

TRANSPORT OF GASES THROUGH BLENDS OF
POLYETHERSULFONE

BY

HARPAL HUNDAL BSc HONS

A Thesis submitted
for the award of the degree of

DOCTOR OF PHILISOPHY
OF THE
UNIVERSITY OF LONDON

and

THE DIPLOMA OF IMPERIAL COLLEGE

Department of Chemistry,
Imperial College of Science and Technology, and Medicine
LONDON SW7 2AY.

ABSTRACT

Transport of gases through blends of Polyethersulfone

The permeability, solubility and diffusivity of carbon dioxide and methane have been determined in blends of Polyethersulfone (PES) - Polyhydroxyether of bisphenol (A) (Phenoxy) and of carbon dioxide in blends of PES-Pu (Polyurethane) in the temperature range 30-50°C.

The PES-Phenoxy system was completely miscible over the entire composition range based on the presence of single composition dependent glass transition temperature indicated by differential scanning calorimetry. All of the blends and pure components were in the glassy state in the temperature range of the transport and solution studies. The sorption of CO₂ exhibited the Langmuir type curvature expected for glassy polymers, however for methane Henry's law was obeyed due to the very low uptake and curvature was observed only at high pressures. The interaction parameter deduced from the solubility data was approaching zero based on the Flory Huggins theory. The permeability was independent of pressures at low penetrant activity and decreased as the pressure was increased. The permeability data also indicated the system to be completely miscible when compared with a number of homogeneous and heterogeneous models for transport. The diffusion coefficients exhibited a minimum around 50% PES while the permeability and solubility increased with increasing PES content. Higher separation factors were achieved at lower temperatures at the expense of lower flow rate.

Sorption and transport of carbon dioxide in blends of PES - Pu strongly suggested mixing for the system when compared with related models. This was further supported by density measurements; however the glass transition temperatures measured by differential scanning calorimetry gave conflicting results.

For my Father

Kartar Singh Hundal (late)

and Mother

Kashmir Kaur Hundal

ACKNOWLEDGEMENTS

I acknowledge with deep gratitude the encouragement and guidance given to me by J.A. Barrie.

I am grateful to Mr Ron Carter, D. Sheppard and to all staff of the Chemistry Department workshops for their helpful technical assistance during the course of this research.

I am also thankful to my younger brother, Bhobinder younger sister Inderjit and friend Ravi for their constant encouragement throughout my research.

I am especially grateful to Mrs. Sue Freedman for her expertise in typing this thesis.

Finally, I acknowledge the award of a bursary from BP Research International, Sunbury Research.

CONTENTS

	<u>Page</u>
List of Figures	10
List of Tables	14
List of Symbols	16
INTRODUCTION	18
 <u>CHAPTER 1 POLYMER BLENDS</u>	
1.1 INTRODUCTION	20
1.2 The Thermodynamics of Polymer-Polymer Miscibility	22
1.3 Phase Separation	28
1.4 Prediction of Miscibility	29
1.41 Glass Transition Temperatures	30
1.42 Scattering and Microscopic Techniques	33
1.43 Spectroscopic Techniques	35
1.44 Thermodynamic Characterization by Vapour Sorption Technique	36
 <u>CHAPTER 2 DIFFUSION IN POLYMERS</u>	
2.0 INTRODUCTION TO METHAMATICS	41
2.1 Permeation	43
2.2 Steady State	44
2.3 Transient State Permeation	45
2.4 Sorption and Desorption Kinetics	46
2.5 Concentration dependent diffusion coefficient	47

2.6	Units of P, D and k	49
2.61	Permeability	49
2.62	Solubility Coefficient	49
2.63	Diffusion Coefficient	50
2.7	Factors Effecting Diffusivity,	
	Solubility and Permeability	50
2.71	Temperature	50
2.72	Glass Transition Temperature	52
2.73	Nature of the Penetrant	55
2.74	Nature of the Polymer	55
2.8	Dual Mode Sorption in Glassy Polymers	56
2.9	Dual Mode Transport	59
2.10	Transport Models for Heterogeneous and	
	Homogeneous	66

CHAPTER 3 EXPERIMENTAL

3.1	Materials	86
3.2	Blend Preparation	89
3.3	Permeation	91
3.31	High pressure side	91
3.32	Low pressure side	93
3.33	High pressure work	93
3.4	The Diffusion Cell	94
3.5	Permeation Measurements	96
3.6	Sorption	97
3.61	Sorption Measurements	100

CHAPTER 4 RESULTS AND DISCUSSION - HOMOPOLYMERS

4.1	INTRODUCTION	102
-----	--------------	-----

4.2	Physical Characterization of films	103
4.3	Equilibrium Sorption	107
4.4	Steady State Permeation	122
4.5	Diffusion	130
4.6	Separation Factors	134
4.7	Equilibrium Sorption for CO ₂ in Pu	140
4.8	Permeation of CO ₂ and CH ₄ in Pu	143
4.9	Diffusion Coefficient for CO ₂ in Pu	143
4.10	Separation Factors	145
4.11	Conclusion	148

CHAPTER 5 RESULTS AND DISCUSSION - PES-PHENOXY BLENDS

5.1	INTRODUCTION	149
5.2	Film Characterization	149
5.3	Equilibrium Sorption	159
5.4	Steady State Permeation	182
5.5	Diffusion Coefficients	193
5.6	Separation Factors	200
5.7	Phase - Separated Blends	207
5.8	Conclusion	208

CHAPTER 6 RESULTS AND DISCUSSION - PES-Pu BLENDS

6.1	INTRODUCTION	211
6.2	Film Characterization	211
6.3	Equilibrium Sorption	215
6.4	Steady State Permeation	218
6.5	Diffusion Coefficients	226
6.6	Separation Factors	232

6.7	Conclusion	232
	Further Study	234
APPENDIX 1	Sample calculation and Error Estimation	235
APPENDIX 2	Selected Data Tables	237
REFERENCES		266

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
<u>CHAPTER 1 POLYMER BLENDS</u>	
1.1 Free energy of mixing diagram for binary mixtures	23
1.2 Phase diagram for PES-Phenoxy system	23
<u>CHAPTER 3 EXPERIMENTAL</u>	
3.1 Permeation Apparatus	92
3.2 The Diffusion Cell	95
3.3 Sorption Apparatus	98
3.4 Microbalance Beam	99
<u>CHAPTER 4 HOMOPOLYMERS</u>	
4.1 FTIR Spectra of Phenoxy film recorded at room temperature	105
4.2 N.M.R. Spectra of Pu	106
4.3 PES/CO ₂ Sorption Isotherms	108
4.4 PES/CH ₄ Sorption Isotherms	111
4.5 Phenoxy/CO ₂ Sorption Isotherms	113
4.6 Phenoxy/CO ₂ Sorption Isotherms at 40°C	115
4.7 Phenoxy/CH ₄ Sorption Isotherms	118
4.8 Phenoxy/CH ₄ Sorption Isotherm at 40°C	119
4.9 Van't Hoff plots of CO ₂ solubility	120
4.10 Van't Hoff plots of CH ₄ solubility	121
4.11 Variation of Isosteric Heat of Sorption for CO ₂ with concentration	123
4.12 Effect of driving pressure on the permeability	

	of CO ₂ in Phenoxy at 40 ⁰ C	127
4.13	Arrhenius plots of CO ₂ permeability	128
4.14	Arrhenius plots of CH ₄ permeability	129
4.15	PES/CO ₂ - Concentration dependence of $\bar{D}$ and D	131
4.16	Phenoxy/CO ₂ - Concentration dependence of $\bar{D}$ and D	132
4.17	Arrhenius plots for Diffusivity of CO ₂	135
4.18	Arrhenius plots for Diffusivity of CH ₄	136
4.19	Pu/CO ₂ Sorption Isotherms	141
4.20	Van't Hoff plot of CO ₂ solubility in Pu	142
4.21	Arrhenius plots of CO ₂ and CH ₄ Permeability	144
4.22	Arrhenius plots for Diffusivity of CO ₂	146
 <u>CHAPTER 5 - PES-PHENOXY BLENDS</u>		
5.1	DSC for PES-Phenoxy Blends cast from DMF solution	151
5.2	Glass-Transition behaviour of PES-Phenoxy blends	152
5.3	Specific volume of PES-Phenoxy Blends	155
5.4	FTIR spectra of PES-Phenoxy blends recorded at room temperature	157
5.5	Plot of the width at half-height versus wt.% PES	158
5.6	Sorption Isotherms of CO ₂ at 30 ⁰ C	160
5.7	Sorption Isotherms of CO ₂ at 40 ⁰ C	161
5.8	Sorption Isotherms of CO ₂ at 50 ⁰ C	162
5.9	50% PES/CO ₂ Sorption Isotherm	163
5.10	Solubility of CO ₂	164
5.11	Henry law parameter for CO ₂ in blends of PES-Phenoxy	168

5.12	Hole affinity parameters	168
5.13	Langmuir capacity parameter for CO ₂	170
5.14	Correlation of measured C _H ' versus (T _g - 40°C) for various blends	170
5.15	Van't Hoff plots of CO ₂ solubility in PES-Phenoxy blends	172
5.16	Sorption Isotherms of CH ₄ at 30°C	175
5.17	Sorption Isotherms of CH ₄ at 40°C	176
5.18	Sorption Isotherms of CH ₄ at 50°C	177
5.19	50% PES/CH ₄ Sorption Isotherms at 40°C	178
5.20	Solubility of CH ₄	179
5.21	Van't Hoff plots of CH ₄ solubility in PES-Phenoxy blends	180
5.22	Pressure dependence of CO ₂ permeability of 50/50 blend of PES-Phenoxy	184
5.23	Permeability of CO ₂ at 30°C - Comparison with Homogeneous models	186
5.24	Permeability of CO ₂ at 30°C - Comparison with Heterogeneous models	188
5.25	Permeability of CH ₄ in blends of PES-Phenoxy	190
5.26	Arrhenius plots of CO ₂ Permeability	191
5.27	Arrhenius plots of CH ₄ Permeability	192
5.28	Activation Energies Pu Permeation of CO ₂	194
5.29	Concentration dependence of $\bar{D}$ and D at 30°C	196
5.30	Steady State Diffusion Coefficients for CO ₂	197
5.31	Steady State Diffusion Coefficients for CH ₄	201
5.32	Arrhenius plots for CO ₂ Diffusivity	202
5.33	Arrhenius plots for CH ₄ Diffusivity	203

5.34	Activation Energies for Diffusion of CO ₂	204
5.35	Activation Energies for Diffusion of CH ₄	204
5.36	CO ₂ /CH ₄ Permeability, Solubility and Diffusivity Ratios	206
5.37	Permeability of CO ₂ at 50°C in Phase-Separated blends of PES-Phenoxy	209

CHAPTER 6 PES-Pu BLENDS

6.1	Variation of specific volume with weight fraction of PES	213
6.2	Sorption Isotherms of CO ₂ at 30°C	216
6.3	Solubility of CO ₂	217
6.4	Van't Hoff plots of CO ₂ solubility in PES-Pu Blends	219
6.5	Heats of Sorption for CO ₂	220
6.6	Permeability of CO ₂ in blends of PES-Pu	221
6.7	Permeability of CO ₂ at 30°C, Comparison with Maxwell Model	223
6.8	Arrhenius plots of CO ₂ Permeability	225
6.9	80% PES Blend/CO ₂ concentration dependence of $\bar{D}$	227
6.10	50% PES blend/CO ₂ concentration dependence of $\bar{D}$	228
6.11	Diffusivity of CO ₂ at 30°C	230
6.12	Arrhenius plots for Diffusivity of CO ₂	231

LIST OF TABLES

<u>Table</u>	<u>Page</u>
 <u>CHAPTER 4 HOMOPOLYMERS</u>	
4.1 Density, and Glass transition temperature of homopolymers	103
4.2 Dual Mode Sorption Parameters for CO ₂	109
4.3 Solubility Coefficients for CO ₂ /PES	110
4.4 Solubility Coefficients for CH ₄ /PES	112
4.5 Dual mode Sorption Parameters for CO ₂ /Phenoxy	114
4.6 Henry's law Solubility Coefficients for CO ₂ and CH ₄	116
4.7 Heats of Dissolution	122
4.8 Permeability Coefficients of CO ₂ and CH ₄ in PES	124
4.9 Permeability Coefficients for CO ₂ and CH ₄ in Phenoxy	125
4.10 Activation Energies of Permeation for CO ₂ and CH ₄	126
4.11 Diffusion Coefficient for CO ₂	133
4.12 Diffusion Coefficient for CH ₄	133
4.13 Activation Energies of Diffusion for CO ₂ and CH ₄	134
4.14 Separation factors (CO ₂ /CH ₄)	138
4.15 Solubility Coefficients for CO ₂ in Pu	140
4.16 Permeability Coefficients for CO ₂ and CH ₄	143
4.17 Diffusion Coefficient for CO ₂	145
4.18 Separation factors	147
 <u>CHAPTER 5 PES-PHENOXY BLENDS</u>	
5.1 Weight fraction, volume fraction and Densities of PES-Phenoxy blends	154
5.2 Solubility Coefficient, k of Carbon Dioxide in blends of PES-Phenoxy	165

5.3	The Dual Mode sorption parameters	167
5.4	The Heat of Dissolution, $\Delta\bar{H}_s$ of CO ₂ in blends of PES-Phenoxy	171
5.5	Isosteric Heat of Sorption of CO ₂ in PES-Phenoxy blends	173
5.6	Henry law solubility coefficient, k, for CH ₄ in PES-Phenoxy blends	181
5.7	Heats of dissolution of CH ₄ in PES-Phenoxy blends	181
5.8	Permeability Coefficient for CO ₂ in PES-Phenoxy Blends	182
5.9	Permeability Coefficient for CH ₄ in PES-Phenoxy Blends	189
5.10	Activation Energies for Permeation of CO ₂ and CH ₄	193
5.11	Diffusion Coefficient ($D_c = 0$) for CO ₂ in PES-Phenoxy blends	198
5.12	Steady State Diffusion Coefficient for CH ₄ in blends of PES-Phenoxy	199
5.13	Permeability of CO ₂ through Phase-Separated blends of PES-Phenoxy	208
<u>CHAPTER 6 PES-Pu BLENDS</u>		
6.1	Weight fractions, volume fractions and Densities of PES-Pu blends	212
6.2	Glass Transition Temperatures	214
6.3	Solubility for CO ₂ in PES-Pu blends	215
6.4	Carbon dioxide Permeabilities in PES-Pu blends	222
6.5	Activation Energies of Permeation for CO ₂	226
6.6	Diffusion Coefficients for CO ₂	229
6.7	Activation Energies of Diffusion for CO ₂	232

LIST OF SYMBOLS

a_i	activity of component i
A	membrane area
b	hole affinity constant
B	Flory-Huggins interaction parameter
c	concentration
C_D	concentration of dissolved species
C_H	concentration of Langmuir species
C'_H	hole saturation constant
D	diffusion coefficient
$\bar{D}$	average diffusion coefficient
D_θ	time-lag diffusion coefficient
D_D	diffusion coefficient of dissolved species
D_H	diffusion coefficient of Langmuir species
G	free energy
ΔG_{mix}	free energy of mixing
ΔH_D	enthalpy of dissolution
ΔH_{mix}	enthalpy of mixing
k_D	Henry's law dissolution constant
k	Henry's law constant derived from dual mode parameters
l	membrane thickness
M_t	Mass of penetrant sorbed at time t
M_∞	Mass of penetrant at equilibrium
p	pressure
P	permeability
R	Universal gas constant
ΔS_{mix}	Entropy of mixing

ΔS_{mix}^*	Combinatorial entropy of mixing
T	absolute temperature
T_g	glass transition temperature
V_i	molar volume of component i
V_s	polymer segmental volume
w_i	weight fraction of component i
Δw_{12}	enthalpy change for forming an unlike contact pair
	coordination number
α_{ij}	separation factor
δ	solubility parameter
ϕ_i	volume fraction of component i
χ	Flory-Huggins interaction parameter
ρ	density
μ	chemical potential
λ	jump length

INTRODUCTION

With the cost of research and development into new polymers becoming prohibitively high, attention has now turned to modifying existing commercial polymers in order that they may fulfil set requirements. Thus the concept of physically blending two or more existing polymers to obtain new products is now attracting widespread interest and commercial application.

Polymer blends may be classified as miscible, partially miscible or immiscible. Mechanical, thermal and rheological properties are determined by the state of miscibility of the system. In more recent years there has been considerable interest in miscible blends. The properties of blends of this kind generally vary smoothly with composition between those of the pure components. Properties are also dependent to some extent on the degree of interaction of the blend components. With the renewed interest in polymer films as potential membranes for the separation of gaseous mixtures, there has also been a number of studies of gas transport in miscible polymer blends. It is with this aspect of miscible polymer blends that the present study is mainly concerned.

The gas barrier properties of polymers are well established and have widespread application in food packaging, bottling of carbonated beverages and other industries. The potential of polymers for the separation of gaseous mixtures was recognized at an early stage but practical application had to await the advent of asymmetric thin film technology to supply the high fluxes

required. Modified asymmetric hollow fibres of polyethersulphone form the basis of the Monsanto "PRISM" separator applied successfully to the recovery of hydrogen waste gas in ammonia synthesis. The potential of polymer membranes for the separation of other gas mixtures, especially CO_2/CH_4 , is also recognized and has resulted in renewed interest in this area.

The main objective of this work is to investigate the transport and solution of carbon dioxide and methane in the engineering plastic polyethersulphone and blends of this polymer with phenoxy polymer and to a lesser extent polyurethane. As well as identifying potentially useful separation membranes, such studies are useful in probing the physical state of a polymer, rubbery or glassy and its morphology.

CHAPTER 1

POLYMER BLENDS

1.1 INTRODUCTION

Polymer blends may be defined as physical mixtures of two or more polymers,⁽¹⁾ and may be subdivided into a number of different categories. However, the most important distinction is between the so-called incompatible and compatible blends. Incompatible blends are those in which the polymeric components exist in well-defined separate phases and domains. Commercially useful examples of such blends are the rubber-modified plastic materials, high impact polystyrene (HIPS) and the acrylonitrile - styrene butadiene (ABS) materials.

While the incompatible blends represent the large majority of all polymer blends, the compatible (also referred to as miscible) blends are in the minority. However, an ever-increasing number of compatible polymer pairs have been discovered and these materials are still attracting considerable attention. An example of an industrially significant compatible blend is the Noryl polymeric material which consists of polystyrene and poly (2, 6-dimethyl - 1, 4-phenylene oxide).⁽²⁾ The heat distortion temperature of the phenylene oxide is decreased by the addition of polystyrene⁽³⁾. Polystyrene is the cheaper of the two components and blending is economically advantageous provided the lower heat distortion temperature is acceptable. Compatibility is often used to describe whether a desired or beneficial result occurs when two materials are combined together and does not necessarily mean they represent

one phase. However, in this case compatibility or miscibility of a miscible blend will be defined as the intimate mixing of polymers on a molecular level to produce macroscopic properties characteristic of a single phase.

This section will discuss, the basic thermodynamics of mixing and briefly the various methods by which miscibility of two polymers may be established. In recent years the technical literature on this subject has greatly expanded and there are a number of detailed accounts. (1, 4-7)

1.2 The Thermodynamic of Polymer-Polymer Miscibility

The thermodynamic criteria for miscibility can be developed in terms of the Gibb's free energy of mixing, ΔG_{mix} . Complete miscibility between mixtures will occur whenever the free energy of mixing, ΔG_{mix} is negative and $\partial^2 \Delta G_{\text{mix}} / \partial \phi^2$ is positive over the entire composition range.

Figure (1.1) shows a typical variation of free energy with composition for completely immiscible, completely miscible and partially miscible binary mixtures represented by curve A, B and C respectively.

Since

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \quad (1.0)$$

there will be contributions to ΔG_{mix} from both ΔH_{mix} , the enthalpy change on mixing and ΔS_{mix} , the entropy change on mixing.

Flory developed⁽⁵⁾ an expression for the combinatorial entropy for the athermal mixing of polymer segments with solvent or other polymer segments using a lattice model approach. The expression for the mixing of two polymer species expressed per unit volume of the mixture is

$$\Delta S_{\text{mix}}^* = -k \left[\frac{\phi_1}{V_1} \ln \phi_1 + \frac{\phi_2}{V_2} \ln \phi_2 \right] \quad (1.1)$$

Where V_i and ϕ_i are the molar volumes and volume fractions of component i respectively. It is clear from equation (1.1), that

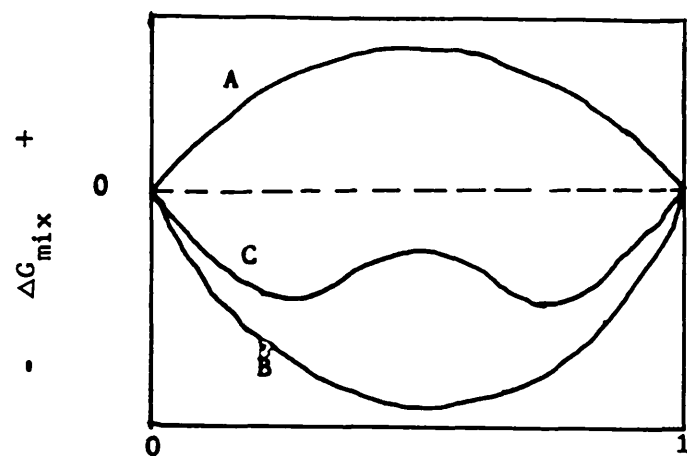


FIG. 1.1 Free energy of mixing diagrams for binary mixtures

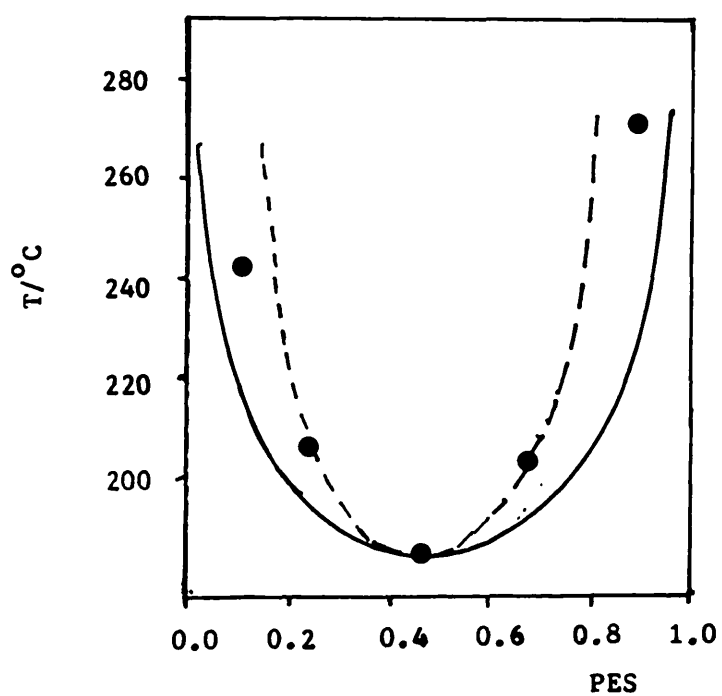


FIG. 1.2 Phase Diagram for PES - Phenoxy system

ΔS_{mix}^* is dependent on the molecular weight since V_i is proportional to molecular weight.

Thus the combinatorial entropy of mixing two polymers is small because of the high molecular weight of commercially important polymers and will tend towards zero with increasing molecular weight.

An estimate of the enthalpy of mixing, ΔH_{mix} depends primarily on the energy change associated with the change in nearest neighbour contacts during mixing⁽⁸⁾ and is independent of molecular weight. When two polymers only interact via dispersive or van der Waals type bonding⁽⁹⁾ the heat of mixing is adequately estimated from the solubility parameters⁽¹⁰⁾ of the components, using equation (1.2).

$$\Delta H_{mix} = V (\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (1.2)$$

Equation (1.2) only predicts a positive or zero enthalpy of mixing and miscibility in such cases is not favourable. It can be seen therefore that ΔG_{mix} is primarily influenced by the sign and magnitude of ΔH_{mix} for high molecular weight mixtures. However, if the solubility parameters of two polymers are closely matched, choosing polymers of similar structure may then lead to an enthalpy of mixing close to zero and a small positive entropy of mixing. This may result in a negative free energy of mixing.

Specific interactions such as intermolecular dipole-dipole interactions or donor-acceptor bonding such as hydrogen bonding when present between chains make an exothermic contribution to

the heat of mixing.

If the strength of these specific interactions outweighs the endothermic contribution for the dispersive forces an overall exothermic heat of mixing may result which favours miscibility. Therefore many miscible mixtures have been examined which have the potential to exhibit specific interaction.

Equation (1.2) does not allow for specific interactions of the kind discussed above nor does it allow for any reduction in volume which often accompanies the formation of miscible mixtures. Bearing in mind that the enthalpy of mixing is associated with change in nearest neighbour contacts between like segments and unlike segments, Hildebrand⁽¹⁰⁾, Van Laar⁽⁹⁾ and Scatchard⁽⁸⁾ derived the following expression for the enthalpy of mixing per unit volume in terms of the energy change Δw_{12} for the formation of an unlike pair of segments

$$\Delta H_{\text{mix}} = z \Delta w_{12} \phi_1 \phi_2 / V_s \quad (1.3)$$

z is the coordination number which accounts for the number of near neighbour segments with which a given segment may interact and V_s is the volume of the segment. Equation (1.3) may also be written as:-

$$\Delta H_{\text{mix}} = \frac{k T \chi \phi_1 \phi_2}{V_s} \quad (1.4)$$

Where k is the Boltzmann constant and χ is the Flory - Huggins interaction parameter and is given by

$$\chi = z\Delta w_{12}/kT \quad (1.5)$$

An alternative expression often seen for the enthalpy of mixing is

$$\Delta H_{\text{mix}} = B \phi_1 \phi_2 \quad (1.6)$$

where B is given by

$$B = z\Delta w_{12}/V_s = kT\chi/V_s = RT\chi/V_1 \quad (1.7)$$

Both χ and B will take negative values when ΔH_{mix} is exothermic, and equation (1.3) and (1.6) may be applied to both exothermic and endothermic heats of mixing unlike equation (1.2) which predicts only positive heats of mixing.

When specific interactions are pronounced the entropy change of mixing cannot be equated to the combinatorial entropy of mixing since the specific interactions will result in an additional entropy contribution arising from an increase in the degree of local ordering in the system. The Δw_{12} may then be redefined as a free energy function given by:

$$\Delta w_{12} = \Delta w_h - T\Delta w_s \quad (1.8)$$

Where Δw_h and Δw_s account for the change in heat content and entropy respectively on forming an unlike segment pair. The interaction parameter in equation (1.5) is no longer simply related to the enthalpy of mixing by equation (1.3) since it contains an entropy contribution.

The total entropy change on mixing, ΔS_{mix} , then has two contributions one which is combinatorial in origin and the other associated with specific interactions and their effect on local ordering. The free energy of mixing remains unchanged by the new definition of the interaction parameter χ so that

$$\Delta G_{\text{mix}}^* = kT \left[\frac{\phi_1}{V_1} \ln \phi_1 + \frac{\phi_2}{V_2} \ln \phi_2 + \frac{\chi}{V_s} \phi_1 \phi_2 \right] \quad (1.9)$$

The corresponding entropy and enthalpy of mixing is given by

$$\Delta S_{\text{mix}}^* = -(\partial \Delta G_{\text{mix}}^* / \partial T)_p \quad (1.10)$$

$$= -k \left[\frac{\phi_1}{V_1} \ln \phi_1 + \frac{\phi_2}{V_2} \ln \phi_2 + \frac{\phi_1 \phi_2}{V_s} \frac{\partial (\chi T)}{\partial T} \right] \quad (1.11)$$

$$\Delta H_{\text{mix}} = -T^2 \left[\frac{\partial (\Delta G_{\text{mix}}^* / T)}{\partial T} \right]_p = \frac{-kT^2}{V_s} \left[\frac{\partial \chi}{\partial T} \right] \phi_1 \phi_2 \quad (1.12)$$

Equation (1.11) and (1.12) must be used if Δw_{12} is temperature dependent. However, if Δw_{12} is independent of temperature, it contains no entropy contribution and the interaction parameter is inversely proportional to temperature, then

$$\Delta S_{\text{mix}}^* = \Delta S_{\text{mix}} \quad (1.13)$$

$$\Delta H_{\text{mix}} = kT \chi \phi_1 \phi_2 / V_2 \quad (1.14)$$

Although attractively simple, the Flory - Huggins lattice model fails to take into account the effect of pressure and volume changes on mixing, also it is unable to predict lower critical solution temperatures. In later work Flory and co-workers⁽¹¹⁻¹⁵⁾

developed an equation of state theory which takes into account these factors, but its application is more complex as it employs several somewhat arbitrary parameters.

1.3 Phase Separation

Mixtures that are miscible at one temperature may undergo a phase separation at other temperatures. In a temperature composition phase diagram, the boundary between the homogeneous and heterogeneous region is termed the cloud point curve since phase separation is accompanied by cloudiness. If, keeping the pressure constant, a homogeneous mixture separates on cooling, then the cloud point curve is concave to the composition axis and the maximum of curve is denoted the upper critical solution temperature (UCST). This behaviour is characteristic of an endothermic heat of mixing and a positive entropy of mixing and can be predicted for polymer systems using the Flory-Huggins theory. A homogeneous mixture may also phase separate on raising the temperature. The cloud point curve is convex to the composition axis and the minimum of the curve is referred to as the lower critical solution temperature (LCST). This behaviour is characteristic of an exothermic heat of mixing and a negative excess entropy of mixing.⁽¹⁶⁾ The Flory-Huggins theory does not account for an LCST and a more recent equation-of-state theory is required.^(17,18) LCST behaviour is encountered with phase separation occurring at sufficiently high temperatures. LCST polymer systems have received much attention recently because of the interest in miscible blends and their likely applications at temperatures at or above room temperatures.

The phase diagram of the system (PES-Phenoxy) in this study is shown in figure (1.2). This is a typical example of a system exhibiting a lower critical solution temperature behaviour. The results are taken from reference (19). The solid curve which separates the stable one phase region from that where the two phases coexist in equilibrium is defined as the binodal. The dashed curve separating the two phase region of the phase diagram into a metastable and unstable region and is defined as the spinodal, where $\partial^2 \Delta G_{\text{mix}} / \partial \phi^2 = 0$. Within the unstable region there is no thermodynamic barrier to phase separation and spontaneous spinodal decomposition occurs. On the other hand in the metastable region, where $\partial^2 \Delta G_{\text{mix}} / \partial \phi^2 > 0$, a small fluctuation in composition increases the free energy of the system, however for phase separation to take place large composition fluctuations are necessary. This mechanism of phase separation in the metastable region is termed as a 'nucleation and growth' since the change of composition generates nuclei which continue to grow once formed.

1.4 Prediction Of Miscibility

There are various ways in which miscibility may be detected, however only a few will be discussed briefly in this section. Before proceeding further, it was mentioned in section (1.3) that on raising the temperature of a compatible blend of two polymers, a lower critical solution (LCST) is reached where phase separation occurs. This in itself is proof that the original clear blend consisted of a single, equilibrium, homogeneous phase. Unfortunately, for the majority of compatible polymer

blends, the LCST is not reached before significant degradation of the pure component polymers occurs. However, exceptions are found for example in blends of ethylene vinyl acetate (EVA) copolymers with either poly (vinyl chloride) (PVC) or chlorinated polyethylene (CPE) which are compatible⁽²⁰⁾ and exhibit LCST's at moderate temperatures (<150°C).

1.41 Glass Transition Temperatures

One method often used to detect miscibility of polymer blends is the determination of glass transition temperature, T_g . It has been well documented that miscible polymer blends show a single composition dependent glass transition temperature. Immiscible or partially immiscible blends have two glass transition temperatures corresponding respectively to those of the two component polymers or of two mixed phases. There are several methods which can be used to determine glass transition temperatures. The two main techniques used in this study were Calorimetric and Dynamic mechanical methods. The Calorimetric methods involve the change in heat capacity of the polymer at the glass transition temperature and is carried out using differential scanning calorimetry, (DSC). This method uses a servo system to supply heat at a same rate to the sample and the reference, so that the temperature of the two stay equal or differ by a constant amount. Also the system is programmed to give a linear rise in temperature with time. When the sample undergoes a transition, the difference in the amounts of heat that must be applied to the sample and the reference changes and is reflected in a change of base line as shown in fig. (5.1).

Care must be taken to ensure samples are properly outgassed and free of solvent as desorption of these on heating may give rise to spurious changes. DSC is one of the most commonly used methods for T_g determination.

The dynamic mechanical experiment yields both the elastic modulus of the material and its mechanical damping, or energy dissipation, characteristics.⁽²¹⁾ These properties can easily be determined as a function of frequency (time) and temperature. The sample is heated at a constant rate; a sinusoidal strain is applied to the sample and the resulting stress, which is out of phase with the strain by a phase angle δ , is measured. The phase angle is measured directly as a function of temperature and the maximum value of $\tan \delta$ is identified with the glass transition temperature.

Other techniques of detecting the glass transition temperature include dielectric methods and dilatometry. The former involves a similar principle to the dynamic mechanical measurements in which the complex dielectric constant (ϵ^*) is determined as a function of temperature and frequency. An alternating electric field produces an alternating electrical polarisation which in the case of polar materials lags behind the applied field by a phase angle δ . The glass transition is determined from the temperature at which $\tan \delta$ has a maximum value. This method allows a wide range of frequencies to be used but it is only applicable to polar polymers. The glass transition temperature measured by dilatometry corresponds to

the temperature at which a change in slope of the specific volume occurs when plotted as a function of temperature. At this point the coefficient of volume expansion of the polymer changes. Various attempts have been made to correlate the dependence of glass transition on blend composition using expressions developed, earlier for random copolymers and polymer solvent systems. According to the Fox relationship the T_g composition dependence is given by⁽²²⁾

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (1.15)$$

Where w_i denotes the weight fraction and T_{g1} , T_{g2} are the glass transition temperatures of the pure components. Other expressions often used are those of Kelly-Bueche⁽²³⁾ and Gordon-Taylor⁽²⁴⁾, namely

$$T_g = \frac{\phi_1 T_{g1} + K \phi_2 T_{g2}}{\phi_1 + K \phi_2} \quad (1.16)$$

$$T_g = \frac{w_1 T_{g1} + K w_2 T_{g2}}{w_1 + K w_2} \quad (1.17)$$

The parameter, K is the ratio of the difference in the thermal expansion coefficient of the rubbery and glassy state for polymers 2 and 1 ie. $K = (\alpha_{1l} - \alpha_{1g})/(\alpha_{2l} - \alpha_{2g})$, and ϕ_i , w_i , T_{gi} are the volume fraction, weight fraction, glass transition temperatures of the respective components and T_g is the transition temperature of the blend. As indicated these

expressions were originally developed to describe the behaviour of random copolymer or polymer-diluent systems.

In general the dependence of T_g on blend composition in miscible polymer blends does not necessarily follow any of the above models.⁽²⁵⁻²⁷⁾ However, in this study the experimental data were well represented by the Fox expression. Jacques et al^(28,29) reported the T_g of the blends to lie below the tie line joining the T_g 's of the pure components. Similar behaviour has been reported for miscible blends of poly(styrene)-poly(vinyl methyl ether)⁽³⁰⁾, poly(styrene) - poly (phenylene oxide)⁽³¹⁾ and PVC with butadiene acrylonitrile copolymer.⁽³²⁾ For some miscible blends a linear variation of the glass transition temperature with composition has been observed⁽³³⁻³⁵⁾, and a more complex behaviour reported by Kwei⁽³⁶⁾ where an S shape dependence of the glass transition temperature was observed. This was described by a combination of the Gordon-Taylor expression with an additional term $(q w_1 w_2)$ which is proportional to the number of intermolecular interactions. When intermolecular interactions are very strong they act as effective links and raise the glass transition more than anticipated on weight or volume average basis. Behaviour of this type has been reported for blends of poly (methyl methacrylate)/poly (vinylidene chloride)⁽³⁷⁾ and poly (vinyl nitrate)/poly (vinyl acetate)⁽³⁸⁾.

1.42 Scattering And Microscopic Techniques

Optically clear films are generally but not necessarily an indication of miscibility. A phase separated blend may appear

similar if domain sizes are small relative to the wavelength of light. For example, Jenckel and Herwing⁽³⁹⁾ reported that the heterogeneous blends of poly (vinyl acetate) (PVA) and poly (methyl methacrylate) (PMMA) were transparent because of the small size of the PVA dispersed domains.

Scattering and Microscopy techniques are two ways in which the miscibility of polymer blends may be investigated bearing in mind the above restrictions. Measurements of the intensity of the scattered light as a function of temperature is commonly used to measure cloud point curves.⁽⁴⁰⁻⁴²⁾ The temperature at which blends show the first sign of turbidity, that is relatively intense scattering, corresponds to the onset of phase separation. Bank et al⁽³¹⁾ demonstrated this for blends of polystyrene-poly(vinyl methyl ether). Also Singh and Walsh⁽¹⁹⁾ used this technique to measure the cloud point curve for the PES-Phenoxy blend system. The same authors used optical microscopy and confirmed that phase separation occurred on heating miscible blends of PES-Phenoxy. Once again it is necessary for the refractive indices of the two phases to be different for this technique to be useful. Different techniques may sometime lead to different conclusions. For example, a system which appears to be one phase by T_g measurements has been found to be two phase by transmission electron microscopy⁽⁴³⁾. This may be because the latter techniques allows small domains of the order of 10^8 Å to be detected.

1.43 Spectroscopic Techniques

Favourable intermolecular interactions between chemically dissimilar polymers have been suggested to contribute to the compatibilization of polymer blends. Spectroscopic techniques allow one to establish the nature of these interactions and can also be used to establish miscibility or phase separation. The most commonly used techniques are infrared and nuclear magnetic resonance. In a Fourier transform infrared (FTIR) study a shift to a lower frequency of the carbonyl absorption was observed for blends of polyester with poly (vinyl chloride)^(44,45), vinylidene chloride copolymers;⁽⁴⁶⁾ poly(bisphenol A carbonate)^(47,48), the poly(hydroxy ether of bisphenol A)⁽⁴⁹⁾. These shifts indicate the presence of specific intermolecular interactions involving the carbonyl bond. FT - IR studies of PES - Phenoxy polymer in this research work give evidence for a hydrogen bonding type interaction involving the hydroxyl groups of Phenoxy. The hydrogen - bonded hydroxyl vibration of Phenoxy was observed to shift to a higher frequency. Similar behaviour has been reported for blends of Phenoxy - poly(ϵ -caprolactone) PCL⁽⁵⁰⁾.

The nuclear magnetic resonance (NMR) technique can provide information on the relaxation times of protons, which depend on the environment of the protons. For a two phase system protons on different chains are in different environments and will exhibit different relaxation times. In a miscible blend the intimate mixing of the polymers results in a single relaxation time since the protons are essentially in the same environment. An excellent example of this approach has been demonstrated by

Kwei, Nishi and Roberts⁽⁵¹⁾ for the blend system poly(styrene) - poly (vinyl methyl ether). The proton relaxation time was measured as a function of temperature, a single relaxation time was observed at low temperatures whereas upon raising the temperature two relaxation times appeared. Miscibility in blends of poly (ethylene oxide) and poly (methyl methacrylate)⁽⁵²⁾ has also been demonstrated using ¹³C NMR.

1.44 Thermodynamic Characterization by Vapour Sorption Technique

Some information on polymer-polymer interactions can be obtained from measurement of the equilibrium sorption of a gas or vapour in a homogeneous blend. Scott^(28,29,50,56-58) developed the Flory-Huggins theory for a ternary system consisting of polymer 1 and polymer 2 and solvent 3. The chemical potential of the solvent in the blend, μ_{3b} , relative to the pure solvent, μ_{3s} is given by

$$\mu_{3b} - \mu_{3s} = RT \ln a_{3b} \quad (1.18)$$

$$= RT [(1 - \phi_3) + \ln \phi_3 + (1 - \phi_3) (x_{31}\phi_1 + x_{32}\phi_2) - x_{12} \phi_1 \phi_2 V_3/V_1] \quad (1.19)$$

Where - a_{3b} is the activity of component 3 in the blend,

ϕ_i is the volume fraction of component i and x_{ij} is the Flory-Huggins interaction parameter between components i and j of the mixture.

The equilibrium activity of vapour in contact with the homogeneous blend of polymer 1 and 2 is given by

$$\ln a_{3b} = (1 - \phi_3) + \ln \phi_3 + (1 - \phi_3) (x_{31} \phi_1 + x_{32} \phi_2) - x_{12} \phi_1 \phi_2 \quad (1.20)$$

$$\text{where } x_{12} = \dot{x}_{12} V_3/V_1 = x_{21} V_3/V_2 \quad (1.21)$$

The volume fraction ϕ_1 of polymer 1 is given by

$$\phi_1 = \frac{V_1}{V_1 + V_2 + V_3} = \frac{V_1}{V_1 + V_2} \frac{V_1 + V_2}{V_1 + V_2 + V_3} \quad (1.22)$$

so that

$$\phi_1 = \phi_{10} (\phi_1 - \phi_2) = \phi_{10} (1 - \phi_3) \quad (1.23)$$

where ϕ_{10} is the volume fraction of component 1 in a blend of 1 and 2 which is free of component 3.

$$\text{Similarly, } \phi_2 = \phi_{20} (1 - \phi_3)$$

$$\ln a_{3b} = \ln \phi_3 + (1 - \phi_3) + (x_{31} \phi_{10} + x_{32} \phi_{20} - x_{12} \phi_{10} \phi_{20}) (1 - \phi_3)^2 \quad (1.24)$$

If the blend of polymers 1 and 2 is now treated as a single component, equation (1.24) may be written in terms of an overall interaction parameter for the blend, x_{3b} so that

$$\ln a_{3b} = \ln \phi_3 + (1 - \phi_3) + x_{3b} (1 - \phi_3)^2 \quad (1.25)$$

$$\text{where, } (x_{3b} = x_{31} \phi_{10} + x_{32} \phi_{20} - x_{12} \phi_{10} \phi_{20}) \quad (1.26)$$

Equation (1.24) may be written as follows in a more general form to give the activity of component 3 in polymer 1, polymer 2 or

the blend,

$$\ln a_{3i} = \ln \phi_3 + (1 - \phi_3) + \chi_{3i} (1 - \phi_3)^2 \quad (1.27)$$

In the limit of Henry law sorption $\phi_3 \rightarrow 0$ and equation 1.27 becomes

$$\ln (\phi_3/a_{3i}) \rightarrow - (1 + \chi_{3i}) \quad (1.28)$$

$$\chi_{3i} \rightarrow - [1 + \ln (\phi_3/a_{3i})] \quad (1.29)$$

Hence from equation (1.26)

$$- [1 + \ln (\phi_3/a_{3b})] = - \phi_{10} [1 + \ln (\phi_3/a_{31})] - \phi_{20} [1 + \ln (\phi_3/a_{32})] - \chi'_{12} \phi_{10} \phi_{20} \quad (1.30)$$

Hence

$$\ln (\phi_3/a_{3b}) = \phi_{10} \ln (\phi_3/a_{31}) + \phi_{20} \ln (\phi_3/a_{32}) + \chi'_{12} \phi_{10} \phi_{20} \quad (1.31)$$

$$\text{Define the Henry's law constants as } k_{3i} = \phi_3/a_{3i} \quad (1.32)$$

$$\ln k_{3b} = \phi_{10} \ln k_{31} + \phi_{20} \ln k_{32} + \chi'_{12} \phi_{10} \phi_{20} \quad (1.33)$$

Thus unless $\chi'_{12} = 0$, a plot of $\log k_{3b}$ as a function of blend composition will deviate from the straight line joining the pure component values of $\ln k_{31}$ and $\ln k_{32}$. For negative values of χ'_{12} , the curve will lie below the line joining the pure component values, the deviation being more pronounced the more negative is the value of χ'_{12} . This is the expected behaviour for miscible

blends. When $\chi'_{12} > 0$, the solubilities will lie above this line. However such blends will be unstable and will tend to phase separate.

Jacque et al^(28, 58) measured the sorption of hexane at different activities in miscible blends of poly(styrene) and poly(2, 6 - dimethyl - 1, 4 - phenylene oxide). At the higher activities of hexane the glass transition temperature of the blends were below the temperature of measurement and a distinct minimum was observed in a plot of $\ln k_{3b}$ against blend composition for a blend containing 75% polystyrene. At lower activities of hexane the blends were still glassy and the curvature in the $\ln k_{3b}$ plot was much less pronounced. These studies indicate that for an effective evaluation of χ'_{12} the probe molecule must not interact strongly with the polymer as it may affect the nature of the blend.

A negative value obtained for χ'_{12} from measurements of the solubility of benzene in blends of poly(styrene) and poly(vinyl methyl ether) was reported by Kwei et al⁽⁵¹⁾. All three interaction parameters, χ_{31} , χ_{32} and χ'_{12} were evaluated as a function of temperature and blend composition and it was suggested that the system exhibit both an UCST and LCST.

Using CO_2 as the molecular probe, Paul et al⁽⁵⁶⁾ fitted their sorption data to equation (1.33) and obtained a negative χ'_{12} for glassy blends of poly(styrene) - poly(phenylene oxide) and blends of bisphenol - A - polycarbonate and a copolyester formed from 1,4 - cyclohexanedimethanol and a mixture of

terephthalic and isophthalic acids. Webb et al⁽⁵⁹⁾ also studied the sorption of CO₂ in miscible blends of chlorinated poly(ethylene) and an ethylene vinyl acetate copolymer. The Henry's law constant was evaluated as a function of blend composition and fitted to equation (1.33). A small negative value for χ_{12} was obtained suggesting only weaker interactions. The interaction parameter decreased slightly in the temperature range 30 - 45°C but increased at higher temperature. Although the results did not cover a wide temperature range it was suggested that above 100°C the interaction parameter will take positive values since the system exhibited a lower critical solution temperature.

A more detailed review of methods for detecting miscibility in polymer blends is given elsewhere^(4,60).

CHAPTER 2

DIFFUSION IN POLYMERS

2.1 INTRODUCTION TO MATHEMATICS

Graham⁽⁶¹⁾ and Mitchell^(62,63) in their pioneering work on the transport of gases and vapour through polymer membranes postulated that the permeation process comprised three consecutive steps;

- 1) dissolution of the gas in the upstream surface of the membrane.
- 2) diffusion of the gas through the membrane.
- 3) evaporation of the gas downstream membrane surface.

In general step (2) is rate controlling and in 1855 Ficks⁽⁶⁴⁾ proposed an equation for mass diffusion by analogy with Fourier's⁽⁶⁵⁾ equation of heat conduction. For unidirectional flow in an isotropic medium, Ficks equation is

$$J = -D \frac{\partial c}{\partial x} \quad (2.0)$$

where J is the rate of transfer of diffusing matter through a section of unit area, c is the concentration of diffusant at point x measured in a direction normal to the section and D is the diffusion coefficient. It was originally treated as a constant but more generally it may be a function of concentration, distance or time. The negative sign arises because the flow of diffusing matter is in the opposite direction to that of the concentration gradient.

From a consideration of the mass balance in a thin section

of the medium Fick obtained his second equation for diffusion treating D as constant,

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (2.1)$$

As indicated, equation (2.1) is only valid if D is constant, however, for many polymers and diffusants D depends on the concentration and equation (2.1) then becomes

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[D \frac{\partial c}{\partial x} \right] \quad (2.2)$$

Provided the flux and concentration are measured in the same units of quantity, the units of D are (length)² (time)⁻¹; common units are cm²s⁻¹ or m²s⁻¹.

For the diffusion coefficient to be properly defined it is also necessary to specify the section through which diffusion occurs. Crank^(66,67) has discussed in detail several frames of references, fixed with respect to the volume or mass of the components which participate in the diffusion process. Diffusion coefficients defined in terms of these volume or mass fixed sections can be related to each other and in particular in the limit of low volume fraction of diffusant the various coefficients become identical to each other. In the present study the solubility of the gases in the membranes was sufficiently low for the diffusion coefficient to be independent of the frame of reference.

Later in 1879, Wroblewski⁽⁶⁸⁾ combined the thermodynamic process of dissolution and the kinetic process of diffusion to yield a relationship,

$$J = Dk \Delta p/l \quad (2.3)$$

where k is the solubility coefficient and Δp the pressure difference across the membranes of thickness l .

Exact solutions for Fick's first and second equations have been obtained for a variety of boundary and initial conditions and geometries and form the subject of a number of texts.⁽⁶⁹⁻⁷¹⁾ In the present study the solution of interest is that for diffusion through a plane sheet.

2.1 Permeation

In a conventional permeation experiment the polymer membrane, initially free of penetrant, is exposed at time $t = 0$ to a concentration c_0 of penetrant in the ingoing face at $x = 0$. The concentration at the downstream face at $x = l$ is also held constant at c_1 and the amount of material diffusing across the downstream face is measured as function of time. The boundary and initial conditions are therefore

$$\begin{array}{lll} c = 0 & 0 < x < l & t = 0 \\ c = c_0 & x = 0 & t > 0 \\ c = c_1 & x = l & t > 0 \end{array}$$

After some time has elapsed a steady state of flow is established.

2.2 Steady State

The steady state condition is given by $\frac{\partial c}{\partial t} = 0$ so that for a constant diffusion coefficient

$$\frac{\partial^2 c}{\partial x^2} = 0 \quad (2.4)$$

Integration subject to the above boundary conditions yields,

$$c = \left[\frac{c_1 - c_0}{1} \right] x + c_0 \quad (2.5)$$

and the concentration changes linearly across the membrane from $x = 0$ to $x = 1$.

In the present study the concentration c_1 in the downstream face is effectively zero relative to c_0 and the steady state flux across the membrane is given by

$$J = \frac{Dc_0}{1} \quad (2.6)$$

The permeability P is the flux normalized to unit thickness of membrane and unit pressure difference across the membrane so that

$$P = \frac{Jl}{p_0} \quad (2.7)$$

where p_0 is the gas pressure at the upstream face.

If sorption obeys Henry's law, i.e. $c = kp$, where k is the

solubility coefficient then it follows from equations (2.6) and (2.7) that

$$P = Dk \quad (2.8)$$

2.3 Transient State Permeation

The region preceeding the establishment of the steady state is referred to as the transient region of flow for which $\frac{\partial c}{\partial t} \neq 0$. The solution of equation (2.1) subject to the boundary conditions and with $c_0 \gg c_1 \sim 0$ is

$$\frac{Q_t}{lc_0} = \frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-)^n}{n^2} \exp\left[-\frac{Dn^2\pi^2 t}{l^2}\right] \dots \quad (2.9)$$

where Q_t is the amount of penetrant which has passed through the sheet in time t .

For sufficiently large t ($t \rightarrow \infty$) the steady state is reached where the exponential terms becomes negligibly small and equation (2.9) reduces to

$$Q_t = \frac{Dc_0}{l} \left[t - \frac{l^2}{6D} \right] \quad (2.10)$$

Hence a graph of Q_t against t yields an asymptotic steady-state straight line which on extrapolation to the time-axis gives an intercept

$$\theta = \frac{l^2}{6D} \quad (2.11)$$

The intercept θ is termed the time lag for diffusion and its

measurement leads directly to a value for the diffusion coefficient. The time lag approach was originated by Daynes⁽⁷²⁾ and developed extensively by Barrer.⁽⁷³⁾

2.4 Sorption and Desorption Kinetics

The boundary conditions for sorption into a plane sheet initially free of penetrant and exposed to the same constant pressure of vapour on each face are;

$$\begin{array}{lll} c = 0 & 0 < x < 1 & t = 0 \\ c = c_0 & x = 0 & t > 0 \\ c = c_0 & x = 1 & t > 0 \end{array}$$

And the corresponding conditions for desorption are

$$\begin{array}{lll} c = c_0 & 0 < x < 1 & t = 0 \\ c = 0 & x = 0 & t > 0 \\ c = 0 & x = 1 & t > 0 \end{array}$$

For a constant diffusion coefficient the solution to Ficks equation for these conditions can be expressed in two forms. The first which is more useful for small times is

$$\frac{M_t}{M_\infty} = \left[\frac{Dt}{l^2} \right]^{0.5} \left[\frac{4}{\sqrt{\pi}} + 2 \sum_{n=0}^{\infty} (-1)^n \operatorname{ierfc} \left[\frac{nl}{2(Dt)^{0.5}} \right] \right] \quad (2.12)$$

and the solution more appropriate to large time is

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp \left[- \frac{D(2m+1)^2 \pi^2 t}{l^2} \right] \quad (2.13)$$

where M_t and M_∞ denote the equilibrium uptake at time t and at

equilibrium respectively.

At sufficiently small times, the summation is negligible compared to $\frac{4}{\sqrt{\pi}}$ and equation (2.12) reduces to

$$\frac{M_t}{M_\infty} = \frac{4}{\sqrt{\pi}} \left[\frac{Dt}{l^2} \right]^{0.5} \quad (2.14)$$

The diffusion coefficient can then be deduced from the initial gradient of a plot of M_t/M_∞ vs $\sqrt{t}$ which is generally linear for values of M_t/M_∞ up to 0.5.

At large times (2.13) is more applicable and the series term converges rapidly so that equation (2.13) reduces to:-

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \exp \left[- \frac{D\pi^2 t}{l^2} \right] \quad (2.15)$$

Then D can be obtained from the slope of a plot of $\ln(1 - M_t/M_\infty)$ vs t .

2.5 Concentration dependent diffusion coefficient

The steady state equation (2.6) is still valid and can be integrated over the membrane to give

$$J l = \int_0^{C_0} D dC \quad (2.16)$$

$$\text{and } \frac{d(J l)}{d C_0} = D_C = C_0 \quad (2.17)$$

Hence the concentration dependence of D may be obtained by differentiation, graphical or otherwise, of a plot of the steady state flux as a function of the concentration in the upstream face C_o .

Also from the definition of the permeability, one has

$$P = \frac{Jl}{p_o} = \frac{C_o}{p_o} \cdot \frac{1}{C_o} \int_0^{C_o} Ddc = \bar{k} \cdot \bar{D} \quad (2.18)$$

where $\bar{D} = \frac{1}{C_o} \int_0^{C_o} DdC$ is some average diffusion coefficient and

$\bar{k} = \frac{C_o}{p}$ is the average solubility.

When D is a function of concentration, exact solutions to Fick's second equation are no longer available. Some average $\bar{D}_s$ may be obtained, however, from the initial linear $\sqrt{t}$ region of the sorption kinetic curve. In general a different average $\bar{D}_d$ is obtained from the corresponding conjugate desorption curve.

Using the $\bar{D}_s$ ($\bar{D}_d$) data as a first approximation to $\frac{1}{C_o} \int_0^{C_o} DdC$,

Crank^(66,67) developed a numerical analysis and successive approximation procedure which enables the concentration dependence of the differential coefficient to be determined. The D - C dependence may then be used to generate the rate curves by numerical analysis to compare with the experimental curves.

Several authors have proposed a number of approximate expressions which relate $\bar{D}_s$ ($\bar{D}_d$) to the differential diffusion coefficient D . Manipulation of the $\bar{D}_s$ - C data again enables the

concentration dependence of D to be determined. These and other aspects of concentration dependent diffusion coefficients have been extensively reviewed by Crank⁽⁶⁷⁾.

2.6 Units of P, D and k

A number of different units have been used especially for P and k and it is pertinent at this stage to define the units of these quantities in the present study.

2.61 Permeability

The permeability coefficient, P, is the amount of gas diffusing per second through unit area of membrane of unit thickness while the system is in steady state and is given by

$$P = V l / [A t (P_1 - P_2)]$$

where V = volume of penetrant [cm³ (stp)]

l = membrane thickness (cm)

t = time (s)

p₁ = ingoing pressure (cm Hg)

p₂ = outgoing pressure (cm Hg)

A = cm²

2.62 Solubility Coefficient

The solubility is the amount of gas (cm³ (stp)) dissolved in a unit volume (cm³) of the membrane when in equilibrium with surrounding gas at unit pressure (cmHg) and is given by

$$k = c/p$$

where c = concentration of penetrant [(cm³ (stp))]

p = pressure of penetrant (cmHg)

2.63 Diffusion Coefficient

The diffusion coefficient, D , is the amount of gas (cm^3 (stp)) diffusing per second through unit cross-sectional area (cm^2) of membrane of unit thickness (cm) with unit concentration difference (cm^3 (stp)/ cm^3) across it and is given by

$$D = V / (A \cdot t \cdot \partial c / \partial x)$$

where

- V = volume of penetrant [cm^3 (stp)]
- A = Area of membrane (cm^2)
- t = time (s)
- c = concentration of penetrant in the membrane [cm^3 (stp) cm^{-3}]
- x = distance (cm)

2.7 Factors Effecting Diffusivity, Solubility And Permeability

There have been numerous studies of gas/vapour diffusion in polymers. Of the many factors investigated which affect the diffusion process some typical examples are, temperature, chemical nature of the polymer and of the diffusant, physical state of the polymer, degree of crystallinity, filler and plasticizer content and degree of cross linking, also both homogeneous and heterogeneous systems have been studied. Much of this work has already been reviewed and only a brief summary is given here of some relevant features.

2.71 Temperature

Barrer⁽⁷⁴⁾ was the first to show the effect of temperature on the diffusion coefficient in a gas/polymer system. He

identified diffusion to be an activated process represented by the following relationship:-

$$D = D_0 \exp(-E_D/RT) \quad (2.19)$$

Where D_0 is the pre-exponential factor, E_D is the activation energy for diffusion and T the absolute temperature. Rewriting equation (2.19) in the following form

$$\ln D_0 = \ln D + E_D/RT$$

Barrer^(75,76) showed that if the range in $\ln D$ was small compared with the range of values of E_D then there was a good correlation between $\ln D_0$ and E_D for many gases in various elastomers.

Later van Amerongen^(77,78) observed that E_D for elastomers was found to decrease with increasing temperature and showed that the temperature - dependence of the activation energy could be interpreted by the Eyring theory of rate processes.

A superficially similar expression exists for the solubility coefficient represented by the Van't Hoff relationship:-

$$k = k_0 \exp(-\Delta\bar{H}_s/RT) \quad (2.20)$$

where k_0 and $\Delta\bar{H}_s$ are the pre-exponential factor and heat of solution respectively. The heat of solution $\Delta\bar{H}_s$ may be regarded as comprising two terms, namely, the latent heat of condensation and the heat of dilution. For permanent gases the heat of condensation is small so that the heat of solution is essentially the heat of dilution and is often small and positive.⁽⁷⁹⁾ However, for organic vapours or for sorption in glassy polymers,

the heat of condensation dominates and $\Delta\bar{H}_s$ values in these cases are usually negative and often quite large. Therefore for positive $\Delta\bar{H}_s$, k will increase with increasing temperature and vice versa. Linear relationships have been observed between the solubility of the gas and various parameters such as the critical temperature,⁽⁸⁰⁾ boiling point⁽⁸¹⁾ and the Leonard - Jones force constant⁽⁸²⁾, all of which reflect the ease of condensability of the penetrant.

If sorption obeys Henry's law and the diffusion coefficient is constant then the permeability is given by $P = D k$ so that

$$P = P_0 \exp (- E_p / RT) \quad (2.21)$$

Where $E_p = E_D + \Delta\bar{H}_s$ is the temperature coefficient permeation or the apparent activation energy for permeation and P_0 the pre-exponential factor. E_p may be positive or negative depending on the relative magnitude of E_D and $\Delta\bar{H}_s$ since permeation is the combined result of diffusion and solution.

2.72 Glass Transition Temperature

Meares^(83,84) studied the effect of glass transition temperature on the gas diffusion in glassy polymers. The Arrhenius plots of the diffusion coefficient and permeability exhibited two distinct changes in slope, one at the glass transition temperature and the other some 10°C lower. Below the glass transition temperature, the activation energy of diffusion was lower compared to the rubbery state. This was attributed to the segmental motions being frozen out below T_g resulting in

smaller jump distances in the glassy state and also lower entropies of activation. Above the glass transition temperature there is large scale segmental motion which results in a greater zone of activation; leading to higher energies and entropies of activation. However, expressed per unit jump length, the activation energy for the glassy state is higher than for the rubbery state.⁽⁸⁵⁾ Michael et al^(86,87) also observed the same effect for gas diffusion in polyethylene terephthalate, and the effect was supported by Ryskin.⁽⁸⁸⁾ Kumin et al⁽⁸⁹⁾ studied water vapour diffusion through plasticised and unplasticised vinyl chloride - vinyl acetate copolymers, and the effect on E_D at the transition of the plasticised and unplasticised films was observed. A change in slope of the Arrhenius plot was also observed by Barrer et al⁽⁹⁰⁾ for the diffusion of neon and hydrogen in unplasticised and plasticised poly(vinyl-chloride). A single break was observed for poly (ethylene terephthalate)^(91,92) poly(acrylonitrile)^(93,94), poly(methylacrylate)⁽⁹⁵⁾ and acrylonitrile-vinyl acetate copolymers⁽⁹⁶⁾.

Later studies of Kumins and Roteman on the diffusion of a series of gases He, H_2 , Ne, NH_4 , O_2 , CO, CO_2 and water vapour through poly (vinylchloride) - poly (vinylacetate) copolymer films⁽⁹⁷⁾ showed no change in slope of the Arrhenius plots except for CO_2 and H_2O . No break was observed in poly(ethylmethacrylate) except with H_2O by Stannett and Williams.⁽⁹⁸⁾ This was attributed to a plasticisation effect occurring through water-polymer interactions and not to penetrant

size. However, they suggested that some polymers would show a change in slope with only large penetrants (e.g. CO_2). The same authors in collaboration with Tikhomirov and Hopfenberg⁽⁹⁹⁾ studied the diffusion of He, Ne, N_2 , CO_2 , O_2 , CH_4 and H_2O in unplasticised poly (vinylchloride) and slope changes were apparent on the Arrhenius plots that were dependent upon penetrant size. However, there was no evidence of a discrete change in activation energy at the glass transition temperature.

A number of models have been proposed for the diffusion process based on energy or free volume fluctuations and were reviewed by Kumin and Kwei.⁽¹⁰⁰⁾ Barrer⁽¹⁰¹⁾ proposed an activated hot zone for diffusion in which the diffusant and surrounding polymer segments acquired sufficient energy for the diffusant molecule to jump.

Brandt,⁽¹⁰²⁾ when estimating the activation energy took into account the molecular structure; where the overall activation energy was the sum of the intermolecular term due to the repulsion which the chains experience from their neighbours on accommodating the penetrant molecules, the intramolecular term arising from the bending of the two neighbouring chains and also the thermal energy. The free volume theory⁽¹⁰³⁾ was based on the concept of density fluctuations in liquids. There were regions of high and low density in the polymer matrix, where the low density regions are regarded as the elements of free-volume. Diffusion of a molecule is then governed by the probability of some critical element of free-volume made available to the molecule for a diffusion step to occur. Di Benedetto⁽¹⁰⁴⁾

proposed a volume fluctuation theory which has since been adapted by Pace and Datyner⁽¹⁰⁵⁻¹⁰⁷⁾ and considers diffusion to occur both along and perpendicular to the axis of the polymer bundles, the former requiring less energy.

2.73 Nature of Penetrant

In general, the larger the penetrant molecule, the larger is the activation energy since a larger hole is needed to be formed in the polymer unit, which results in a smaller diffusion coefficient. The pre-exponential factor, D_0 will also increase, since it includes both the entropy of activation and the jump length (λ). The jump-length arises in the pre-exponential term as $\longrightarrow D_0 = e\lambda^2 \frac{KT}{h} \exp^{\Delta S^* / R}$ ⁽¹⁰⁸⁾

where R and T have their usual significance and K is the Boltzmann constant, ΔS^* is the entropy change associated with a unit diffusion step and h is the Planck constant.

However, there appears to be a critical size of penetrant for a given polymer; above the critical value, penetrant size seems to have little effect on E_D ⁽¹⁰⁶⁾; but below it there appears in some cases to be an almost linear correlation between E_D and penetrant molecular diameter.⁽¹⁰⁹⁾ Branching in the molecular structure of the penetrant is another important factor.⁽¹¹⁰⁻¹¹¹⁾

2.74 Nature Of The Polymer

The correlation between the diffusivity of gas and the nature of the polymer is very complicated since it is impossible to change any feature of the polymer without affecting others.

Stannett⁽¹¹²⁾ has given an excellent review on the effect of the nature of the polymer on the diffusion process. Briefly, since density can be regarded as a measure of the "looseness" of the polymer, then generally the lower the density the higher the rate of permeation and diffusion.

Other factors that will effect the diffusion process, are the addition of plasticizers, degree of cross-linking and crystallinity. The addition of plasticizer to a polymer membrane effectively lowers the glass transition temperature and increases the diffusivity. The increase in degree of crosslinking on the other hand, decreases the diffusivity due to the decrease in mobility of some of the polymer chains. The permeability will also decrease as the degree of crosslinking increases, however, crosslinking has little effect on the solubility.

Finally, the crystallites in polymers also act as giant crosslinks which tend to immobilize the chains thus reducing any flow through the chains. This subject has been studied in detail by Michaels et al.⁽¹¹³⁾ and other authors.^(114,115)

2.8 Dual Mode Sorption in Glassy Polymers

To account for the isotherm shape in the glassy state Barrer et al. proposed that the dissolution mode be described by Henry's law and the microvoid sorption by the Langmuir isotherm equation. The development of the dual mode sorption theory has been reviewed several times^(85,86,116-118) and is only discussed here briefly.

Essentially the equilibrium sorption isotherm is represented as:-

$$C = C_D + C_H \quad (2.22)$$

$$= k_D p + \frac{C'_H b p}{1 + b p} \quad (2.23)$$

C_D represents the concentration of the dissolved species and k_D is the Henry's law solubility coefficient in $(\text{cm}^3(\text{stp})/\text{cm}^3 \text{cmHg})$. C_H represents the concentration of the microvoid component to the sorption where C'_H is the hole saturation constant in $(\text{cm}^3(\text{stp})/\text{cm}^3)$. b is the hole affinity constant (cmHg^{-1}) and represents the ratio of the rate constants for sorption and desorption of penetrant in the holes.

At sufficiently high pressures, $b p \gg 1$, a linear asymptote is approached corresponding to the saturation of Langmuir sites and equation (2.23) reduces to:-

$$C = k_D p + C'_H \quad (2.24)$$

At low pressures such that $b p \ll 1$ equation (2.23) reduces to Henry's law.

$$C = k_D p + C'_H b p = k p \quad (2.25)$$

$$\text{where } k = k_D + C'_H b \quad (2.26)$$

The dual mode sorption parameters, k_D , C'_H and b , may be determined by a graphical analysis of the sorption isotherm⁽¹¹⁸⁾. The parameter k_D can be determined from the limiting high

pressure slope of the isotherm using equation (2.24) and extrapolating the linear portion back to the concentration axis, gives the hole saturation constant as the intercept. Once k_d is evaluated, C_D follows as a function of pressure and hence from equation (2.22) C_H is obtained as a function of pressure by subtraction of C_D from C .

By rearranging the Langmuir part of equation (2.23) in the form

$$\frac{1}{C_H} = \left[\frac{1}{C_H' b} \right] \frac{1}{p} + \frac{1}{C_H'} \quad (2.27)$$

and constructing a plot of $\frac{1}{C_H}$ vs $\frac{1}{p}$, the hole affinity parameter b is obtained. The main drawback of the above method is in ensuring the equilibrium sorption isotherms have been measured at pressures sufficiently high for the limiting linear region of the isotherm to be established accurately.

A more accurate method of determination of the dual mode sorption parameters has been developed by Koros et al.⁽¹¹⁹⁾ and more recently by Barrie et al.⁽¹²⁰⁾ This method involves evaluation of the parameters by the non-linear regression analysis of the sorption isotherm.

The temperature dependence of k_D , given by:-

$$k_D = k_{D_0} \exp (- \Delta \bar{H}_D / RT) \quad (2.28)$$

Where $\Delta \bar{H}_D$ is the enthalpy change in transferring one mole of

sorbate from the gas phase to the dissolved state. As indicated the heat of dissolution for the glassy state is generally more exothermic than for the rubbery state, since some of the sorption occurs in pre-existing microvoids.

The temperature dependence of b is given by

$$b = b_0 \exp(-\Delta\bar{H}_H/RT) \quad (2.29)$$

where $\Delta\bar{H}_H$ is the heat of sorption in the microvoids.

The overall heat of sorption $\Delta\bar{H}_s$ which is generally dependent on concentration can be evaluated using the Clapeyron-Clausius equation

$$\left[\frac{\partial \ln p}{\partial 1/T} \right]_C = \frac{\Delta\bar{H}_s}{R} \quad (2.30)$$

In the Henry's law limit ($p \rightarrow 0$),

$$\Delta\bar{H}_s = \frac{k_D}{k} \Delta\bar{H}_D + \frac{k_H}{k} \Delta\bar{H}_H \quad (2.31)$$

From eqn. 2.26 $k_H = C_H b$

2.9 Dual Mode Transport

It is assumed that local equilibrium is maintained between the dissolved species of the penetrant and those species sorbed in the microvoids at all times throughout the medium. Also the earlier developments of the model regarded the penetrant sorbed according to the Langmuir mode as totally immobilized.⁽¹²¹⁾ The contribution to the total flux is solely from the dissolved species and may be written as:

$$J = -D_D \frac{\partial C_D}{\partial x} = -D \frac{\partial c}{\partial x} \quad (2.32)$$

Where D is the experimentally determined diffusion coefficient and D_D is the diffusion coefficient of the dissolved species which is independent of concentration.

Therefore from equation (2.32), it follows that

$$D = D_D \frac{\partial C_D}{\partial c} \quad (2.33)$$

The differential $\frac{\partial C_D}{\partial c}$ is easily evaluated from partial

differentiation w.r.t. p of equation 2.23

$$\frac{\partial C_D}{\partial c} = \frac{\partial C_D}{\partial p} \frac{\partial p}{\partial c} = \frac{k_D}{k_D + C_H b / (1 + bp)^2} \quad (2.34)$$

Substituting (2.33) into (2.34) yields

$$D = D_D \left[1 + \frac{C_H b}{k_D (1 + bp)^2} \right]^{-1} \quad (2.35)$$

The two limiting cases of low and high pressure are such that when $p \longrightarrow 0$

$$D = D_D \left[1 + \frac{C_H b}{k_D} \right]^{-1} = D_D k_D / k \quad (2.36)$$

and when $p \longrightarrow \infty$

$$D = D_D \quad (2.37)$$

i.e. at sufficiently high pressures the experimentally measured diffusion coefficient is identified with the diffusion coefficient of the mobile species.

In the present study, measurements were not made at sufficiently high pressures for D_D to be determined. The permeability is given by (eqn. (2.8))

$$\bar{P} = \bar{D} \frac{C}{P} \quad (2.38)$$

where $\bar{D} = \frac{1}{C_0} \int_0^{C_0} D dC$. It follows from eqn. 2.35 and 2.23 that

$$\bar{D} = \frac{P}{C} D_D k_D$$

$$\text{and so } \bar{P} = D_D k_D \quad (2.39)$$

The permeability is therefore independent of pressure.

A detailed account of the dual mode transport model has been given by Vieth and Sladek.⁽¹²¹⁾

In later developments⁽¹²⁴⁾ the constraint of total immobilization of the Langmuir component was removed. The flux is then written formally as

$$J = -D \frac{\partial C}{\partial x} = -D_D \frac{\partial C_D}{\partial x} - D_H \frac{\partial C_H}{\partial x} \quad (2.40)$$

so that

$$D = D_D \frac{\partial c_D}{\partial c} + D_H \frac{\partial c_H}{\partial c} \quad (2.41)$$

and so

$$D = (D_D - D_H) \frac{\partial c_D}{\partial c} + D_H \quad (2.42)$$

Koros et al.^(118,122-123) later developed an expression for the permeability which is now pressure dependent and is given by

$$P = k_D D_D \left[1 + \frac{FK}{1 + bp} \right] \quad (2.43)$$

Where $F = D_H/D_D$ and $K = C'_H/k_D$. In the limit of total immobilization, $D_H=0$ and equation (2.43) reduces simply to equation (2.39). Also in the limit of high pressure $P = k_D D_D$.

Evaluation of D_D and D_H is possible using sorption kinetic or high pressure permeability data. A molecular interpretation of the possible steps in the diffusion process were given by Chen et al.⁽¹²³⁾ They considered that four unit jumps steps contributed to the overall process, namely, jumps in the dissolved state, jumps from dissolved state into microvoids, jumps from microvoids into dissolved state and jumps from microvoids to microvoid.

Barrer⁽¹²⁵⁾ from a quantitative analysis of these four different jump processes showed that the flux could be expressed normally as in equation (2.40). The diffusion coefficients D_D

and D_H however are not simply related to a single unit process.

The dual mode sorption model has been extensively applied and has satisfactorily represented the solubility, steady-state and transient transport of gases and vapours in a number of glassy polymers. However the temperature dependence of the hole saturation constant C_H' as the temperature is raised towards T_g still remains unresolved. For example, Koros et al.⁽⁹¹⁾ measured the sorption of carbon dioxide in poly(ethylene terephthalate) at various temperatures and found that the hole saturation constant, C_H' approached zero as the temperature was raised to the glass transition. This suggested that the microvoid component to the sorption decreases to zero as the transition temperature is approached. A similar effect was reported for poly(carbonate) polymer^(126,119) and has been observed by other authors for gas and vapour sorption in many glassy polymers^(127,117). The variation of C_H' through annealing the polymer sample close to its T_g or conditioning it with high penetrant pressures prior to the sorption experiment has also been studied. Chan and Paul⁽¹³¹⁾ annealed a sample of polycarbonate at 135°C (close to its $T_g \approx 145^\circ\text{C}$) for a day, and observed a reduction in the Langmuir component in the sorption of CO_2 . Annealing sheets of poly(acrylonitrile)⁽⁹⁴⁾ and poly(styrene)⁽¹³²⁾ below their respective glass transition temperatures also showed the same effect. An opposite effect was observed on conditioning the sheet of poly(ethylene terephthalate)⁽⁹¹⁾ and poly(carbonate)⁽¹³³⁾ at high carbon dioxide pressures. It was suggested that carbon dioxide dilated the polymer structure which

resulted in an increase in the hole saturation constant C_H' . However, for both cases k_D and b remained relatively unchanged. The same effect has been reported for sorption of sulphur dioxide in Kapton poly(imide)⁽¹³⁴⁾, carbon dioxide in cellulose acetate⁽¹³⁵⁾ and for various gases in poly(phenylene oxide).⁽¹³⁶⁾ The sorption in the above polymers was described in terms of the partial immobilization model.

More recent application of the dual mode sorption theory has been the prediction of the permeabilities⁽¹³⁷⁾ of gases in a mixture from the single component dual mode sorption parameter, and of the isotherms⁽¹³⁸⁾ of mixed gases using a model based on dual mode sorption theory which includes competition between the two penetrants for Langmuir sites in the polymer. As interest grows in the application of polymer membranes to gas separation, mixed permeation and sorption^(139,140-142) is now receiving considerable attention. Excellent agreement between the experimental results and model prediction was reported for mixed gas sorption and transport in glassy polymers when nonideality in the gas phase was taken into account.^(123,143)

As indicated above, the dual mode sorption theory has had considerable success in modelling sorption and transport data for single component glassy polymers. However, the use of dual mode theory for gas sorption and transport in polymer blends has also attracted interest.^(184, 199, 200) The variation of the dual mode parameters, k_D , C_H' and b , with blend composition has been demonstrated.

Raucher, Sefcik and co-workers⁽¹⁴⁸⁻¹⁵⁰⁾ have recently proposed an alternative gas - polymer - matrix model which describes the sorption and diffusion process in glassy polymers. Briefly, the matrix model assumes that (a) there is only one population of sorbed gas molecules in polymers at any pressure, (b) the physical properties of the polymers are perturbed by the presence of sorbed gas and (c) the perturbation of the polymer matrix arises from gas-polymer interaction. The equilibrium sorption isotherm is represented by

$$C = \frac{\theta_o \cdot p}{1 + \chi c} \quad (2.44)$$

The concentration dependent diffusion coefficient is given by

$$D_{(c)} = D_o (1 + \beta c) \quad (2.45)$$

χ , β are constants and θ_o , D_o are the solubility and diffusion coefficient in the limit of zero concentration respectively. The resulting permeability is given by

$$P = D_o \theta_o \cdot \frac{1 + \beta c}{1 + \chi c} \quad (2.46)$$

Barbari et al⁽¹⁵¹⁾ measured the sorption of N_2 , CH_4 & CO_2 gases in various amorphous polymers based on bisphenol A and analysed the data in terms of the dual-mode sorption model and the gas-polymer matrix model. They concluded that the former provided a better fit of the experimental sorption isotherms compared with the gas-polymer matrix model. This was a result of the dual mode

sorption containing three adjustable parameters compared to the gas-polymer matrix with only two. Furthermore, the parameters from the dual mode model could easily be correlated with both gas and polymer properties. A weakness of the matrix model is that the choice of equation 2.44 and 2.45 is somewhat arbitrary and apparently does not rest on any model for the sorption and transport process in the glassy state.

2.10 Transport Models for Heterogeneous and Homogeneous Media

Heterogeneous polymer systems include block and graft copolymers, partially crystalline polymers, filled polymers, fibre-reinforced plastic and immiscible or partially immiscible polymer blends. Models for gas transport in heterogeneous media have been derived by analogy with the earlier developments of electrical permittivity, electrical conductance and thermal conductivity. Detailed reviews of the various models are given elsewhere.⁽¹⁵²⁻¹⁵⁴⁾ In the following section, a few models have been selected for discussion and are confined to dispersions of one phase in a continuum of another. The following notations are used:-

P_m : The permeability of the composite media.

P_c : The permeability of the continuous phase.

P_d : The permeability of the disperse phase.

ϕ_c : Volume fraction of the continuous phase.

ϕ_d : Volume fraction of the dispersed phase.

Maxwell⁽¹⁵⁵⁾ derived an exact expression for a single sphere embedded in a continuous medium which has been applied to a

dilute dispersion of identical spheres in a continuous phase. The separation between spheres is sufficient to prevent any mutual perturbation of fluxes.

The permeability of the medium is given by

$$P_m = P_c \frac{P_d + 2P_c - 2\phi_d (P_c - P_d)}{P_d + 2P_c + \phi_d (P_c - P_d)} \quad (2.47)$$

The Maxwell expression is found to be valid for small volume fractions up to 0.1 but may be a fair approximation up to volume fractions approaching 0.5 of the disperse phase.

When $P_c \gg P_d$ equation (2.47) reduces to

$$P_m = P_c \cdot 2(1-\phi_d)/(2+\phi_d) \quad (2.48)$$

When $P_d \gg P_c$ equation (2.47) reduces to

$$P_m = P_c \cdot (1+2\phi_d)/(1-\phi_d) \quad (2.49)$$

There have been a number of extensions and modifications to the Maxwell model by other authors, ⁽¹⁵⁶⁻¹⁵⁹⁾ for example the following:

Bruggeman ⁽¹⁵⁹⁾ allowed for the interaction between fluxes as the volume fraction of the disperse phase increased and obtained

$$\phi_c = \frac{(P_d - P_m)}{(P_d - P_c)} \left[\frac{P_c}{P_m} \right]^{1/3} \quad (2.50)$$

Since the Bruggeman expression was an extension of the Maxwell model, it simplified to give, when $P_c \gg P_d$

$$P_m = P_c \cdot \phi_c^{3/2}$$

$$\text{and when } P_d \gg P_c \quad (2.51)$$

$$P_m = P_c / (1 - \phi_d) \quad (2.52)$$

This expression also allows for the disperse phase to comprise a large range of domain sizes, but does not correspond to any specific, well defined structure.

Higuchi^(157,158) also allowed for the interaction of fluxes and neighbouring spheres for a random dispersion of spherically uniform particles. His expression was

$$P_m = P_c \frac{(P_d + 2P_c - X) - \phi_d(2P_c - 2P_d - X)}{(P_d + 2P_c - X) + \phi_d(P_c - P_d + X)} \quad (2.53)$$

$$\text{where } X = k (P_d - P_c)^2 / (2P_c + P_d)$$

The parameter k is the radial distribution function for a random dispersion of spheres and is a function of volume fraction but is generally unknown. Higuchi found the expression to be relatively insensitive to k , and a value of $k = 0.78$ gave a good fit to the experimental data in a wide range of systems. For $k=0$, in the limit where particle-particle interactions are absent, ie in the limit of infinite dilution, the Higuchi expression reduces to Maxwell's model. A weakness of eqn. (2.52) is that it does not reduce to the Maxwell expression for a dilute dispersion.

The limiting cases for this model are

When $P_c \gg P_d$

$$P_m = P_c \cdot 3.22\phi_c / (6 - 2.78\phi_c) \quad (2.58)$$

and when $P_d \gg P_c$

$$P_m = P_c \cdot (3 - 2.78\phi_c) / 0.22\phi_c \quad (2.55)$$

Böttcher⁽¹⁶⁰⁾ derived the following expression for a dispersion of ellipsoidal or spherical particles.

This expression is of interest in that unlike the Maxwell, Higuchi models it is symmetric with respect to the disperse and continuous phase and so is applicable in principle over the whole of the component range.

$$P_m - P_c = 3 P_m \phi_d \frac{(P_d - P_c)}{(P_d + 2P_m)} \quad (2.56)$$

The simplest, empirical model applicable to a homogeneous mixture was suggested by Lichtenecker⁽¹⁶¹⁾ and was later justified by Lichtenecker and Rothér⁽¹⁶³⁾ and is given by:-

$$\ln P_m = \phi_c \ln P_c + \phi_d \ln P_d \quad (2.57)$$

Paul⁽¹⁶²⁾ has developed models for gas transport in homogeneous blends in terms of activated state theory and free volume theory.

Treating diffusion through polymer as an activated process one has equation (2.19)

$$D = D_0 \exp(-E_D/RT)$$

where E_D is the activation energy for diffusion and D_0 is a pre-exponential factor. Assuming that the activation energy for the blend can be expressed as

$$E_D = \phi_1 E_{D_1} + \phi_2 E_{D_2} + \Delta E_{12} \quad (2.58)$$

where subscripts 1 and 2 denote the pure components and ΔE_{12} accounts for the departure from the simple additivity relationship.

The following empirical relation has also been established between the activation energy and the pre-exponential term. (165,226,227)

$$\ln D_0 = a E_D + b \quad (2.59)$$

where a and b are constants.

Inserting eqn (2.58) into (2.19) and (2.59) yields

$$\ln D = \phi_1 \ln D_1 + \phi_2 \ln D_2 + (a RT - 1) \Delta E_{12}/RT \quad (2.60)$$

The solubility coefficient for a mixture has been shown to be related to those of the components by equation (1.33) by the ternary solution theory.

$$\ln k_{3b} = \phi_1 \ln k_{31} + \phi_2 \ln k_{32} + \frac{BV_3 \phi_1 \phi_2}{RT} \quad (1.33)$$

Where $B = V'_{12} RT/v_3$, is the binary interaction parameter mixing of component 1 and 2, and V_3 is the molar volume of the penetrant.

Since $P = Dk$, combining eqn (2.60) and (1.31) yields

$$\ln P = \phi_1 \ln P_1 + \phi_2 \ln P_2 + (aRT - 1) \frac{\Delta E_{12}}{RT} + \frac{BV_3}{RT} \phi_1 \phi_2 \quad (2.61)$$

Equation (2.61) reduces to the Lichtenecker expression when the transport and thermodynamic interaction parameter terms, ΔE_{12} and B are both zero. Furthermore, B takes on negative values (1,129,164) for miscible blends of high molecular weight, thus giving rise to a decrease in the solubility coefficient relative to the weighted geometric mean defined by the first two terms in equation (1.33). A positive value of B would increase the solubility coefficients and this behaviour is possible for random co-polymers. A typical value for B is in the order of $\pm 20.92/\text{cm}^3$. McGregor⁽¹⁶⁵⁾ has shown that for many polymers, aRT takes a value in the region 1.67 to 2.09 hence $(aRT - 1)$ is about -2.09. Hence depending on the magnitude and the energetic interactions between the component polymers, one might expect a homogeneous multicomponent system to deviate from equation (2.61) in either direction. However, miscible blends are expected to fall below the predicted line.

The transport behaviour of a mixture in terms of free volume concepts has appeared in various forms. In one of the simplest approaches proposed by Lee⁽¹⁶⁶⁾, the permeability was given by

$$P = A e^{-B/(V - V_0)} \quad (2.62)$$

where A and B are constants, V is the specific volume of the

polymer and V_o is the volume "occupied" by the polymer chains. To formulate a mixtures rule for a multicomponent polymer system from equation (2.62) it is necessary to know the variation in free volume, $(V-V_o)$ with composition.

It is assumed that the free volume for the mixture follows the additive relationship,

$$(V-V_o) = \phi_1 (V-V_o)_1 + \phi_2 (V-V_o)_2 \quad (2.63)$$

Inserting equation (2.63) into (2.62) and rearranging yields

$$\ln (P/A) = \left[\frac{\phi_1}{\ln (P_1/A)} + \frac{\phi_2}{\ln (P_2/A)} \right]^{-1} \quad (2.64)$$

It can be shown that when $\ln A \gg \ln P$ or $\ln P_i$ equation (2.64) reduces to the simple Lichtenecker expression. However, in most cases the value of $\ln A$ is not sufficiently high enough to permit the use of the simple form. It is of interest that equation (2.64) predicts positive deviations from equation (2.57).

However, for miscible blends when there is strong interactions between dissimilar chains then in general a loss of free volume is observed on mixing.⁽¹⁶⁷⁾ Equation (2.63) is now replaced by

$$(V - V_o) = \phi_1 (V - V_o)_1 - \phi_2 (V - V_o)_2 + \Delta V_{\text{mix}} (\phi_1) \quad (2.65)$$

where $\Delta V_{\text{mix}} (\phi_1)$ allows for a small negative volume change on mixing. The permeability thus becomes

$$\ln (P/A) = \left[\frac{\phi_1}{\ln(p_1/A)} + \frac{\phi_2}{\ln(P_2/A)} - \frac{\Delta V_{\text{mix}}(\phi_1)}{B} \right]^{-1} \quad (2.66)$$

In general for a heterogeneous blend a plot of P (or $\log P$) against ϕ_1 (or ϕ_2) will be sigmoidal in shape as a result of phase inversion which will usually occur around a composition of $\phi_1 = 0.5$. With homogeneous blends the corresponding plot may follow the Lichtenecker expression or deviate from it in either direction but the variation of P with composition is generally monotonic.

The literature published on the transport of gases through polymer blends has been extensive in the last few years. All these studies have been involved with blends of three different categories, namely (a) purely rubbery blends, (b) blends that are rubbery over part of the composition range and glassy over the remainder and (c) glassy over the entire composition range. In the following section, a literature survey is given of the studies carried out in blends in the above categories.

Ranby and co-workers were the first to study gas transport in mechanically prepared miscible polymers.⁽¹⁶⁸⁾ In all of the studies polyvinyl chloride (PVC) was one of the components. Gas transport in miscible blends of PVC and ethylene-vinyl acetate copolymer EVA-45 prepared mechanically by milling the polymers together at high temperature, was studied. The permeabilities of helium, argon and carbon dioxide were widely scattered and when plotted against weight fraction, an S-shaped trend was obtained. This suggested that the blends were immiscible and showed that

phase inversion occurred when the EVA-45 content was about 6%; EVA-45 was believed to form the continuous phase even at such low levels by covering the available surface area of the PVC particles. Phase separation may have been induced by the high temperature used during processing.

In a later study Shur and Ranby⁽¹⁶⁹⁾ showed that the miscibility of PVC and EVA was improved when the vinyl acetate content of the EVA was increased to 65% as opposed to 45% in the earlier study. Blends of PVC and EVA-65 exhibited a single composition-dependent glass transition temperature consistent with miscibility. Further confirmation came from the densities which were higher than calculated from volume additivity and from the permeabilities of O_2 and N_2 which were lower than those estimated from the Lichtenecker expression.

Similar behaviour was observed for the permeation of He, O_2 , N_2 and CO_2 in blends of PVC with Acrylonitrile-Butadiene copolymer (NBR).^(170,171) As the acrylonitrile (AN) content of the copolymer was increased plots of $\log P$ ($\log D$) against blend composition approached linearity whereas at low levels of AN, there was indication of phase inversion. The corresponding permeability-composition plots for several gases in blends of PVC and chlorinated polyethylene (CPE) also approached linearity and the phase inversion was observed at low levels of chlorination. For blends of PVC and Acrylonitrile-Butadiene-styrene (ABS) copolymer, the permeation data suggested that the system was heterogeneous.⁽¹⁷³⁾

Finally for blends of PVC and poly(ϵ -caprolactone), the

permeability-composition plots were linear, consistent with miscibility. Analysis of this system was complicated by the fact that the blends were rubbery over part of the composition range and glassy over the remainder. A further complicating factor in a number of these studies was the presence of crystallinity.

The effect of crystallinity on gas permeation in miscible blends of polycarbonate and a copolyester (composed of 1,4-cyclohexane dimethanol and a mixture of terephthalic and isophthalic acid units) was reported by Preston et al.⁽¹⁷⁵⁾ The permeability of CO₂, CH₄ and He in both annealed and unannealed samples was measured and owing to crystallization of the copolyester, the permeability of annealed specimens showed a progressively larger decline relative to the unannealed film as the copolymer content of the blends increased.

The relative rates of permeation varied greatly with blend composition, but for a given pair of gases the selectivities were essentially the same for the totally amorphous or semi-crystalline polymers.

The permeation behaviour of CO₂ and O₂ in heterogeneous blends of Polystyrene (PS) and Poly(1,1,1-tris(trimethylsiloxy) methylacrylate propylsilane (PTMPS) was studied by Kang et al.⁽¹⁷⁶⁾ The permeability coefficient for both gases increased rapidly with increasing content of PTMPS in the blends, however, the selectivity calculated from the ratio of the permeabilities of CO₂ and O₂ approached unity. It was also reported that the addition of graft copolymer (prepared by the reaction of PTMPS

and styrene monomer) improved the compatibility and the permselectivity but at the expense of a reduced permeability.

Barnaboes et al.⁽¹⁷⁷⁾ investigated the transport of CO₂ and O₂ in poly(methylacrylonitrile-styrene) block and random copolymers. For random copolymers there was reasonable agreement with the Lichtenecker expression (equation (2.57)) but with a small positive deviation. For the block copolymers plots of log P against composition were sigmoidal, indicating a heterogeneous system. Paul⁽¹⁶²⁾ analysed these data further in terms of equation (2.64) based on additivity of free volume and obtained an excellent agreement between the experimental and predicted values using the appropriate values of A from Lee's results.⁽¹⁶⁶⁾

The transport of hydrocarbon vapours for a series of heterogeneous graft copolymers and also block copolymers of polydimethylsiloxane (PDMS) containing polystyrene was studied by Barrie and Munday.⁽¹⁹⁸⁾ In these blends PDMS comprised the continuous phase and good agreement was obtained well with various heterogeneous models. The activation energies for a given penetrant were virtually constant for the blends and were equal to that of PDMS suggesting that the transport was governed by the continuous PDMS phase. Sorption in the graft copolymers followed the dual mode sorption mechanism, particularly at low pressures and with high PS content. However, the sorption in block copolymers were linear in all cases with no curvature even at low pressures. The relatively low glass transition temperature of the PS phase in the block copolymers may be responsible for the absence of a Langmuir component.

Barrie and Ismail⁽¹⁷⁹⁾ studied the transport of propane in heterogeneous blends of poly(dimethyl siloxane) and poly(ethylene-co-propylene) elastomers. The solubility coefficient and the heat of sorption followed the simple additivity relationship. The permeability coefficients were pressure independent and were in agreement with the various heterogeneous models.

The sorption and diffusion of propane in alternating block copolymers of poly(bisphenol-A carbonate) (BPAC) and Poly(dimethylsiloxane) (PDMS) in terms of blend composition and PDMS block length were studied by Barrie and Williams.⁽¹⁸⁰⁾ These systems are essentially heterogeneous and consist of BPAC domains dispersed in PDMS-rich continuum. The continuum is not pure PDMS as some BPAC units are incorporated in it. In general the permeability-composition curve for a given PDMS block length lay below that predicted by the Maxwell-type expressions. The departure from the Maxwell-type expressions became more pronounced as the PDMS block length increased. This was explained as due to the changing nature of the continuous phase brought about by incorporation into it of varying amounts of BPAC units.

Barbier⁽¹⁸¹⁾ studied the transport of nitrogen in blends of natural rubber and various synthetic elastomer. The permeability results indicated good agreement with the Maxwell model for blends of natural rubber and butadiene-acrylonitrile copolymer containing 25% w/w acrylonitrile with natural rubber as the disperse phase. Ziegel⁽¹⁸²⁾ showed several poly(urethanes) to be

heterogeneous by gas transport studies.

Blends of cellulose nitrate and Polyethylene glycol (PEG)⁽¹⁸³⁾ exhibited a single composition dependent glass transition temperature and the permeability coefficient for N_2 , O_2 and CO_2 increased with increasing PEG content while the selectivity ratio P_{CO_2}/P_{N_2} remained constant. This behaviour is common as any increase in permeability is generally at the expense of lower selectivity.

Masi et al.⁽¹⁸⁴⁾ reported on the gas sorption and transport in blends of polycarbonate and a copolyester made from 1,4-cyclohexane-methanol and mixture of terephthalic and isophthalic acids. Density data suggested that the additivity of volumes was valid for this system. However, application of equation (2.64) gave a permeability-composition curve lying about the Lichtenecker line (equation (2.57)) where as the experimental results showed strong negative deviations.

The solubility and diffusion of propane in blends of Polystyrene and Poly(vinyl methyl ether) at temperature above the glass transition temperature and low diffusant pressures was studied by Spencer et al.⁽¹⁸⁵⁾ The solubilities were described by Henry's law as expected for rubbery polymers and the diffusion was characterized by Fick's equation with concentration independent diffusion coefficients. The permeability coefficient followed the linear relationship (equation (2.57)) when plotted against blend composition.

Webb et al⁽⁵⁹⁾ reported the transport of CO₂ and CH₄ through miscible blends of ethylene vinylacetate copolymer (EVA-45) and chlorinated polyethylene (H-48). Miscibility was established by differential scanning calorimetry (DSC) and also by dynamic mechanical thermal analysis. The deviation of specific volume for the blends from the additivity line was insignificant and suggested a weak interacting system. The solubility coefficients analysed in terms of the Flory-Huggins solution theory showed a slight negative departure from the theoretical values suggesting a small negative value for χ'_{12} (interaction parameter). The permeability of CO₂ was independent of the ingoing pressure. The permeation data were tested in terms of the free-volume theory and the simple additivity rule as applied to miscible blends.

Sorption and transport of various gases (He, Ar, N₂, CH₄, CO₂) at high pressures in miscible blends of Poly(methyl acrylate) and Poly(epichlorohydrine) were reported by Chiou et al.⁽¹⁸⁶⁾ The permeability coefficients for He, Ar, N₂, CH₄ remained constant with ingoing pressure, whereas those for CO₂ increased with ingoing pressures. This was caused by concentration dependent increase of the diffusion coefficient, since the solubility coefficients were found to be independent of equilibrium sorption pressure, ie sorption obeyed Henrys law. All these parameters, namely solubilities, diffusion coefficients and permeabilities for these gases followed a simple additivity rule, equations (1.33), (2.60) and (2.57).

Chiou and Paul⁽¹⁸⁷⁾ reported the sorption and transport of CO₂ at high pressures in miscible blends of Poly(vinylidene fluoride)

(PVF₂) and Poly(methyl methacrylate) (PMMA) at 35°C. Blends rich in PMMA were glassy and blends rich in PVF₂ were rubbery. Thus the sorption isotherms at high PVF₂ content were linear and at high PMMA were concave to the pressure axis as expected for glassy polymers. However, the sorption in the intermediate blends was more complex with the initial stage of the isotherm (at low pressures) concave to the pressure axis and linear at higher pressures. It was proposed that CO₂ acts as a plasticizer reducing the glass transition temperature so that glassy blends became rubbery at sufficiently high CO₂ pressures giving rise to linear isotherms. A further complication in these systems was crystallization of PVF₂ which could be induced by CO₂ plasticization. In general the permeability decreases with pressure in glassy polymers, however in this case an increase in permeability was observed due to plasticization by CO₂.

The sorption and transport of the inert gases He, Ar, N₂ and CH₄ in the same blends was also studied by the same authors⁽¹⁸⁸⁾. The sorption isotherms were nonlinear for the glassy blend (PMMA-rich) and linear for the rubbery blends (PVF₂-rich). The Henrys law solubility coefficient showed a negative deviation from equation (1.33) and the permeabilities were independent of pressure for all blend compositions. The effect of crystallinity at high PVF₂ on both the permeability and diffusion coefficient was observed. However from the sorption and permeation behaviour it was obvious that these gases did not plasticize any of these materials in contrast to CO₂.

The effect of the addition of tricresyl phosphate (TCP), N-phenyl-2-naphthylamine (PNA) and 4,4-dichlorodiphenyl sulfone (DDS) to polysulfone on the transport and sorption properties of various gases was also studied.⁽¹⁸⁹⁾

In general, the extent of sorption in glassy polymers decreased as the measurement temperature approached the glass transition temperature. In this case the addition of diluent had the same effect on the isotherms as raising the temperature of measurements. That is, the capacity of the Langmuir mode of sorption was found to decrease monotonically with diluent addition in a fashion entirely explained by the reduction in T_g of the mixture. The permeability coefficients for CO_2 decreased as the driving pressure increased which was a typical for glassy polymers, however, in the case of 30% TCP mixture, the reverse trend was observed due to strong plasticization by CO_2 . Overall, the addition of diluent caused a significant decrease in both the permeability and mobility.

The same authors also studied the effect of antiplasticization on gas sorption and transport in Poly(phenylene oxide) (PPO) by adding a wide range of liquid diluents to PPO.^(190,191) From a mechanical point of view, it appeared that PPO did not show as strong antiplasticization behaviour as did Polysulfone, however a significant reduction in gas solubility and permeability did occur as a result of adding diluent to PPO, particularly in the case of TCP which reduced CO_2 mobility more in PPO than in Polysulfone.

Blends of Poly(methyl methacrylate) (PMMA) with bisphenol chloral polycarbonate have also been shown to be miscible over the entire composition range, using various techniques which include gas permeation.⁽¹⁹²⁾ The gas permeability of all gases studied (He, H₂, O₂, Ar, N₂, CH₄, and CO₂) were lower than those from the linear additivity rule and the extent of deviation increased with gas molecular size, and was smallest for He and largest for CH₄. The permeabilities predicted from the free volume theory were significantly higher than the measured ones. On the other hand, both the permeability and diffusion coefficient for the same gases in homogenous blends of PMMA with each of two SAN (Styrene/Acrylonitrile) random copolymers showed positive deviation from the semilogarithmic additivity rule, but was well described by the free volume theory (equation (2.64)).⁽¹⁹²⁾ This was attributed to the very weak net interaction between PMMA and SAN produced by repulsion between styrene and acrylonitrile units in the SAN random copolymer. However, in this case the solubility coefficient and the ideal separation factors followed the semilogarithmic additivity rule well. The sorption and permeation of phase separated blends were also studied which showed similar behaviour to those of the corresponding homogeneous blends.

Stalling et al.⁽¹⁹⁴⁾ characterized the transport behaviour of neon, argon and krypton at low penetrant activities through solution cast, annealed, glassy blends of poly(2,6-dimethyl-1,4-phenylene) oxide (PPO) and polystyrene (PS). The permeability data for argon and krypton, exhibited the monotonic variation

with composition expected for a homogeneous system. However, this was not so for the neon permeability, although there was a considerable amount of evidence that the PPO-PS polyblend system was completely compatible over the entire composition range. (195,196)

The sorption and transport of CO_2 gas in amorphous glassy blends of poly(phenylene oxide), PPO, and polystyrene (PS) was measured at 35°C over the entire range of blend composition. (199) The equilibrium sorption of CO_2 in the homopolymers and in the blends was well described by the dual sorption model (eqn. (2.23)). The affinity parameter, b , showed a minimum when plotted against blend composition. The Langmuir capacity parameter increased with increasing PPO content as expected and revealed that C'_H was well predicted by the notion that Langmuir sorption occurred by filling the excess volume of the glassy state with liquid like CO_2 . (91, 133, 184, 200) The Henry's law parameter (k_D) for the blend deviated markedly from a simple linear additivity rule as expected for miscible polymer blends and a reasonable value of the interaction parameter was deduced from the mixing rule (equation (1.33)). The permeability composition curve showed a strong negative deviation from the Lichtencker expression whereas the additive free-volume expression predicted a positive deviation. Some improvement was obtained by allowing for volume contraction on mixing although even here the experimental results were lower than the predicted values.

Muruganandam and Paul^(197,198) studied the gas sorption and

transport in miscible blends of tetramethyl bisphenol-A polycarbonate (TMPC) and polystyrene (PS). The sorption isotherms were non-linear as expected of glassy polymers and the Langmuir capacity parameter increased with TMPC in the blend owing to the higher T_g of TMPC than that of PS. The permeability coefficient for He, CO_2 , O_2 , CH_4 and N_2 passed through a minimum when plotted against blend composition. This behaviour was attributed to the volume change on mixing for this system. Although corrections were made for volume contraction on mixing, the deviation in the experimental permeabilities from the simple additivity and free volume theory was still greater than predicted. Similar effect were observed for the diffusion coefficient. There were slight maxima in the selectivity composition curve for He/ CH_4 , CO_2/CH_4 , O_2/N_2 gas pair. However, there were no strong advantages for gas separation offered by blending in their case.

Taylor⁽²⁰¹⁾ has recently reported on the transport and sorption of the CO_2 and CH_4 in miscible blends of Polyethersulphone (PES) and Polyethylene oxide (PEO). The sorption isotherms for CO_2 showed negative deviation from Henry's law expected for glassy polymers. However, due to the very low uptake of the CH_4 the negative deviation was not detected. The Henry's law solubility coefficients obtained from the initial slope of the isotherms showed negative departure from the simple additivity line. The permeability of both gases were independent of the ingoing pressure.

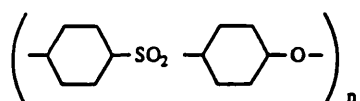
Due to the PEO being a crystalline material, problems were encountered in obtaining a film suitable for the permeation measurements. A minimum for the permeability when plotted against blend composition was observed. The average diffusion coefficients, $\bar{D}$, were calculated using equation (2.18) and were found to increase linearly with concentration. The variation of D with blend composition was not shown.

CHAPTER 3

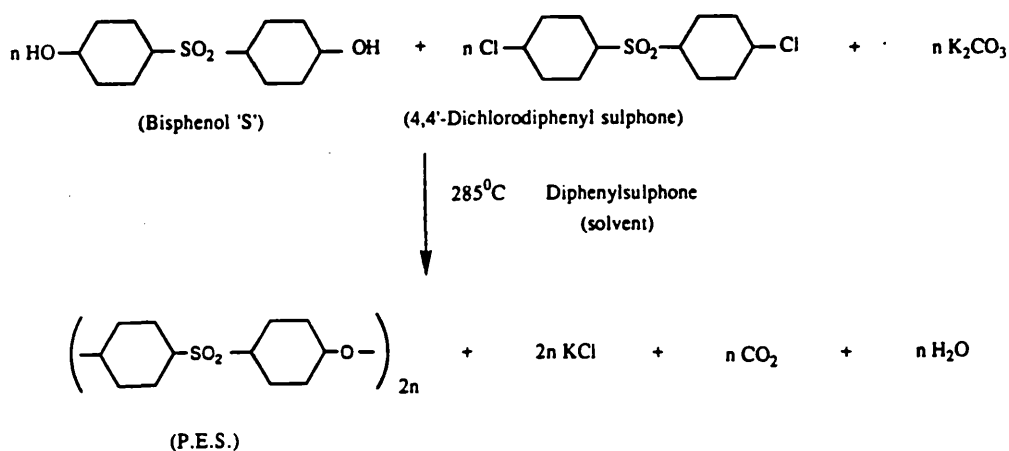
EXPERIMENTAL

3.1 Materials

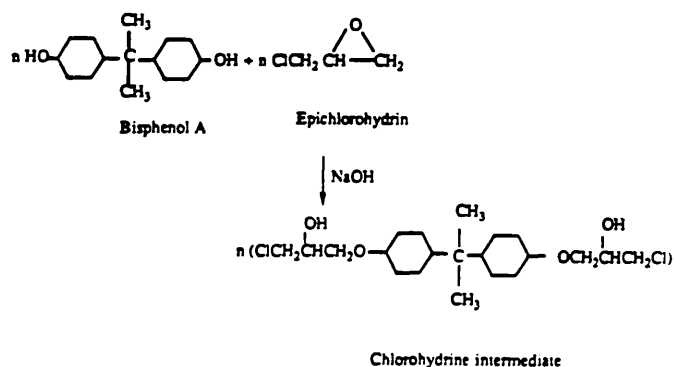
The Polyethersulfone (PES) (also referred to as Poly (oxy - 1, 4 - phenylenesulphonyl - 1, 4 - phenylene) was supplied by ICI (Victrex 200P). It has a quoted density of 1.37gcm^{-3} and a glass transition temperature, T_g , of 226°C . PES has the following repeat unit:-



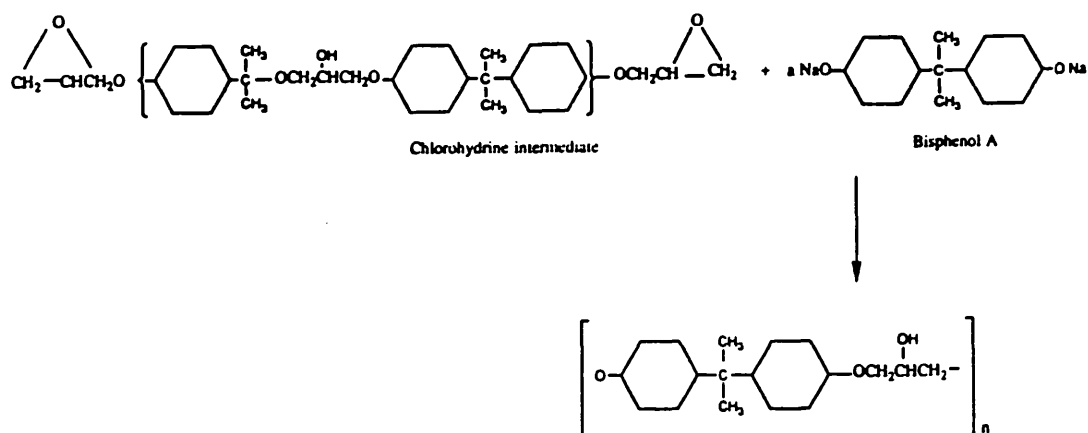
There are number of ways in which PES may be synthesized which are well described in the literature.^(202,203) These include self-condensation of certain dinuclear arylsulphonyl chlorides catalysed by ferric chloride⁽²⁰⁴⁾ and the polycondensation of halogenophenylysulphonyl phenoxide.⁽²⁰⁵⁾ A more general route used by ICI⁽²⁰⁶⁾ is the reaction of Bisphenol's with 4, 4 -Dichlorodiphenyl sulphone as shown below:-



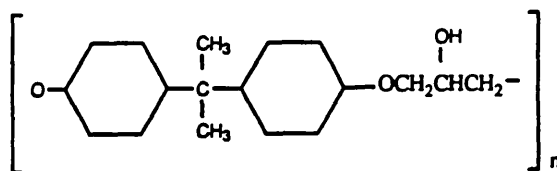
Phenoxy resins (alternatively referred to as the polyhydroxy ether of bisphenol (A)) are the reaction products of epichlorohydrin with bisphenol A. The basic reaction scheme is shown below:- (129,130)



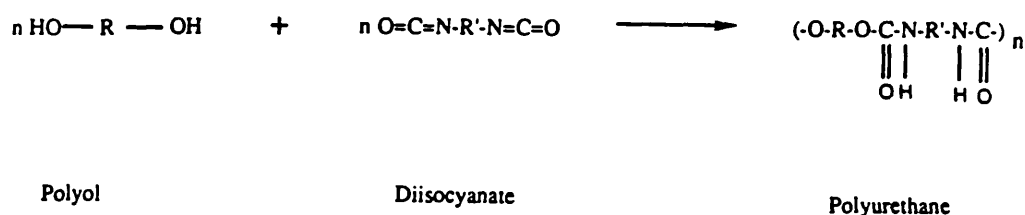
The chlorohydrine intermediate reacts with NaOH to form Diglycidylether of Bisphenol DGEBA, the raw material for the commercial synthesis of phenoxy. The DGEBA reacts with the dianion of the bisphenol to give phenoxy polymer as shown by the following reaction.



Phenoxy polymer was supplied by Union Carbide (grade PKHH) and has a density of 1.18gcm^{-3} , T_g 90°C and a repeat unit of:-



Polyurethane elastomer is a commercially synthesized material and was supplied by BP. Polyurethane results from the reaction between alcohols with two or more reactive hydroxyl groups per molecules (diols or polyols) and isocyanates that have more than one reactive isocyanate group per molecules (a diisocyanate or polyisocyanate).⁽²⁰⁷⁾ This type of polymerisation is called "addition polymerization"; and the basic reaction is given below:-



The molecular structures of polyurethane polymers vary from rigid cross-linked polymers to linear, highly extensible

elastomers. Flexible polyurethanes include, flexible foams, and many elastomers having a segmented structure consisting of long flexible chains (eg of polyether or polyester oligomers) joined by the relatively rigid aromatic polyurethane polyurea segments.

Polyurethane was supplied as a viscous liquid in Methyl ethyl Ketone (MEK) solvent. The MEK was removed by either direct evaporation under vacuum or by precipitation technique. The precipitation method was more useful as the very small traces of the MEK were easily removed by water. The solid polymer was then dried in a vacuum oven at room temperature for several weeks prior to use.

Research grade carbon dioxide and methane (purity of 99.995%) were supplied by Matheson Gas Products plc and were used without further purification.

3.2 Blend Preparation

There are three main methods of preparing homogeneous polymer blends namely, by mixing in the melt, by mixing in solution in a common solvent followed by evaporation or precipitation and by in-situ- polymerization. The technique of mixing in solution in common solvent followed by evaporation was used in this study.

Polyethersulfone (PES) and Polyhydroxyether of Bisphenol (A) resin (Phenoxy) were dried in a vacuum oven at 50°C for several days before use. Whereas polyurethane (Pu) was dried under vacuum for several weeks. Stock solutions of the pure components

were prepared separately by dissolving in dried Dimethylformamide (DMF) at room temperature to form 10-20wt% solution and then appropriate mixtures were prepared for individual blends.

Thin films were produced using the casting technique in which the polymer solution (10cm³) was filtered through a millipore filter onto a glass plate. A glass rod with tape evenly wound on both ends was then passed across the glass plate to obtain a uniform thickness. The plate was quickly placed in a desiccator to prevent any uptake of H₂O which caused phase separation and was left for 2 - 3 days in a vibration free environment.

After most of the solvent had evaporated, a clear thin film was formed on the glass surface; the film was kept under vacuum for further removal of solvent. The film was removed from the glass plate by immersing in water; left in a desiccator under vacuum for a further day and was out gassed in a vacuum oven at 40 - 50°C for several weeks prior to use.

Thermogravimetric analyses up to temperature of ~400°C indicated that the samples were completely solvent - free. The glass transition temperatures of the pure component and the PES/Phenoxy blends were measured using a DSC Du Pont 990 thermal analyser at a heating rate of 10°C/min and also using a DMTA (Polymer Laboratories) at a heating rate of 3°C/min with a strain of x1 and a frequency of 10Hz. However, the glass transition temperatures of the Pu/PES system were measured at BP Research Centre.

The densities of all of the films were measured at BP Research Centre. The method used was to find an aqueous KI solution in which a piece of the film tended neither to sink nor to float. The density of the aqueous KI was determined using a Paar DMA 60/60 2H digital density meter.

The film thickness was measured using a digital micrometer and an accuracy of $\pm 0.001^{\text{cm}}$ was obtained.

The Fourier Transform Infra Red (FTIR) spectra of the PES-Phenoxy blends and the pure component were recorded using a Mattson Instruments, ALPHA Centuri at room temperature.

Attempts to record the FTIR spectra of the PES-Pu system were unsuccessful due to the sample being relatively thick and a strong absorbance of the carbonyl band was observed.

3.3 Permeation

The permeation apparatus illustrated in Figure (3.1), was of conventional design.⁽⁷⁴⁾ The apparatus consisted of two main sections, namely the high pressure side and high vacuum side which were connected via a diffusion cell.

3.31 High pressure side

The high pressure side comprised a gas reservoir (GR), buffer volume (BV) and pressure transducer (PT). The gas reservoir contained approximately 50 cmHg of gas under study which could be frozen back after each run using the cold finger (CF) attached to the gas bulb. The buffer volume (BV) with a capacity of 1000cm^3 was used to maintain the ingoing pressure constant during the

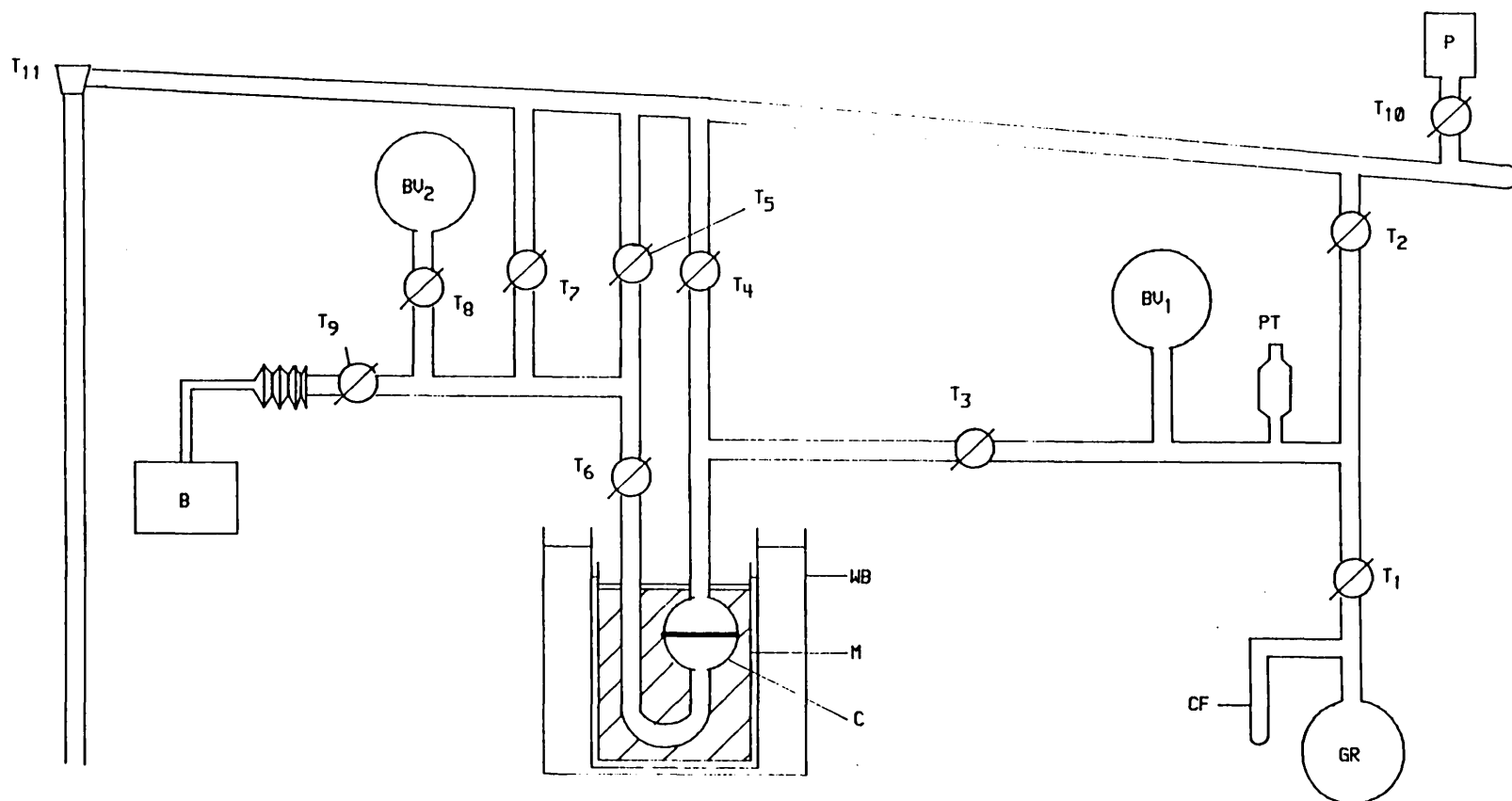


Fig. 3.1 Permeation Apparatus

course of each permeation run.

The ingoing pressure was monitored using a pressure transducer (PT) (model 4-327-0003, Bell and Howell Ltd, 0-76cmHg). The transducer was connected to a stable 10 volts (DC) power supply, and the output was monitored on a digital voltmeter (Excel XL35). The transducer was calibrated against a mercury manometer and the output was found to be directly proportional to pressure with a calibration constant of 1.103cmHg/mV. The calibration constant was checked periodically thereafter.

3.32 Low Pressure side

The low pressure side consisted of an outgoing buffer volume (BV) and a "Baraton" manometer. The buffer volume was used to maintain the outgoing pressure below 1% of the ingoing pressures. The outgoing pressure was monitored using a "Baraton" capacitance manometer (B) (MKS Type 310BHS -1, range 1 Torr) which was connected to a digital pressure indicator, type 170M-6B.

In the later stage of the research, the downstream pressure was measured using a Baraton (MKS type 96H-3E) connected via an IEEE interface microcomputer (Commodor PET 2001) which stored and analysed the data.

3.33 High Pressure Work

Pure gas permeation measurements were carried out in a constant volume apparatus. The permeation cell was of all metal construction with the membrane supported by a filter paper resting upon a fine steel mesh screen. This work was conducted

using a high pressure system at BP Research Centre.

3.4 The Diffusion Cell

The diffusion cell (C) shown enlarged in Figure (3.2) consisted of two separate parts made out of glass with an area of 3.301cm^2 . In the lower part of the cell, a piece of copper gauze (CG) was sealed using Araldite to form the support for the membrane. To prevent the seration of the membrane a piece of filter paper (FP) (Whatmen No. 4) was placed between the gauze and the membrane (M). The two sections of the cell were sealed using Araldite (A), which was also placed around the join to give extra support. The diffusion cell was glass blown on to the permeation rig and was immersed in a mercury beaker to provide an effective seal as well as a good heat transfer medium. A thin layer of silicone oil was poured onto the mercury and the top of the beaker covered with plastic film to reduce the level of Hg vapour. The mercury beaker containing the cell was placed in a water bath (as shown in Figure (3.1)) which was thermostatically controlled using a Gallenkamp Thermo Stirrer.

These three sections, namely, the high pressure side, the high vacuum side and the diffusion cell were all connected to a main vacuum line attached to which was a Pirani gauge, (Edwards G5C-2).

The whole of the system was evacuated via the main vacuum line using a mercury diffusion pump in conjunction with a rotary oil pump (Edward ES 20).

The main section of the apparatus was protected from the Hg

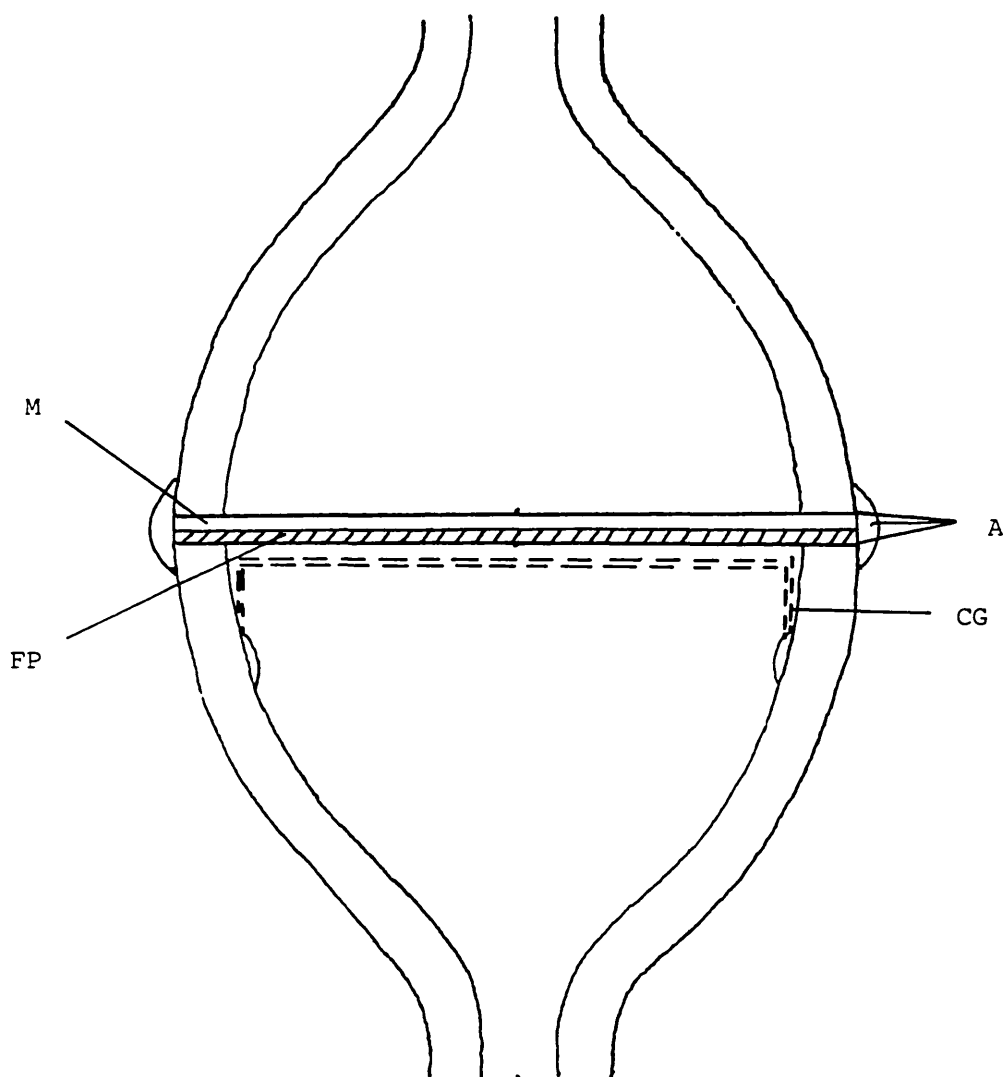


FIG 3.2 : DIFFUSION CELL

diffusion pump via a liquid nitrogen trap. The trap prevented the mercury vapour (by freezing) from entering into the main vacuum line and rest of the system.

3.5 Permeation Measurements

Prior to measurements the whole system was completely evacuated for 2 days with the cell at 50°C. The vacuum was monitored using the "Baratron".

Before the start of the first run (on a new membrane), the desired bath temperature was set using the thermo stirrer and the membrane was left to equilibrate (usually 12 hr). The outgoing volume was then measured by the gas expansion technique. Before each run, the leak rate was measured by closing taps (T_2 , T_4 , T_5 , T_7) and the build up of pressure was monitored on the "Baratron" digital output. A leak rate of less than 1/2% of the total expected flow-rate was considered to be acceptable. At the start of each run taps T_2 and T_3 were closed and a charge of gas admitted from the gas reservoir (GR) into the ingoing side of the apparatus. The pressure of the gas was monitored by the pressure transducer. Taps (T_4 , T_5 and T_7) were then closed and T_3 was opened to allow gas into the membrane and the starting time ($t = 0$) was recorded. The output on the "Baratron" was monitored as a function of time and the reading was noted at regular intervals in both the steady and transient state.

Once the steady state was reached, the penetrant was frozen back from the ingoing side into the gas reservoir using liquid nitrogen. The membrane was outgassed for a minimum period of ten

- times the estimated timelag before proceeding with the next run.

The method of calculating the Permeability, Solubility and Diffusion Coefficient is presented in Appendix (1), for CO₂ in the 50/50 blend of PES-phenoxy. High pressure permeation measurements were made at 40°C for CO₂ at pressures (0-6 bars) in Phenoxy and the 50/50 PES-Phenoxy blend.

3.6 Sorption

The sorption apparatus consisted of a vacuum line and balance assembly as shown schematically in Figure (3.3).

The vacuum line was made up of a gas reservoir (R), Pirani Gauge (P) and a pressure transducer (PT), where all have the same function as described in the section (3.31). The vacuum line was once again connected to a pumping system comprising a mercury diffusion pump backed with a rotary oil pump and was protected using a liquid nitrogen trap.

The vacuum electronic sorption microbalance (Sartorius model No. 4102) operates on the principle of automatic torque compensation. The main feature of the balance (as shown in Figure (3.4)) are the tabular quartz beam (B), the rotating coil (RC) and an oscillator coil (OC). The beam is always maintained in the null position and when displaced from the horizontal an error signal is induced in the rotating coil from the oscillator coils. This AC signal is rectified and regulated in the amplifier and fed back into the coil to enable the balance to return to null position again. This compensating current is a

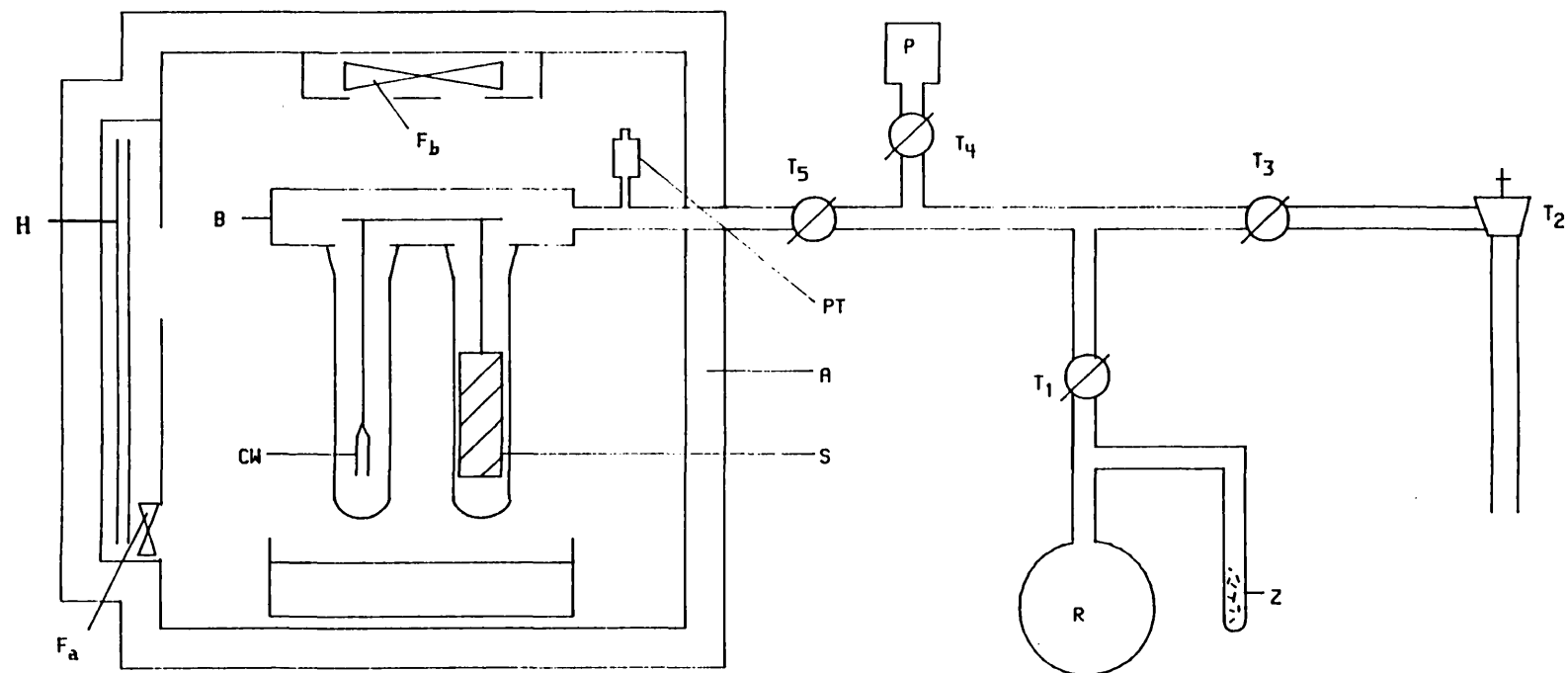


Fig. 3.3 Sorption Apparatus

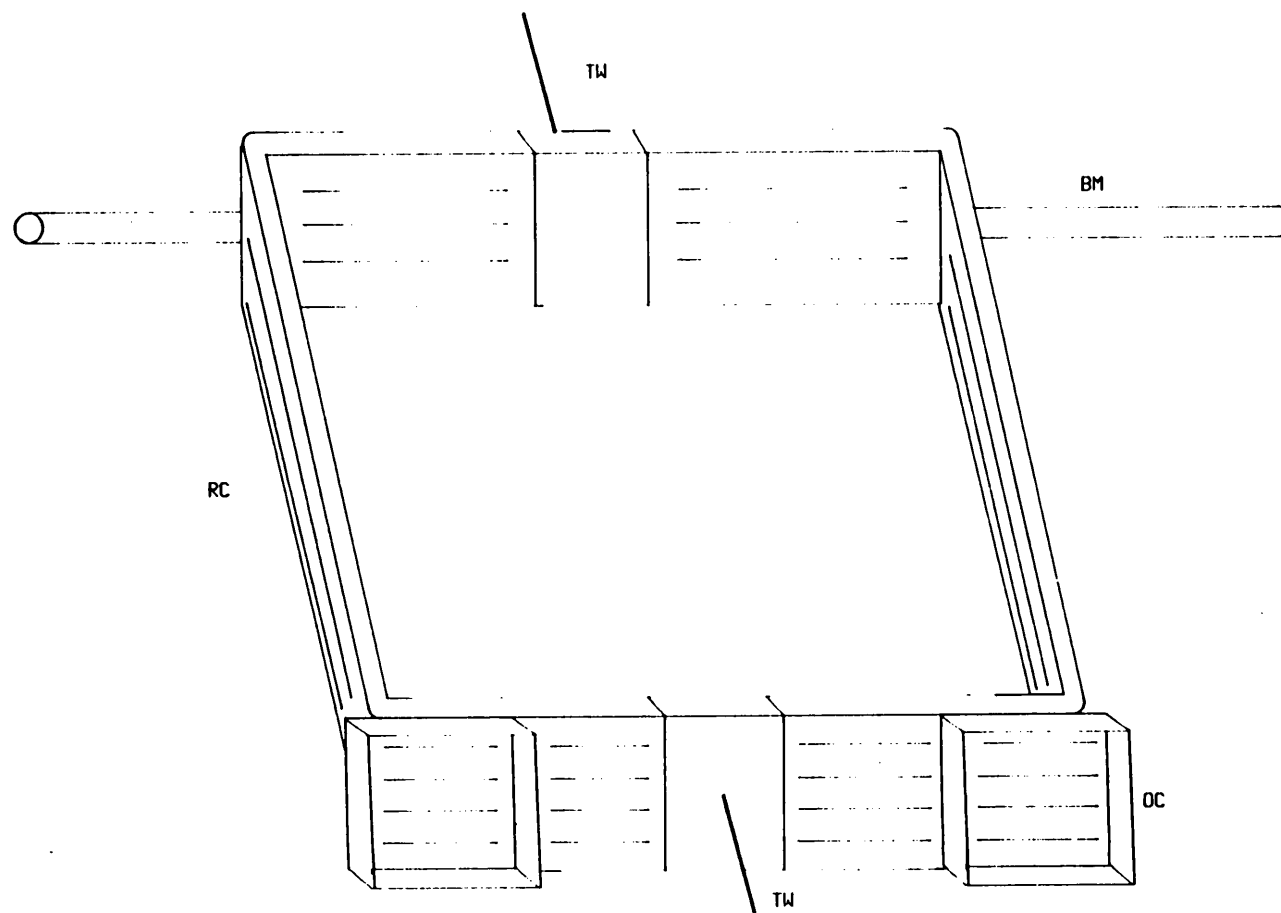


Fig. 3.4 Microbalance Beam Assembly

function of the load. The sample and counterweight were attached to platinum hangdown wires suspended from aluminium stirrups resting on diamond pins at each end of the beam. A complete vacuum seal was maintained using two Pyrex hangdown tubes as shown in Figure (3.3).

The microbalance was enclosed in a closed metal cabinet and mounted on wall brackets to maintain stability and temperature constancy.

The temperature was regulated to within $\pm 0.5^{\circ}\text{C}$ with a column of 500W heaters, H, controlled by a mercury contact thermometer. Air circulation was maintained by the two fans, (FA) and (FB). The output from the microbalance was monitored with a chart recorder (Bryans Model No. 28000).

3.61 Sorption Measurements

A thin rectangular sheet of uniform thickness and known weight (approx. 0.3g) coiled by copper mesh was suspended from the right hangdown wire. The copper mesh was necessary to act as a spacer and a support, for the thin film used to give a reasonable equilibrium time, and also allow for sufficient sample to be used due to the low level of sorption especially with CH_4 . A thin film was used to give reasonable equilibrium time. Hence to get sufficient weight of sample on the balance it was necessary to coil the thin film with copper gauze as a spacer. A copper counter weight was suspended from the left hangdown wire to bring the balance readout on to scale. The sample and rest of the system was fully evacuated and allowed to attain thermal

equilibrium.

Once the sample was fully out gassed, the zero drift was measured over a period of time and was found to be negligible. The leak rate was measured by isolating the balance from the pumping system and was also found to be very small, generally less than 10^{-2} mmHg over several hours.

To start a run, tap (T_3) was closed, the balance tared and a charge of gas was admitted from the gas reservoir. The pressure of the gas was monitored by the pressure transducer. The weight change was recorded continuously on the chart recorder and sorption equilibrium was indicated by constant weight. At this point, the penetrant was either frozen back into the gas reservoir, (R) or alternatively another vapour charge admitted for a new equilibrium sorption measurement. At the end of runs the sample was outgassed for a period of 12 hours before the next set of runs. Solubility of both CO_2 and CH_4 in Phenoxy and 50/50 PES-phenoxy blend at pressures up to 6 atmospheres was also measured using a high pressure microbalance at BP Research Centre. A sample calculation is presented in the Appendix (1.1) together with the buoyancy correction at a given temperature and gas pressure resulting from introducing the penetrant vapour calculated from the mass of the sample, the hook and the counter weight and the relative molecular mass of the gas.

CHAPTER 4

RESULTS AND DISCUSSION

HOMOPOLYMERS

4.1 Introduction

PES (Polyethersulfone) is a high performance engineering thermoplastic with good mechanical and electrical properties. It is amorphous with a high glass transition temperature and is, tough and thermally stable.

Phenoxy resins (alternately referred to as the polyhydroxyether of bisphenol A) are also tough, ductile thermoplastics with high impact resistance. Phenoxy resins are thermally stable materials that can be processed at high temperature and high speed.

Both polymers are glassy in the temperature range in which the sorption and transport measurements were made. Relatively few measurements have been reported on the transport and sorption of CO_2 , CH_4 and other gases in both of these polymers.^(151,208) Both polymers show high selectivity⁽¹⁵¹⁾ for these gases, but all the measurements were made at high pressures (0 - 25 atmospheres). Taylor^(201,208) has reported on the transport and sorption of CO_2 and CH_4 in PES at low pressures, however, no measurements have been reported for Phenoxy and the effect of low pressures on the separation properties of the material will be discussed.

On the other hand Polyurethane (PU) was rubbery in the

temperature range at which the sorption and transport measurements were made. The number of diffusion studies in PU is limited and concerned mainly with the effect of varying the structure and the length of the soft and hard block.^(221,220) Once again the transport of gases, namely CO₂ and CH₄ through Pu based on dense flat sheet membrane will be reported.

4.2 Physical Characterization of Films

Films of PES , Phenoxy and PU were transparent. The densities and glass transition temperature of the three polymers are given in Table (4.1).

Table (4.1) Density and Glass Transition Temperature of homopolymers.

Membrane	$\rho/\text{g/cm}^3$	$T_g/^{\circ}\text{C}$
PES	1.378	222
Phenoxy	1.180	92
Polyurethane	1.251	-32

Glass transition temperatures were determined by DSC. Attempts were made to measure the T_g of the films using the Dynamic mechanical thermal analyser, however this was unsuccessful since the films were too thin. Thermogravimetric analyses up to 400^oC showed no weight loss suggesting that samples were completely solvent free.

As mentioned in section (3.2), Fourier Transform Infra-red (FTir) was recorded for Phenoxy since the presence of internal hydrogen bonding for the material has been reported.⁽¹⁵¹⁾ Fig (4.1) shows scale expanded spectra of a Phenoxy film in the 3000 to 3800 cm^{-1} region, recorded at room temperature. The spectra exhibits a very broad band centered at 3400 cm^{-1} , indication of extensively hydrogen bonded hydroxy groups. This is entirely consistent with self-association of the polymer chains through intermolecular hydrogen bonding of the hydroxyl group. The minor contribution, observed as a shoulder at 3570 cm^{-1} is attributed to unassociated (free) hydroxyl groups. Coleman et al⁽²¹⁶⁾ recorded the FTir spectra of Phenoxy as a function of temperature. An increase of the relative contribution of the 3570 cm^{-1} band was observed upon heating the sample in a stepwise fashion to 150°C. This behaviour was explained in the following manner. Above the T_g of the polymer, there is sufficient energy to disrupt a significant number of the intermolecular hydrogen bonds, thus yielding a higher concentration of the unassociated (free) hydroxyl groups. Furthermore the broad band attributed to hydrogen-bonded hydroxyls shifted to a higher frequency reflecting a smaller difference between the frequencies of the unassociated (free) and self-associated hydroxyl groups, indicating a weaker hydrogen bonded system.

^1H nuclear magnetic resonance (nmr) of polyurethane was recorded using a Bruker WM250 MHz spectrometer with d^6 - DMSO (99.9 atom % D) as solvent. The ^1H n.m.r. spectrum shows (figure (4.2)) that the polyurethane consists of (diphenylmethane)

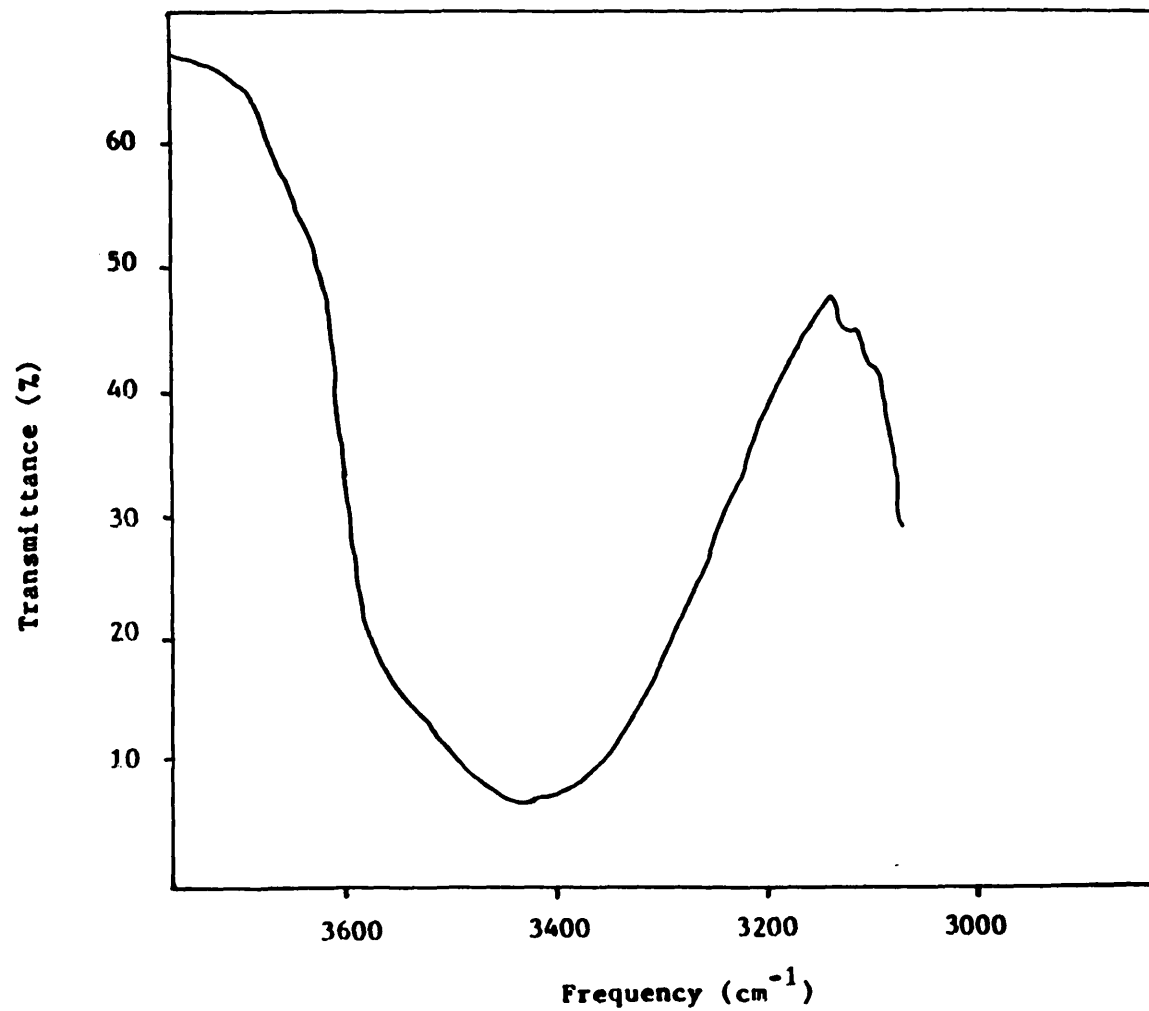


Fig. 4.1
FTir spectra of Phenoxy
film recorded at room
temperature

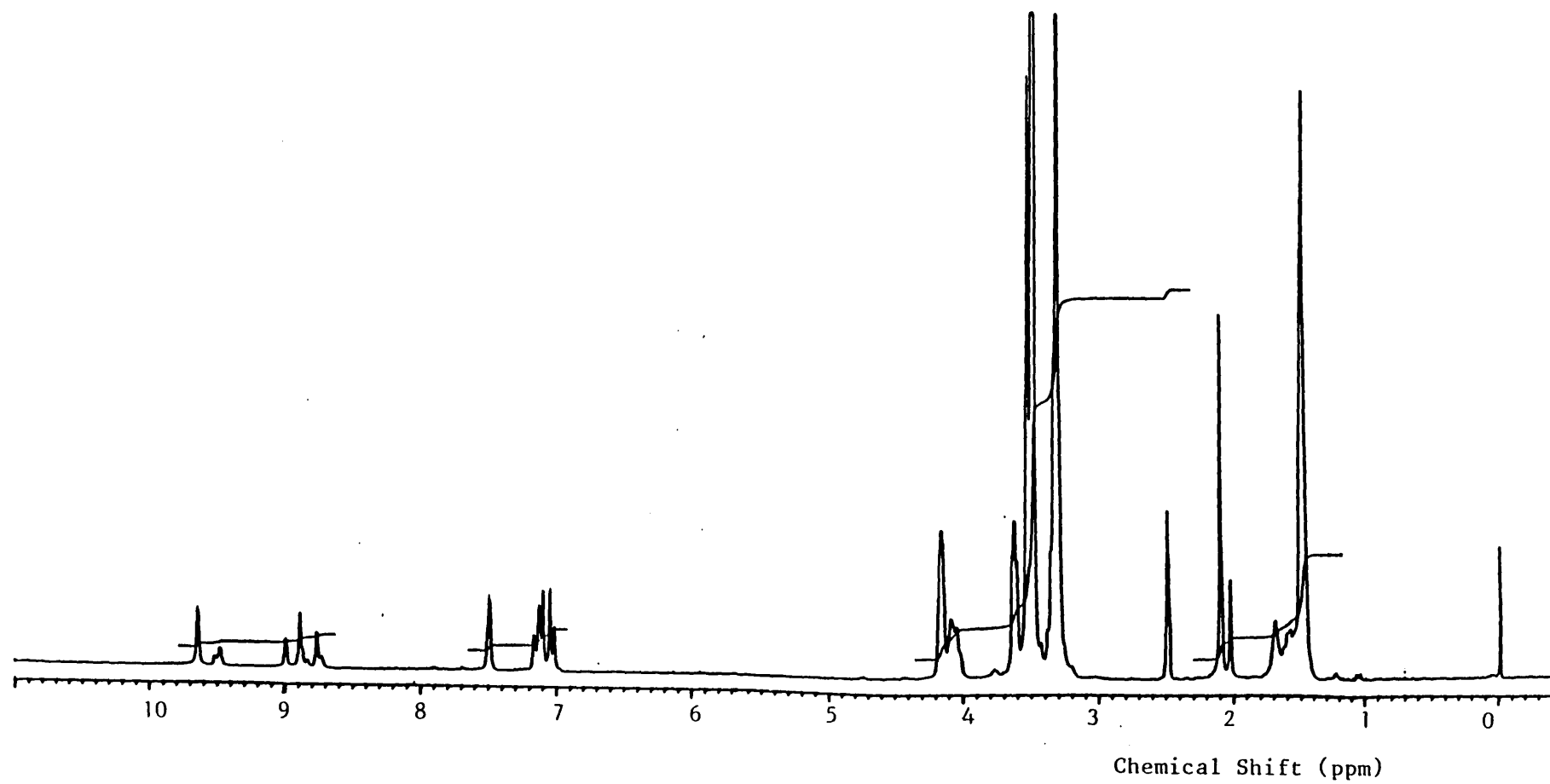


Figure (4.2) ^1H -NMR Spectra of Pu

diisocyanate (MDI), polyethylene glycol (PEG) and possibly butanediol used as a chain extender.

The ^1H n.m.r. spectrum of polyurethane (MDI - PEG - Butanediol) was assigned in ppm from up - field to down - field as follows:-

CH_3 (Butanediol) 1.3 - 2.2 ppm, CH and CH_2 (PEG) 3.2 - 3.6 ppm, CH_2 (MDI) 3.6 - 3.8 ppm, CH (Butanediol) 4.0 - 4.2 ppm, Aromatics (MDI) 7.0 - 7.6 ppm, and N - H at 8.7 - 9.0 ppm and 9.4 - 9.7 ppm.

The peak at 2.45 - 2.55 ppm is due to d^6 - DMSO, the solvent used for n.m.r..

A reasonable spectrum could not be obtained for the infra - red study of the polyurethane, due to the film being moderately thick for this experiment and a strong absorbance of carbonyl bands in Pu was observed. To obtain a better result, a very thin film is required, however this was not possible since the polyurethane was uncrosslinked and very viscous.

An attempt was made to investigate the mechanical strength of the Pu using a Minimat (Polymer Laboratories UK) tensile testing machine, however due to the material being viscous this was unsuccessful.

4.3 Equilibrium Sorption

The equilibrium sorption isotherms for CO_2 in PES film were measured at 30, 40, 50°C and for pressures up to 50cmHg and are shown in figure. (4.3). The Langmuir type curvature is observed

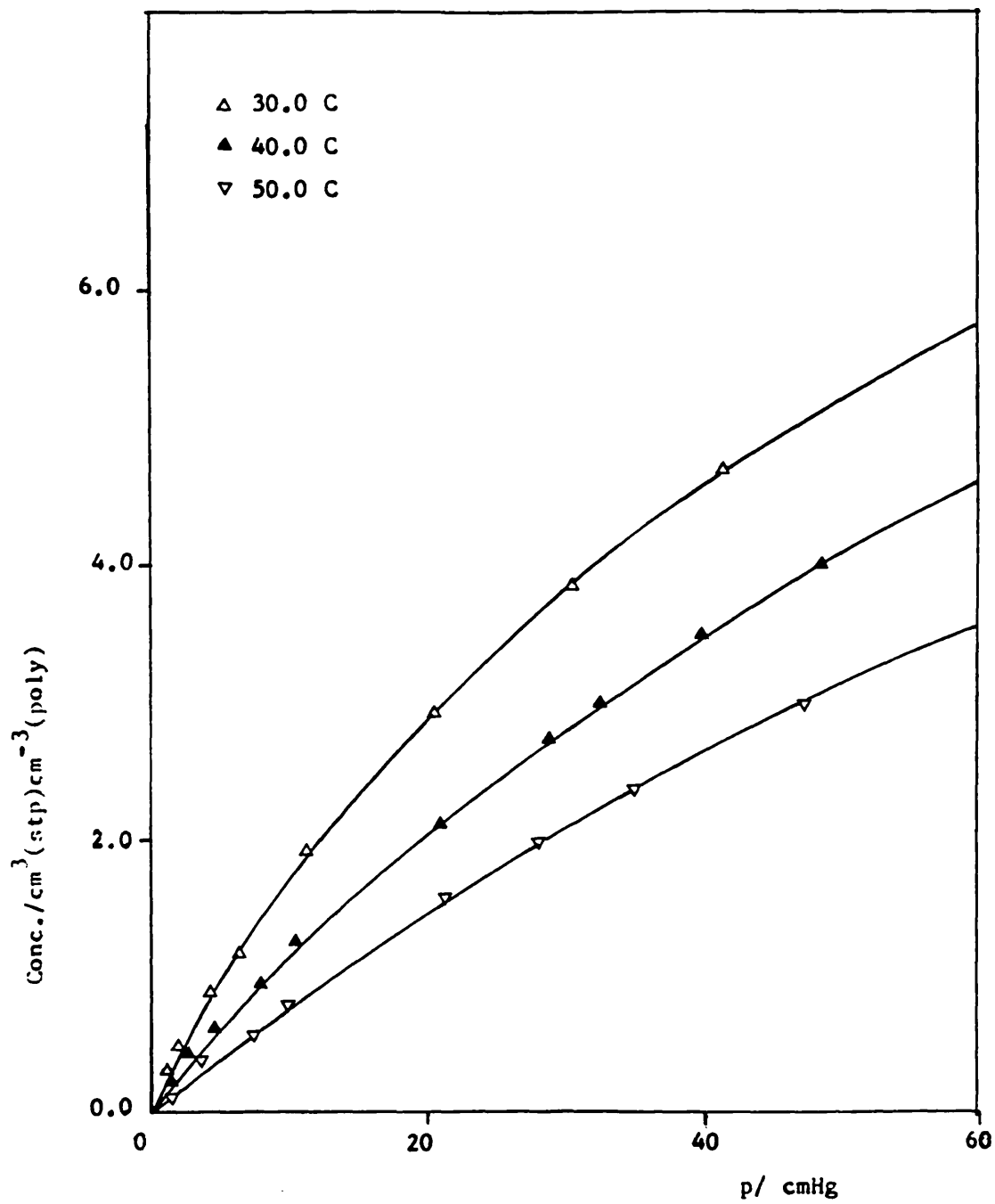


FIG. 4.3 PES/CARBON DIOXIDE SORPTION ISOTHERMS

as expected for gas sorption in the glassy state. The solid lines were calculated using the dual-mode sorption equation (2.23). The agreement with the experimental points is good and the dual mode sorption parameters obtained from the individual isotherms using a non-linear regression computer programme developed in this laboratory⁽¹²⁰⁾ are shown in table (4.2).

Table (4.2) Dual Mode Sorption Parameters for CO₂ in PES

T/°C	10 ² k _D	C' _H	10 ² b	C' _H b
30	5.87 (49%)	3.33 (90%)	4.96 (66%)	0.165
40	5.47 (28%)	1.92 (88%)	5.03 (72%)	0.097
50	3.28 (100%)	2.78 (100%)	2.14 (100%)	0.059

$$k_D : \text{cm}^3(\text{stp})\text{cm}^{-3}(\text{poly})\text{cmHg}^{-1}$$

$$C'_H : \text{cm}^3(\text{stp})\text{cm}^{-3}(\text{poly})$$

$$b : \text{cmHg}^{-1}$$

The uncertainty attached to each parameter is given in brackets. The error is large particularly at higher temperatures since the curvature in the isotherm was relatively weak. Limiting solubility coefficients were estimated from the initial slope of the isotherms and are collected in table (4.3) and compared with those of Taylor⁽²⁰¹⁾. There is excellent agreement between the two sets of data made on two separate samples of polymers and different equipment. Also included for comparison are the limiting k values obtained from $k = k_D + C'_H b$.

Sanders⁽²⁰⁸⁾ studied the sorption of CO₂ in PES at high pressures (1-15 atmospheres). A dual-mode analysis of his results gives lower values for the dual-mode parameters. For example at 35°C, $k_D = 8.31 \times 10^{-3} \text{ cm}^3(\text{stp})\text{cm}^{-3}(\text{poly}) \text{ cmHg}^{-1}$, $C_H b = 1.61 \times 10^{-3} \text{ cm}^3(\text{stp})\text{cm}^{-3}(\text{poly})\text{cmHg}^{-1}$ and $k = 9.92 \times 10^{-3} \text{ cm}^3(\text{stp})\text{cm}^{-3}(\text{poly})\text{cmHg}^{-1}$. This was due to CO₂ being a strong plasticiser,

Table (4.3) Solubility Coefficients ($\text{cm}^3(\text{stp})\text{cm}^{-3}(\text{poly}) \text{ cmHg}^{-1}$)
for CO₂/PES; $\text{cm}^3(\text{stp})\text{cm}^{-3}(\text{poly})\text{cmHg}^{-1}$

T/°C	k(HUN)	($k_D + C_H b$)	k(Taylor)
30	0.250	0.224	0.270
40	0.156	0.151	0.189
50	0.110	0.092	0.120

which reduced the glass transition temperature of the polymer at high pressures thus reducing its Langmuir sorption capacity. Therefore these measurements were complicated by the presence of plasticization effects and cannot be compared directly with the data obtained in this study.

The equilibrium sorption isotherms for CH₄ measured in the same temperature and pressure range are shown in figure. (4.4). Although there is a slight scatter in the data, it is obvious that sorption obeyed Henry's law. This is a result of the very low uptake of CH₄, and it is anticipated that at sufficiently

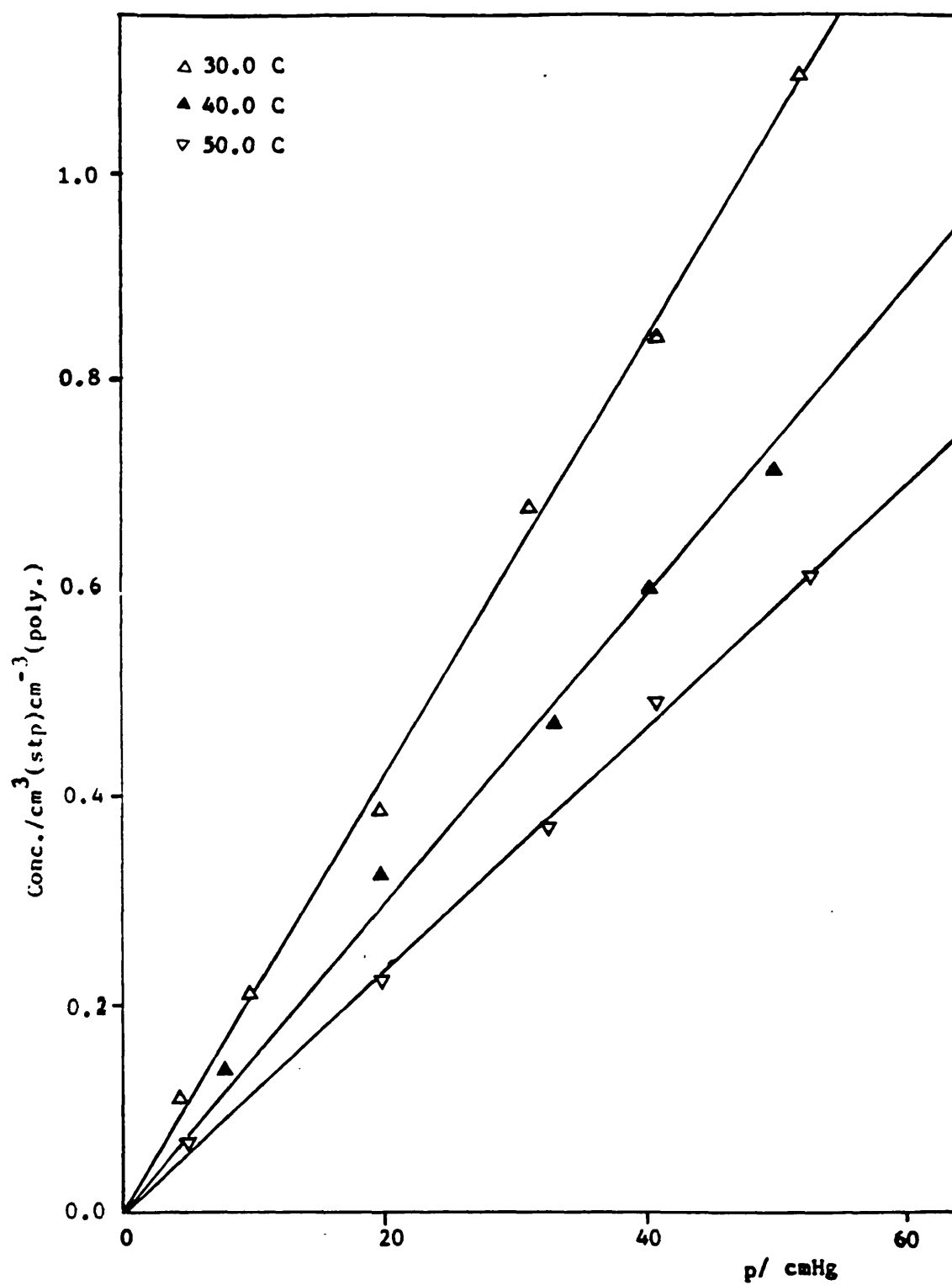


FIG. 4.4 PES/ METHANE SORPTION ISOTHERMS

high pressures the usual curvature would be observed. Sanders⁽²⁰⁸⁾ measured the sorption of CH₄ in PES at pressures up to 40 atmospheres and a distinct negative deviation from Henry's law was reported. The Henry's law solubility coefficients (k) of this study were obtained from the best fit straight line constrained to pass through the origin and are listed in table (4.4) together with values reported by Taylor⁽²⁰¹⁾.

Table (4.4) Solubility Coefficients (cm³(stp)⁻³(poly)cmHg⁻¹) for CH₄/PES,

T/°C	k _{Hundal}	k _{Taylor}
30	0.0210	0.0260
40	0.0149	0.0180
50	0.0119	0.0130

There is a slight discrepancy between these values compared to those of CO₂ solubilities, because the level of CH₄ sorbed was very low and is subject to larger uncertainty.

The equilibrium sorption isotherms for CO₂ in Phenoxyl films were measured at five temperatures in the range of 30° - 50°C and pressures up to 50cmHg. The isotherms are shown in figure (4.5). The curvature, characteristic of glassy state sorption is less pronounced, especially at the higher temperatures where the isotherms are almost linear. The dual mode sorption parameters

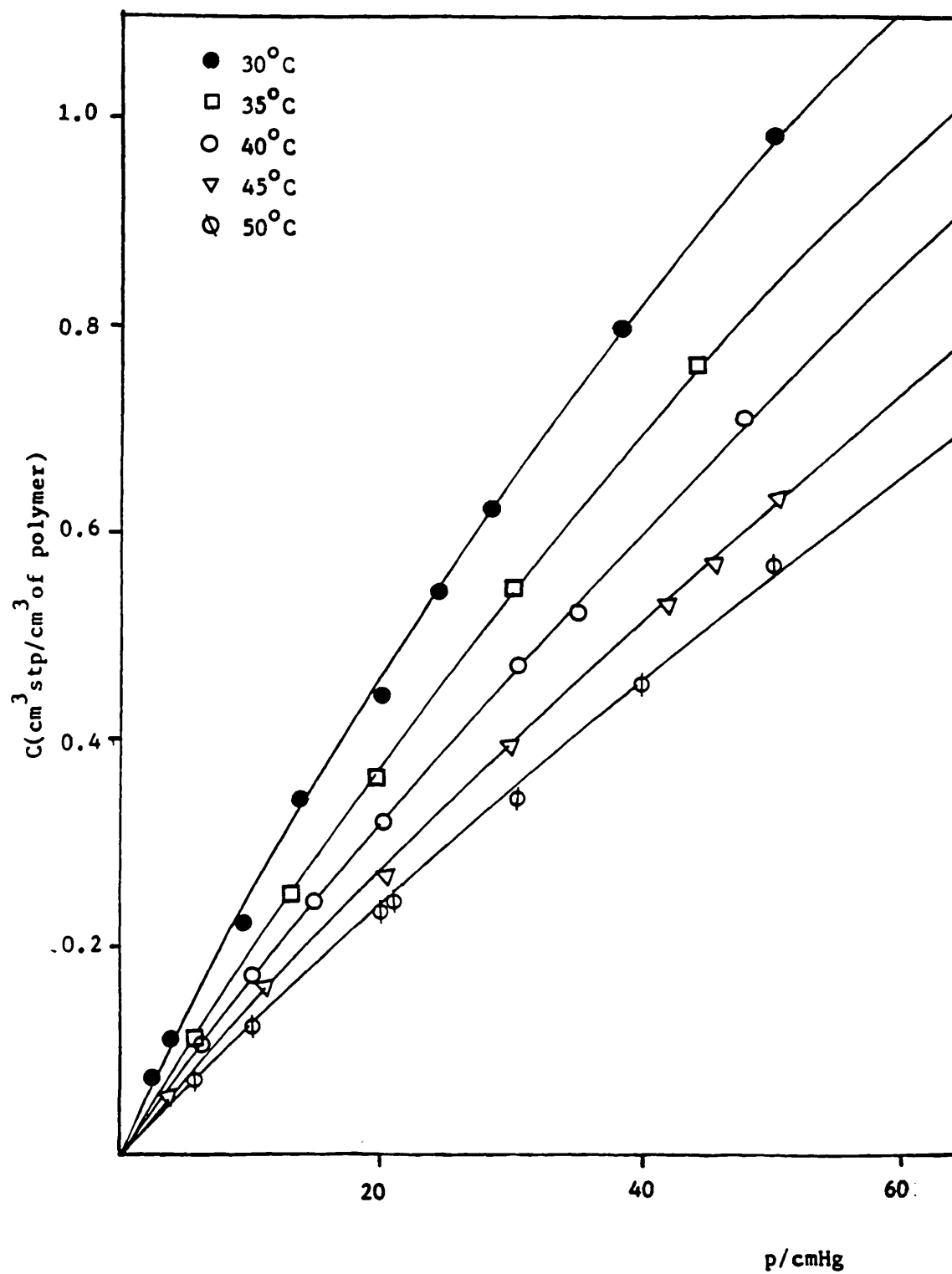


FIG. 4.5 PHENOXY/CARBON DIOXIDE SORPTION ISOTHERMS

are listed in table (4.5).

Table (4.5) Dual Mode Sorption Parameters for CO₂/Phenoxy

T/°C	10 ² k _D	C' _H	10 ³ b	C' _H b
30	0.89	1.960	7.81	0.0153
40	1.07	0.626	9.29	0.0058
50	1.10	0.042	21.6	0.0000

$$k_D : \text{cm}^3 (\text{stp}) \text{cm}^{-3} (\text{poly}) \text{cm Hg}^{-1}$$

$$C'_H : \text{cm}^3 (\text{stp}) \text{cm}^{-3} (\text{poly})$$

$$b : \text{cm Hg}^{-1}$$

In general k_D decreases with increasing temperature, however an increase is observed in this case. This is probably due to the large error involved in estimating these parameters at higher temperatures (40 and 50°C) since the isotherms were almost linear.

In all cases the error of estimation exceeded 100%. Limiting solubility coefficients deduced from the initial slope of the isotherms are given in table (4.6).

The equilibrium sorption isotherm (shown in Figure (4.6)) for CO₂ in Phenoxy films measured at 40°C with pressures up to 6 atmospheres showed a pronounced Langmuir type curvature. The dual mode sorption analysis gave the values for $k_D = 6.15 \times 10^{-3}$

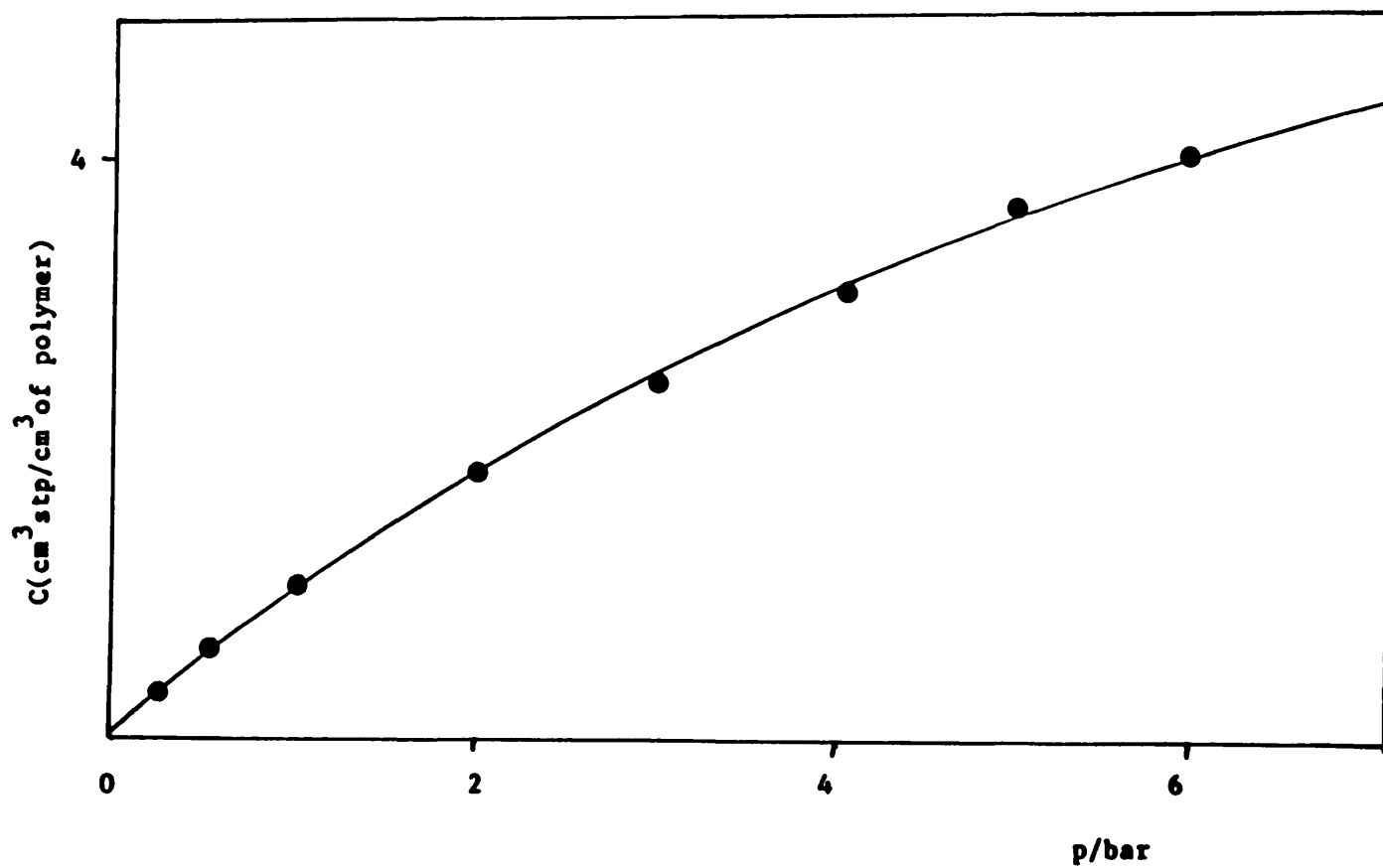


FIG. 4.6 PHENOXY / CARBON DIOXIDE SORPTION ISOTHERM AT 40°C

Table (4.6) Henry's Law Solubility Coefficients; ($\text{cm}^3(\text{stp})\text{cm}^{-3}(\text{poly})\text{cmHg}^{-1}$)
for CO_2 and CH_4 in Phenoxy polymer.

$T/^{\circ}\text{C}$	$k(\text{CO}_2)$	$k(\text{CH}_4)$	$k_D + C'_H b (\text{CO}_2)$
30	0.0285	0.0041	0.0242
40	0.0185	0.0035	0.0113
50	0.0133	0.0027	0.011

$\text{cm}^3(\text{stp}) \text{cm}^{-3}(\text{poly}) \text{cmHg}^{-1}$, $C'_H = 1.73 \text{ cm}^3(\text{stp}) \text{cm}^{-3}(\text{poly})$ and $b = 7.18 \times 10^{-1} \text{ cmHg}^{-1}$ which are considerably greater than the low pressure values from the low pressure isotherms. However the error in these parameters was fairly large. The solubility coefficient, $k = 0.0119 \text{ cm}^3(\text{stp}) \text{cm}^{-3}(\text{poly}) \text{cmHg}^{-1}$, estimated from the initial slope of the isotherm was comparatively low from that estimated from the low pressure isotherms. However the limiting solubility ($k_D + C'_H b = 0.0186$) estimated from the dual mode parameters agreed well with the solubility coefficient, $k = 0.0185 \text{ cm}^3(\text{stp}) \text{cm}^{-3}(\text{poly}) \text{cmHg}^{-1}$, obtained from the initial slope of the low pressure isotherm.

Barbari et al⁽¹⁵¹⁾ studied the sorption of CO_2 in Phenoxy at pressures 1 - 25 atmospheres. Dual mode sorption analysis in this case gave lower values for the parameters, for example $k_D = 3.8 \times 10^{-3} \text{ cm}^3(\text{stp}) \text{cm}^{-3}(\text{poly}) \text{cmHg}^{-1}$, $C'_H b = 3.19 \times 10^{-4} \text{ cm}^3(\text{stp}) \text{cm}^{-3}(\text{poly}) \text{cmHg}^{-1}$ and $k_D + C'_H b = 4.12 \times 10^{-3} \text{ cm}^3(\text{stp}) \text{cm}^{-3}$

(poly) cmHg⁻¹.

The equilibrium sorption of CH₄ in Phenoxyl obeyed Henry's law as shown by the isotherms in figure (4.7) and the solubility coefficients obtained from these isotherms are also given in table (4.6). High pressure sorption of CH₄ was also studied in Phenoxyl and the isotherm is shown in figure (4.8). As can be seen the sorption of CH₄ up to 6 atmospheres obeys Henry's law. Barbari et al reported the sorption of CH₄ in Phenoxyl at pressures up to 25 atmospheres and the usual curvature expected for glassy polymers, was observed even for CH₄.

The overall sorption for both gases in Phenoxyl was much lower than that in PES. This may be attributed to the lower glass transition temperature of the Phenoxyl polymer as well as the existence of internal hydrogen bonding for the material. Dual mode analyses of gas sorption in glassy polymers shows that the Langmuir parameter C'_H tends to zero as the temperature is raised towards the glass transition.

The solubility decreased with increasing temperature and the temperature dependence of the limiting solubility coefficient in the form of a Van't Hoff plot is shown in figures (4.9) and (4.10) for CO₂ and CH₄ respectively. The corresponding heats of dissolution, $\Delta\bar{H}_S = -R(d\ln k/d(1/T))$ were obtained and are given in table (4.7).

There is excellent agreement between the values obtained here and those of Taylor⁽²⁰¹⁾, (CO₂ = -32.1 kJmol⁻¹ and CH₄ = -28.2 kJmol⁻¹).

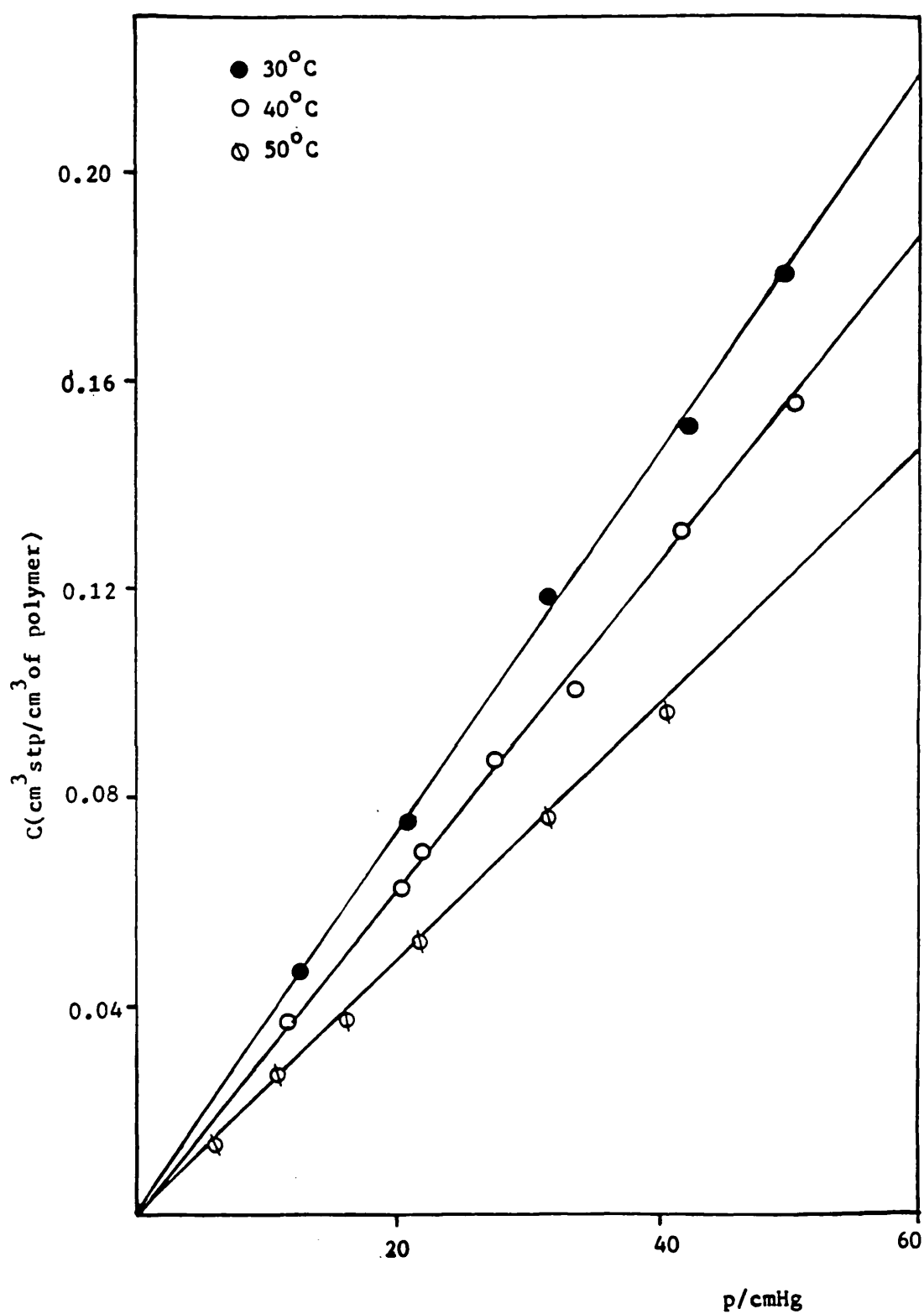


FIG. 4.7 PHENOXY/ METHANE SORPTION ISOTHERMS

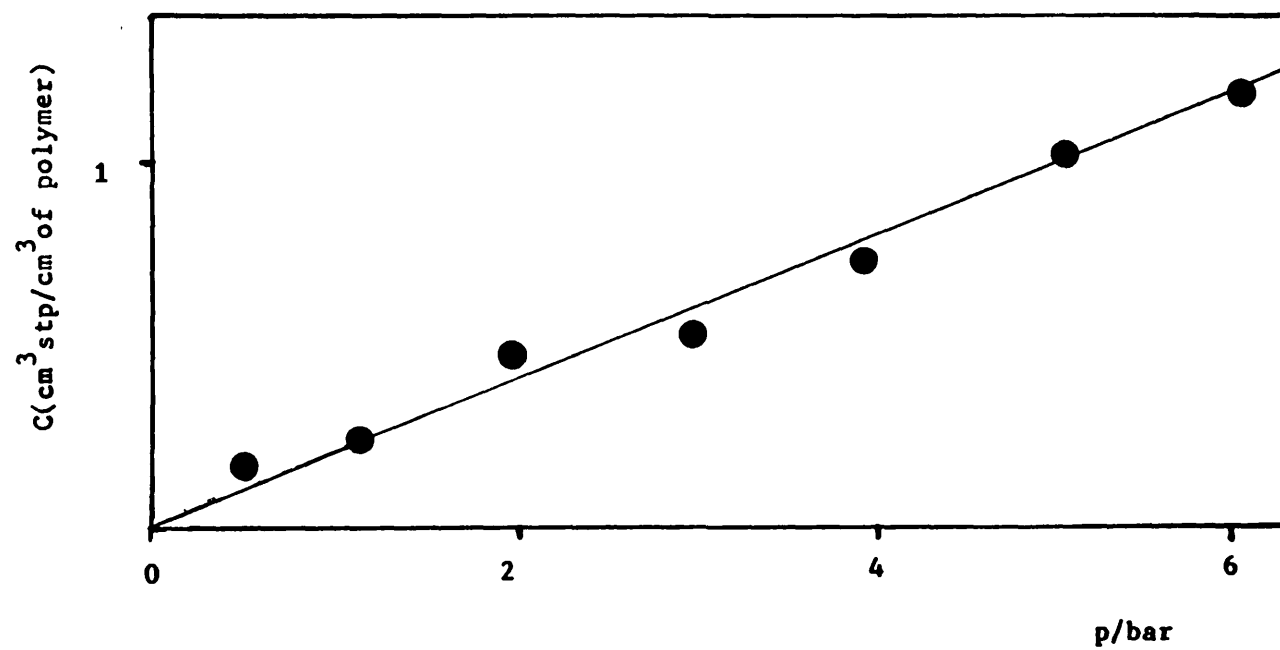


FIG. 4.8 PHENOXY/ METHANE SORPTION ISOTHERM AT 40°C

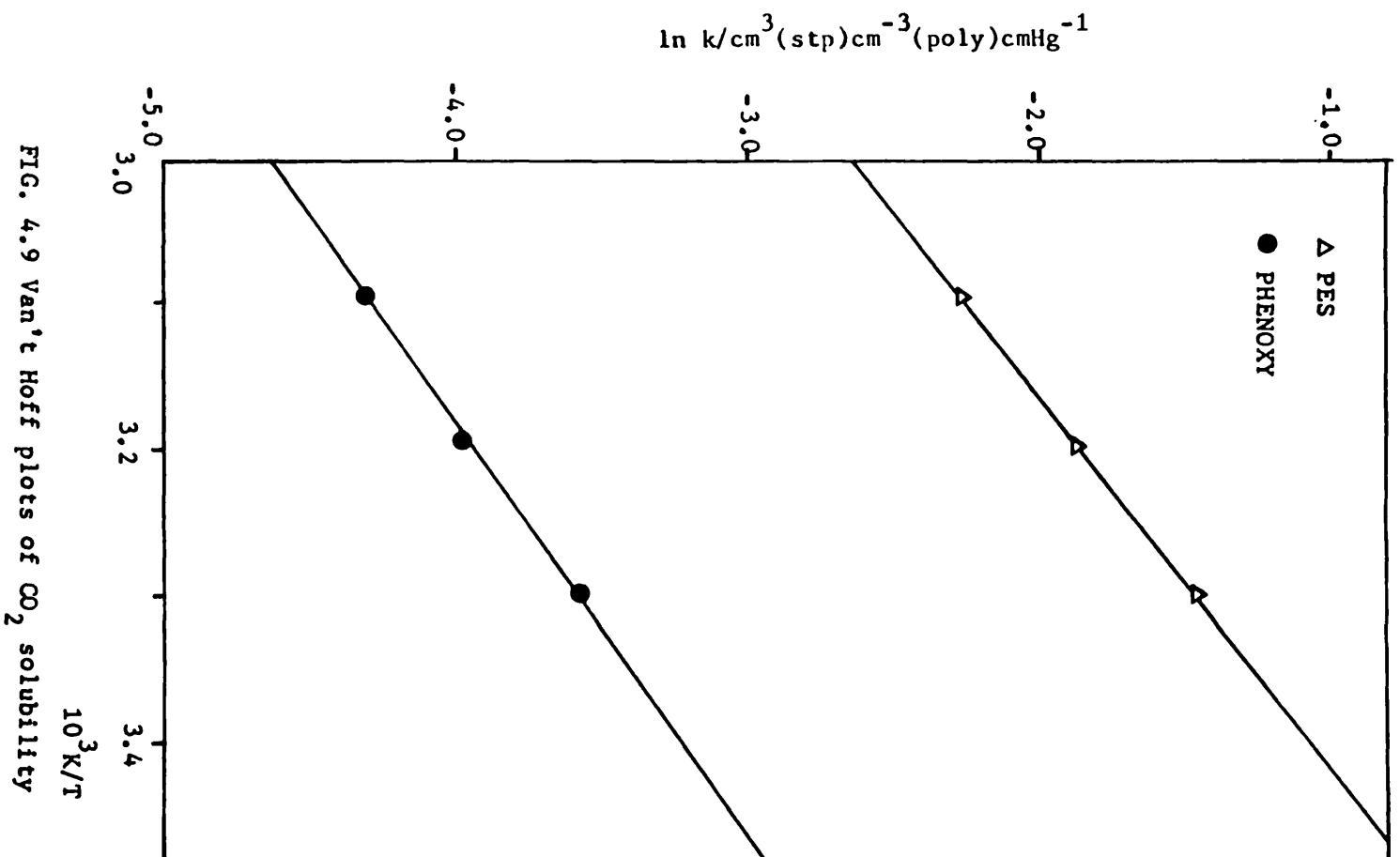


FIG. 4.9 Van't Hoff plots of CO_2 solubility

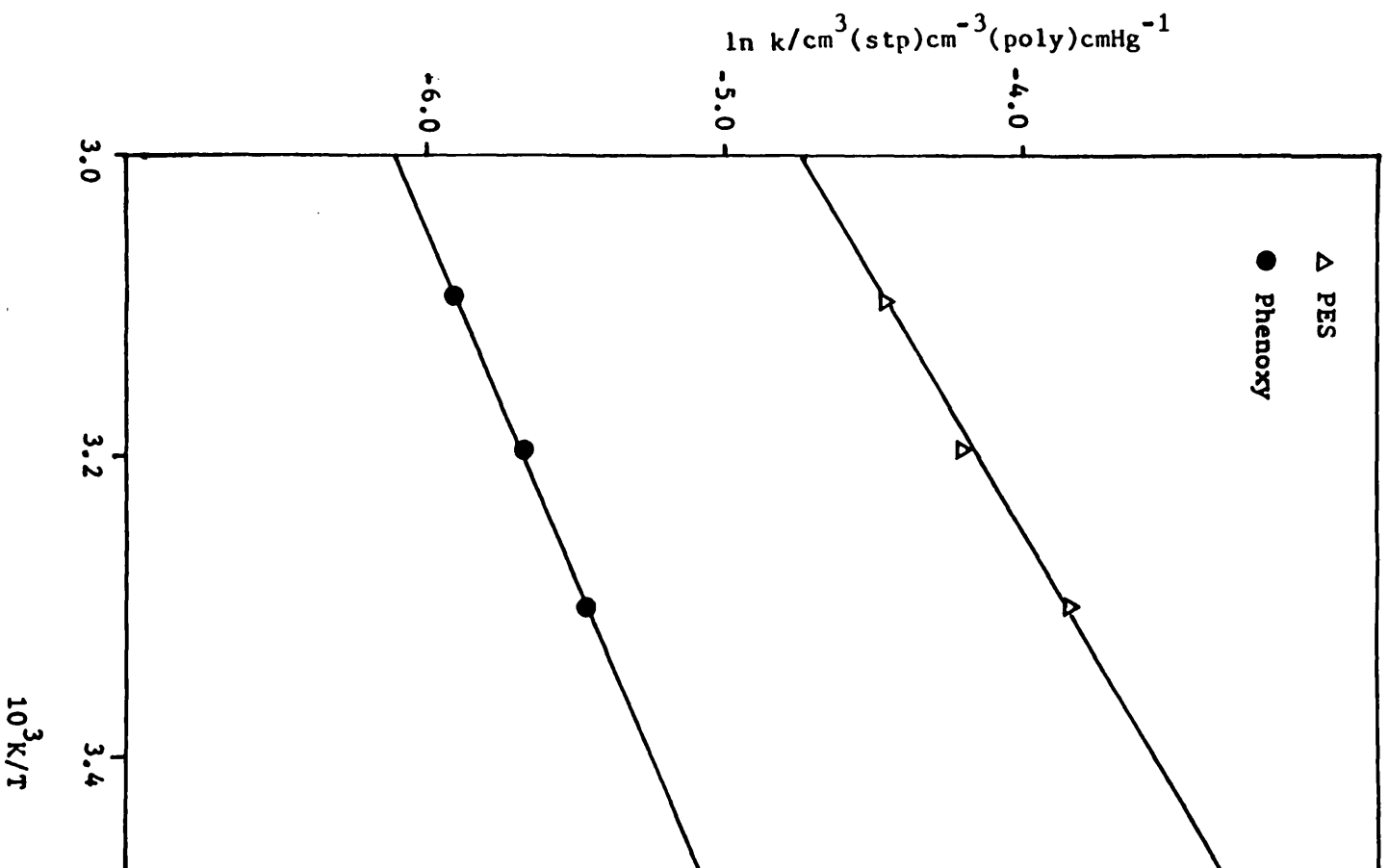


FIG. 4.10 Van't Hoff plots of CH_4 solubility

Table (4.7) Heats of Dissolution (kJmol^{-1})

Sample	$\Delta\bar{H}_{S\text{CO}_2}$	$\Delta\bar{H}_{S\text{CH}_4}$
PES	-32.74	-28.84
Phenoxy	-30.14	-15.85

Since the sorption of CO_2 in both PES and Phenoxy is non linear the heat of sorption, $\Delta\bar{H}_s$, may be a function of concentration. To test for concentration dependence of $\Delta\bar{H}_s$, values were obtained at different levels of sorption using the relation

$$\frac{\Delta\bar{H}_s}{R} = \left[\frac{\partial \ln p}{\partial (1/T)} \right]_c \quad (4.1)$$

The variation of the heat of sorption with concentration for both polymers is shown in figure (4.11) and it is clear that it is virtually concentration independent.

4.4 Steady State Permeation

The permeabilities of CO_2 and CH_4 in both PES and Phenoxy were measured in the temperature range of $30^\circ - 55^\circ\text{C}$ and pressures up to 25cmHg. The permeabilities of both gases were independent of the ingoing pressures. However, a decrease in permeabilities with an increase in pressures has been reported for most glassy polymers^(126,127,162,200,209-212) at much higher pressures, and in some cases an increase is also observed due to plasticization of the polymer by the gas.⁽²⁰⁸⁾ Barbari et

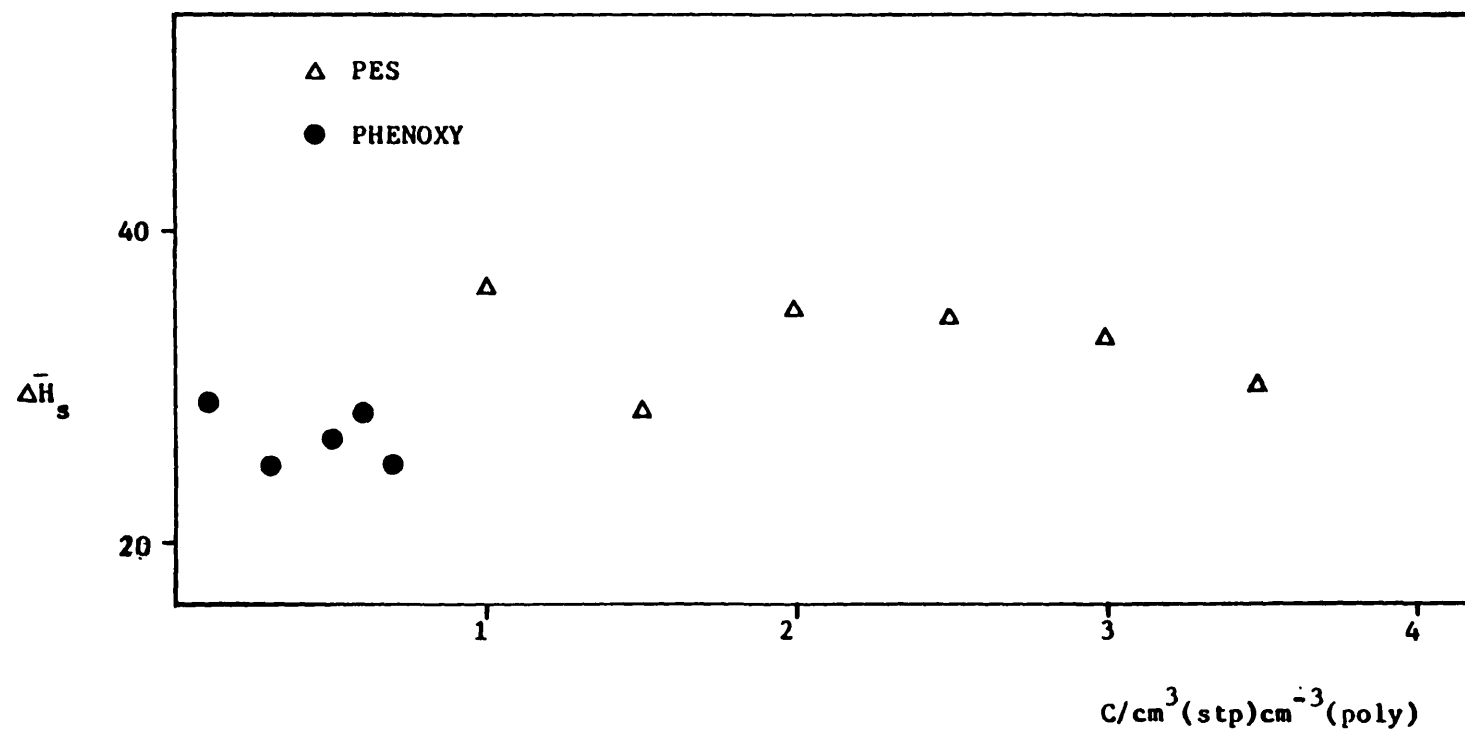


FIG. 4.11 Variation of Isosteric Heat of Sorption for CO_2 with concentration

al⁽¹⁵¹⁾ studied the permeation of CO₂ and CH₄ through Phenoxyl and other glassy polymers at pressures up to 15 atmospheres and a decrease in permeability was observed. Similar behaviour was reported by Sanders⁽²⁰⁸⁾ and Chiou et al^(192,193) for gas permeation through PES. Taylor⁽²⁰⁹⁾ has recently measured the permeability of CO₂ and CH₄ through PES in the same temperature and pressure range as in this study. Pressure independent permeabilities were reported. The permeability coefficients for CO₂ in PES estimated from the average of 3 to 4 measurements are collected in table (4.8) and compared with the values obtained by Taylor.⁽²⁰¹⁾

Table (4.8) Permeability Coefficients of CO₂ and CH₄ in PES;
 $10^{11} P (\text{cm}^3 (\text{stp}) \text{cm cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1})$

T/°C	P _{HUNDAL}		P _{TAYLOR}	
	CO ₂	CH ₄	CO ₂	CH ₄
30	53.0	1.30	51.1	1.14
40	59.3	1.68	58.9	--
50	65.1	2.58	64.0	2.35

The agreement is excellent between the two set of data. Also extrapolation of Sanders data to zero pressure yields a permeability of PES to CO₂ at 25°C $\sim 4.1 \times 10^{-10} \text{ cm}^3 (\text{stp}) \text{cm cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$ which falls within the range of results obtained in this study. The result of Chiou et al gave a value of 4.8×10^{-10}

$\text{cm}^3(\text{stp})\text{cmcm}^{-2}\text{s}^{-1}\text{cmHg}^{-1}$ at zero concentration for the permeability of CO_2 in PES at 35°C which is lower than the values measured here at 30°C . This may be due to the fact that in Chiou's measurement the films were prepared by compression moulding.

The permeability coefficients for both CO_2 and CH_4 in Phenoxo are listed in table (4.9).

Barbari et al⁽¹⁵¹⁾ reported a value of 5.5×10^{-11} $\text{cm}^3(\text{stp})\text{cmcm}^{-2}\text{s}^{-1}\text{cmHg}^{-1}$ at zero pressure for the permeation of CO_2 in Phenoxo at 35°C which is in reasonable agreement compared to the value obtained in this case at 30°C .

Table (4.9) Permeability coefficients for CO_2 and CH_4 in Phenoxo, [$10^{12}P(\text{cm}^3(\text{stp})\text{cmcm}^{-2}\text{s}^{-1}\text{cmHg}^{-1})$]

$T/^\circ\text{C}$	$P(\text{CO}_2)$	$P(\text{CH}_4)$
30	56.4	1.68
40	71.8	2.32
45	88.0	---
50	93.3	3.52
55	10.32	---
60	---	5.71

The permeability of CO_2 to phenoxo decreased with increasing pressures when measured at pressures up to 6 atmospheres as can

be seen in figure (4.12). This was an expected behaviour for glassy polymers and has been well described by many authors. The decrease in permeability is explained on the basis of a partially mobile microvoid phase and a site-saturation mechanism. This states that at low pressures, a highly microvoid environment is available for sorption and permeation. However, at sufficiently high pressures the microvoids become saturated reducing the available pathway for permeation.

As can be seen from figure (4.12), it was not possible to get reasonable results over the entire pressure range since the membrane ruptured after the initial three runs. A similar effect was observed by Barbari et al⁽¹⁵¹⁾ for gas permeation through phenoxy.

The temperature dependence of the permeability for both gases, is shown in the form of Arrhenius plots in figure. (4.13) and (4.14) respectively. The Arrhenius plots were linear over the temperature range from which the activation energies for permeation were estimated and are given in table (4.10).

Table (4.10) Activation Energies of Permeation
for CO₂ and CH₄ (kJmol⁻¹)

sample	E _p (CO ₂)	E _p (CH ₄)
PES	11.4	37.6
Phenoxy	22.6	42.3

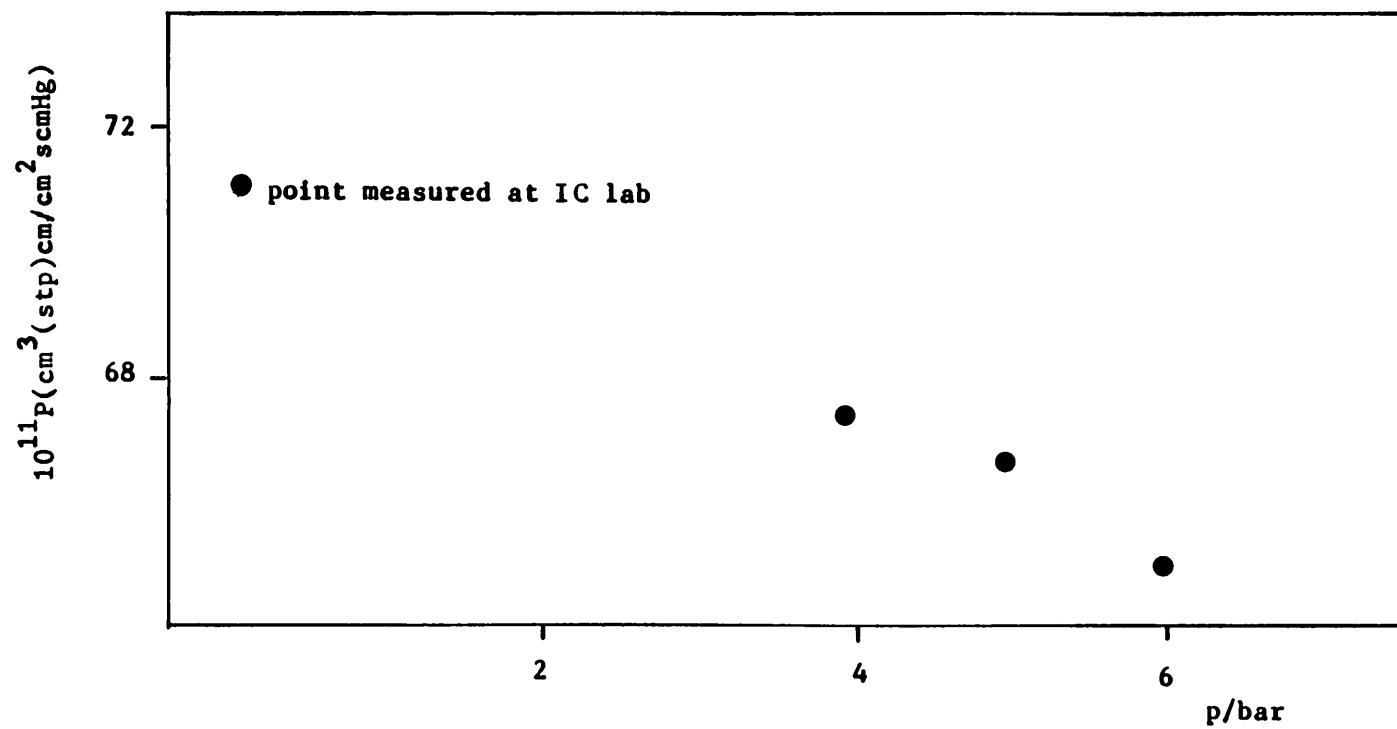


FIG. 4.12 Effect of driving pressure on the permeability of CO_2 in Phenoxyl at 40°C

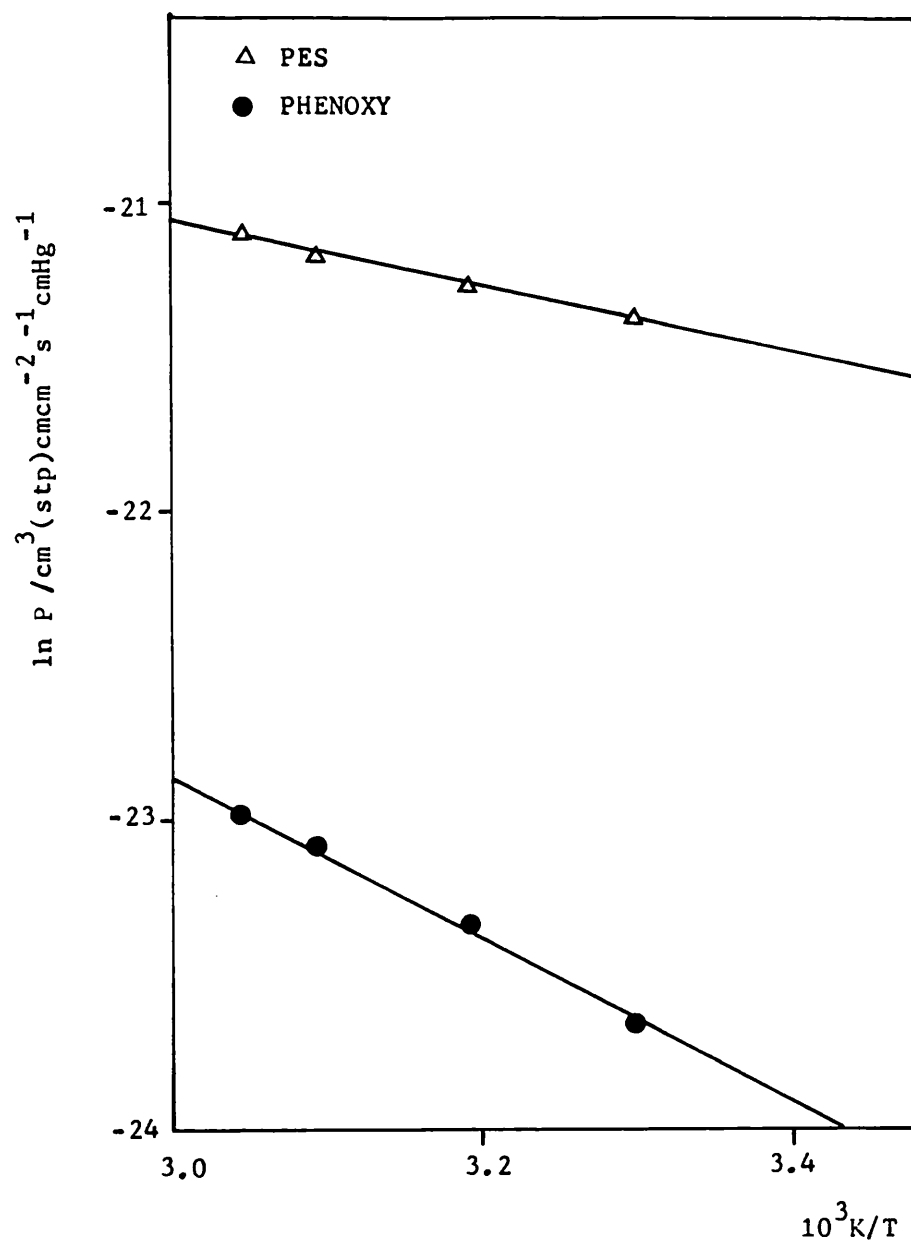


FIG. 4.13 Arrhenius plots of CO₂ permeability

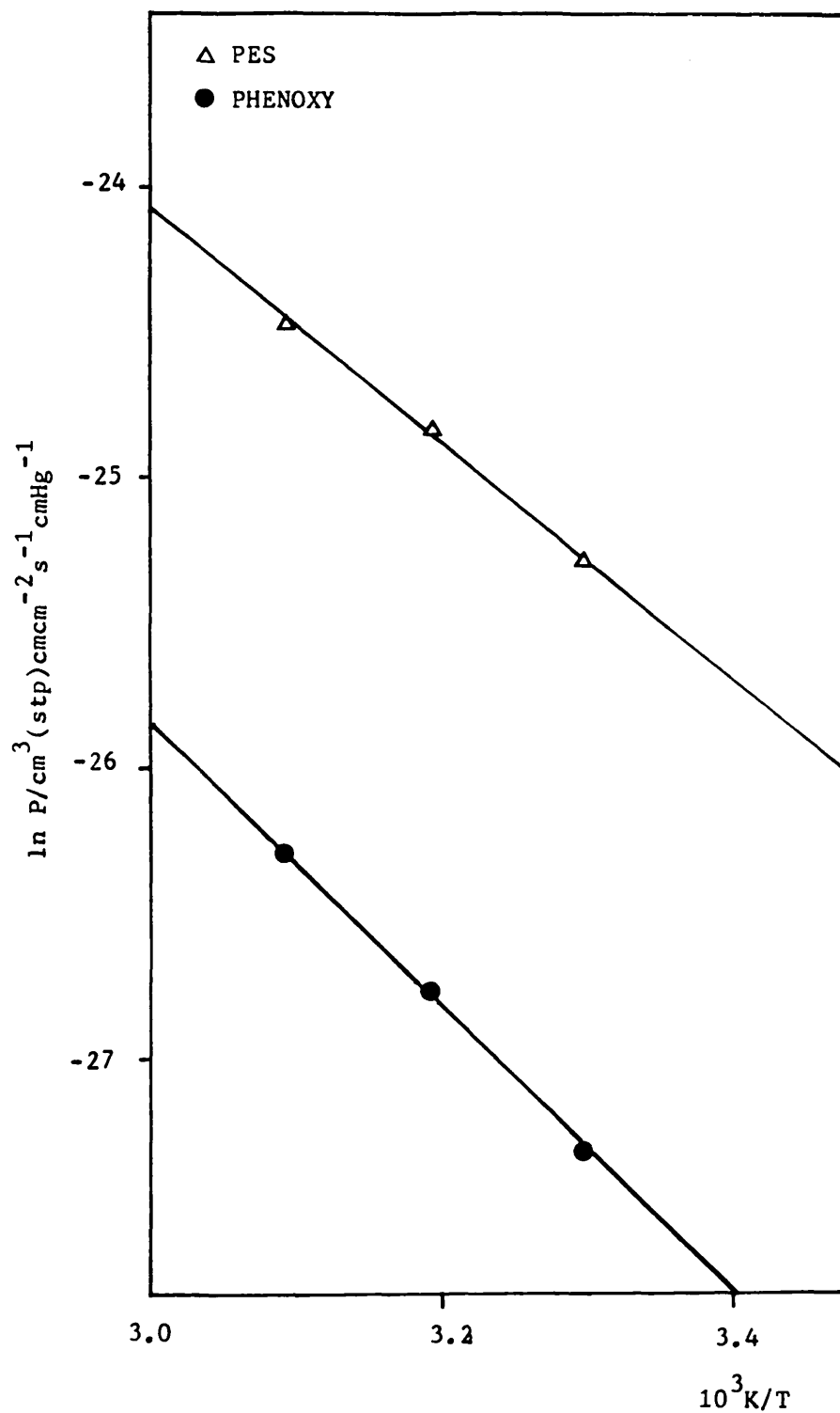


FIG 4.14 Arrhenius plots of CH_4 permeability

The permeability for both gases in phenoxy is lower than in PES. This is largely due, as seen from the following analysis of the diffusion coefficients, to the much lower sorptive capacity of the phenoxy polymer relative to PES. The dual mode sorption analysis suggests that both the dissolution and microvoid components to the sorption are smaller in the Phenoxy polymer.

4.5 Diffusion

Although the permeability of CO₂ in both PES and Phenoxy was independent of the ingoing pressures, the non-linear isotherms indicated that the measured diffusion coefficients are concentration dependent. Since P was independent of pressure, an average diffusion coefficient $\bar{D}$ was obtained from $\bar{D} = \bar{P}/\bar{k}$ where $\bar{k} = c/p$. This average coefficient is related to the differential diffusion coefficient by;

$$\bar{D} = \frac{1}{c_0} \int_0^{c_0} D \, dc \quad (2.18)$$

Differentiating and rearranging with respect to c yields,

$$D = \bar{D} + c_0 \frac{d\bar{D}}{dc_0} \quad (4.0)$$

Experimental plots of $\bar{D}$ versus c were constructed at each temperature. Each curve was fitted with a polynomial and differentiated to obtain $d\bar{D}/dc_0$ at different values of c_0 . Using equation (4.0) the corresponding D versus C curves were established. These curves are shown in figures (4.15) and (4.16) for PES and Phenoxy respectively. Extrapolation of $\bar{D}$ and D to c = 0 in these plots gave the same value for $D_{c=0}$ and are listed in table (4.11).

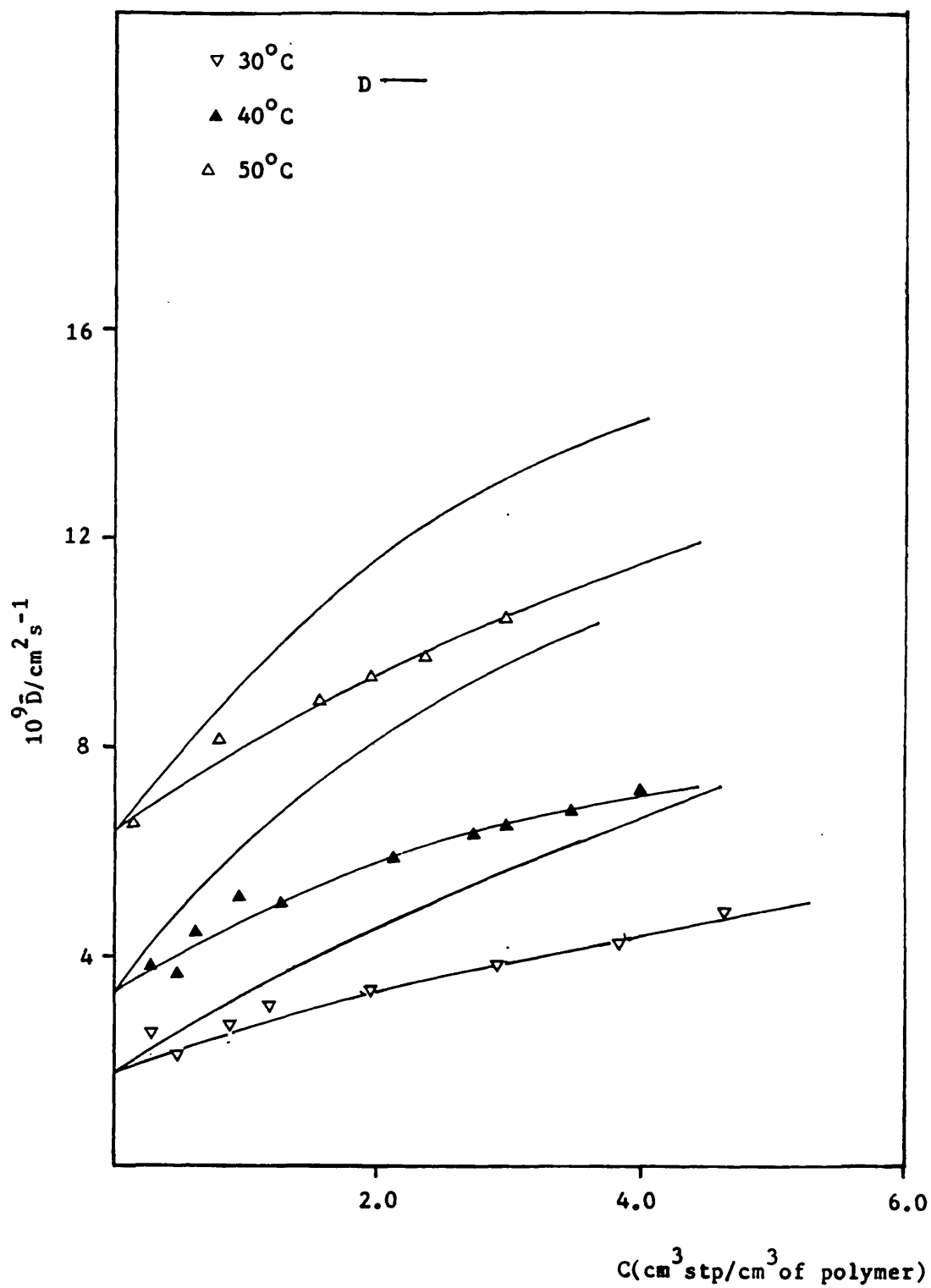


FIG.4.15 PES/CO₂ - Concentration dependence of $\bar{D}$ and D

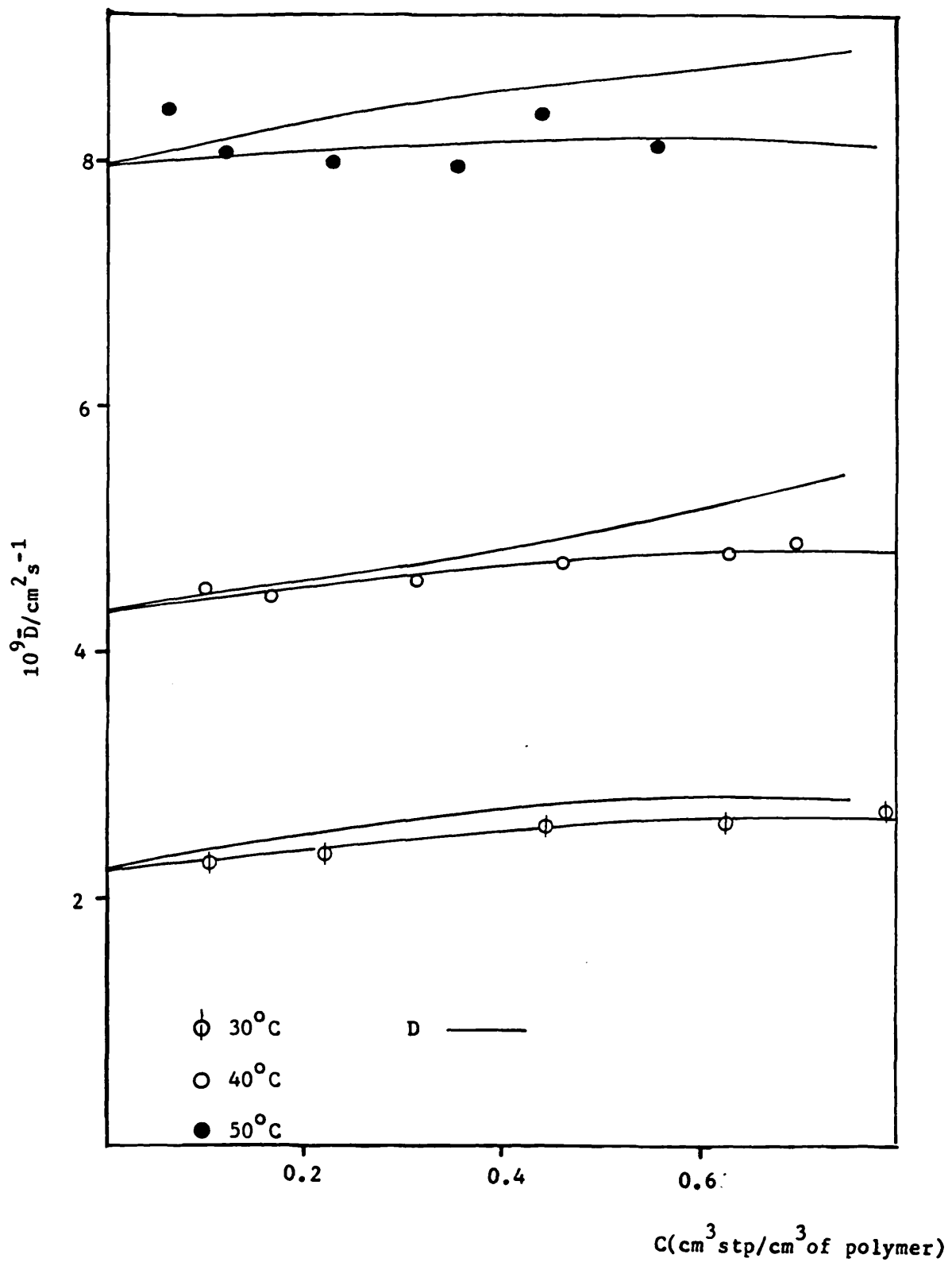


FIG. 4.16 PHENOXY/CO₂ - Concentration dependence of $\bar{D}$ and D

Table (4.11) Diffusion Coefficients for CO₂ (10⁹D/cm²s⁻¹)

T/°C	PES	Phenoxy
30	2.0	2.0
40	4.01	4.0
50	6.95	6.88

Although the rate of permeation and the amount of sorption of CO₂ by the two polymers differ approximately by a factor of 10, the diffusion coefficients of the two polymers are quite similar. The analysis confirms that the lower permeability for phenoxy is largely due to the lower sorptive capacity of this polymer.

The diffusion coefficients for CH₄ are shown in Table (4.12) were independent of concentration and simply calculated from the solubility coefficients and the permeability coefficients using $P = kD$ since Henry's law was obeyed.

Table (4.12) Diffusion Coefficients for CH₄ (10⁹D/cm²s⁻¹)

T/°C	PES	Phenoxy
30	0.5	0.34
40	1.1	0.7
50	2.0	1.5

It was not possible to evaluate the diffusion coefficients for either gas from sorption kinetics as described in section (2.4), since the initial uptake of the penetrant was too rapid and the time lag between the digital to analog convertor was relatively long.

The diffusion coefficient decreased with decreasing temperature and the temperature dependence of the diffusion coefficient is shown in the form of Arrhenius plots in Figure (4.17) and (4.18) from which the activation energies of diffusion were obtained and are collected in table (4.13).

Table (4.13) Activation Energies of Diffusion For CO_2 and CH_4
(kJmol^{-1})

Sample	$E_D(\text{CO}_2)$	$E_D(\text{CH}_4)$
PES	47	51.2
Phenoxy	47	56.1

4.6 Separation Factors

The separation of gas mixtures by polymer membranes was first demonstrated by Graham.⁽⁶¹⁾ However, a successful design for a membrane separation process required the use of membranes with as high flux and separation factors as possible and was not achieved until recently. The separation of gases using asymmetric hollow fibre polymer membranes have become more

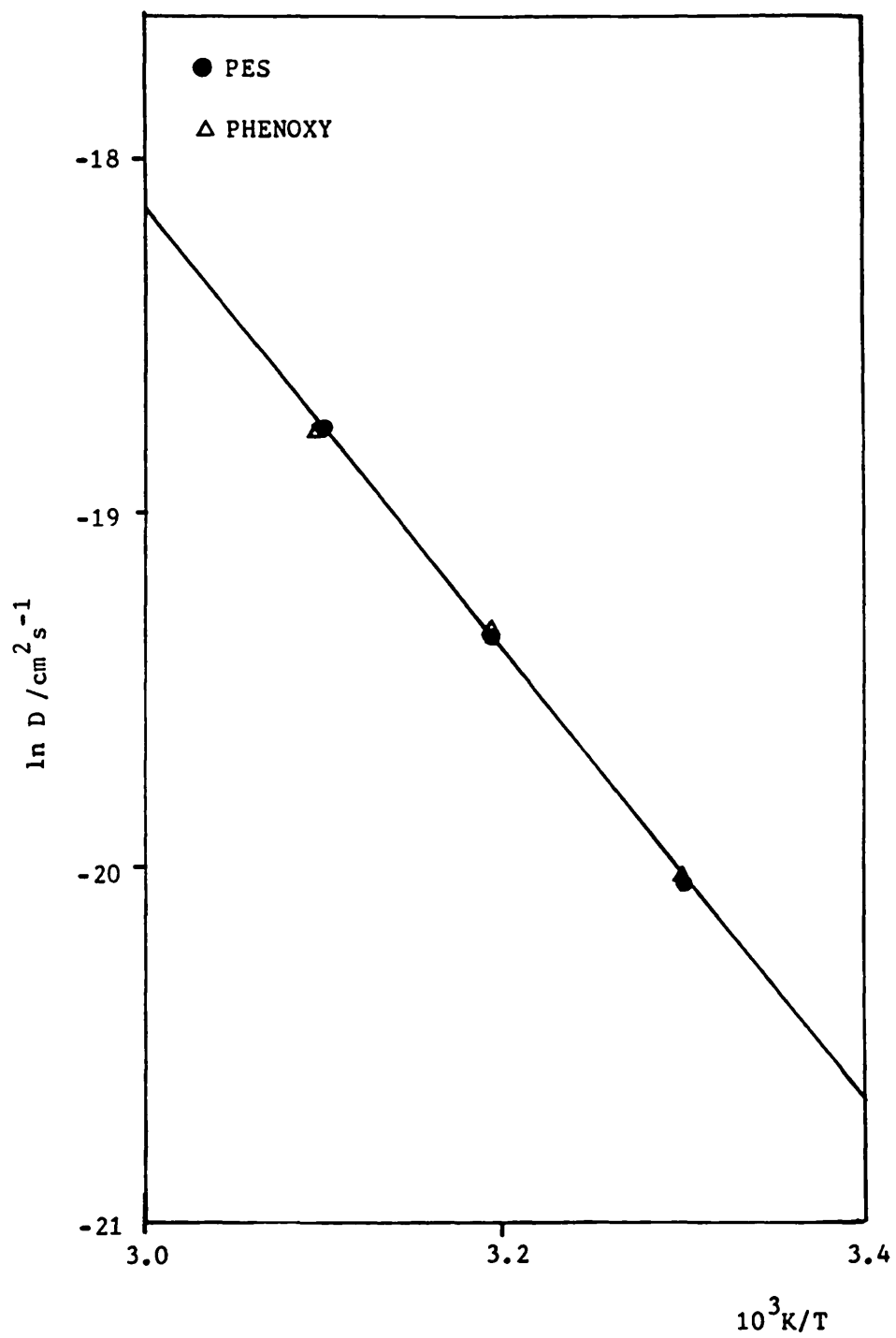


FIG. 4.17 Arrhenius plots for Diffusivity of CO_2

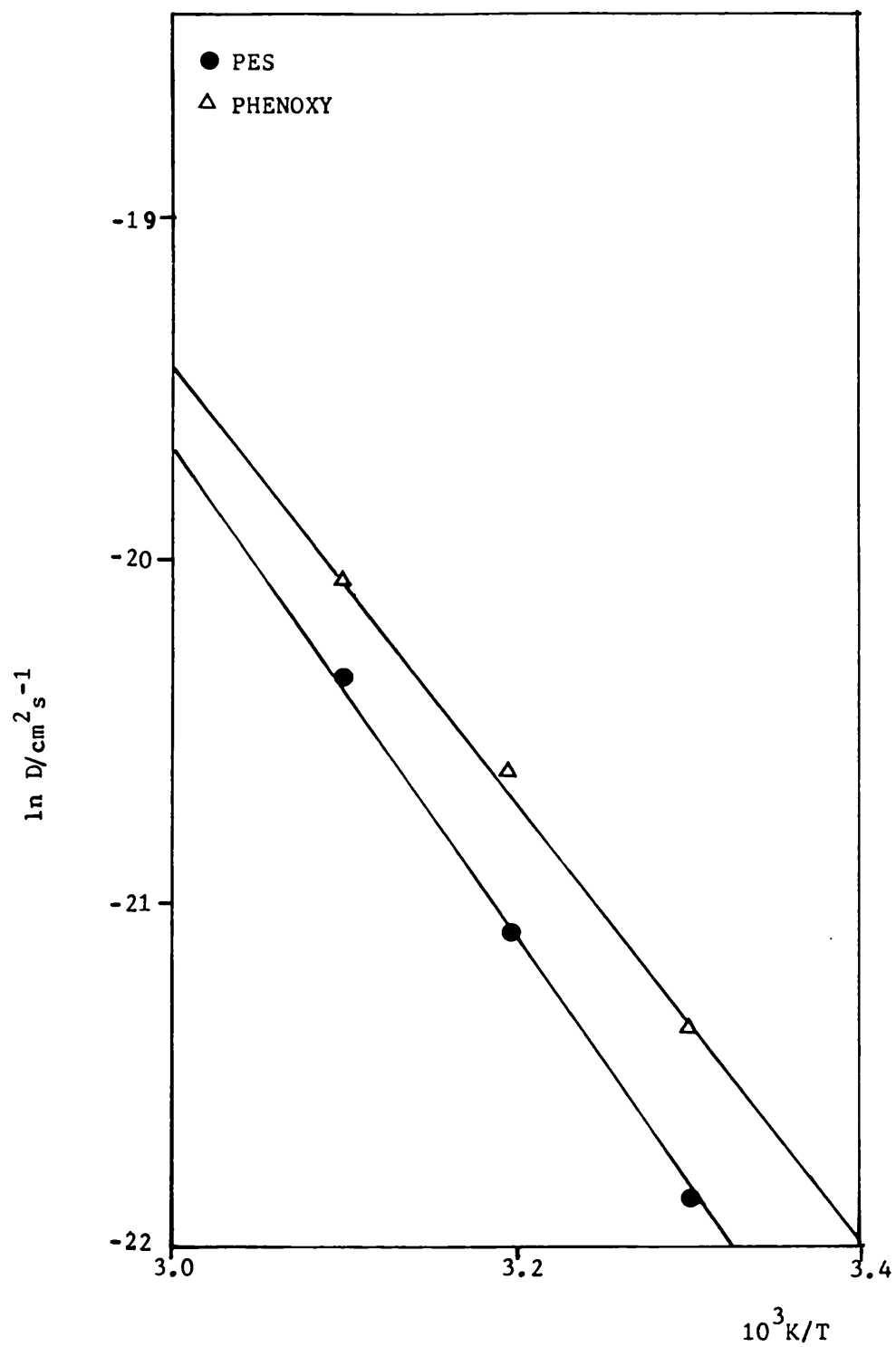


FIG. 4.18 Arrhenius plots for diffusivity of CH_4

economical.

The degree of separation expressed in terms of selectivity or separation factors is defined by the following concentration ratio:

$$\alpha^* = \frac{y_A/y_B}{x_A/x_B} \quad (4.1)$$

where y_A and y_B are the downstream concentration of the component A and B of the gas mixture and x_A and x_B are the upstream concentration. However, when the concentration of the penetrant at the down stream side of the membrane is small compared with upstream side and when diffusion is Fickian and Henry's law is valid, then the separation factor becomes the ideal separation factor. (213)

$$\alpha = \frac{P_A}{P_B} = \frac{k_A}{k_B} \cdot \frac{D_A}{D_B} \equiv k(A/B) \cdot D(A/B) \quad (4.2)$$

Where $k(A/B)$ and $D(A/B)$ are the solubility and mobility selectivity for gas A and B respectively. When the diffusion coefficient and/or the solubility coefficient are concentration dependent, the above definition provides only an approximation to the separation factors.

The ideal separation factors may differ from those obtained from mixed gas experiments, because competition between gases for sorption sites in glassy polymers may change the sorption and transport behaviour from that of pure component. (137,214) Also the plasticizing effect of one gas due to high solubility may

change the diffusion coefficients of the other gas. Table (4.14) contains the permselectivity, solubility and mobility selectivity for both PES and phenoxy at all three temperatures

Table (4.14) Separation Factors (CO_2/CH_4)

T/ $^{\circ}\text{C}$	PES			Phenoxy		
	α	β	γ	α	β	γ
30	47	4.3	11.7	38.4	5.8	6.9
40	35	3.7	10.4	30	5.8	5.3
50	26	3.6	8.8	24	5.8	4.8

α : ideal separation factor = $(P(\text{CO}_2)/P(\text{CH}_4))$

β : mobility selectivity = $(D(\text{CO}_2)/D(\text{CH}_4))$

γ : solubility selectivity = $(k(\text{CO}_2)/k(\text{CH}_4))$

The same sheet of the membrane was used for all the measurements. Therefore any errors in the membrane area, thickness and the downstream volume are reduced when calculating the various parameters namely, the permeability, solubility and diffusivity. It is clear that the separation ability of the two polymers does not differ greatly, however a better separation is achieved at lower temperature. Furthermore, the ratio of the diffusion coefficient $D(\text{CO}_2)/D(\text{CH}_4)$ does not vary much with temperature compared to the solubility ratio $S(\text{CO}_2)/S(\text{CH}_4)$ suggesting that the solubility constitutes the process controlling factor.

Barbari et al⁽¹⁵¹⁾ obtained the values of $\delta = 21.2$, $\beta = 3.6$, and $\gamma = 5.9$ for pure gas measurements at pressures up to 10 atmospheres in phenoxy at 35°C. When comparing their data with the values obtained in this study, it is clear that a better separation is achieved at lower penetrant pressure although the flow rate is low.

4.7 Equilibrium Sorption for CO₂ in Pu

The equilibrium sorption for CO₂ in Pu film measured at 30°, 40° and 50°C is shown in figure (4.19). All the isotherms were linear, indicating that sorption obeyed Henry's law which was not unexpected since Pu was well above its glass transition temperature. The Henry's law solubility coefficients, k , obtained from best-fit straight lines are given in table (4.15).

Table (4.15) : Solubility Coefficients for CO₂ in Pu

$k : (\text{cm}^3 \text{ (stp)} \text{ cm}^{-3} \text{ (poly)} \text{ cmHg}^{-1})$

$T/^{\circ}\text{C}$	k
30	0.0153
40	0.0133
50	0.0120

Clearly the solubility does not change greatly with temperature. The temperature dependence of k , as shown in figure (4.20), obeyed the relationship, $k = k_0 \exp (-\Delta\bar{H}_s/RT)$, and the heat of dissolution was estimated to be -9.98 kJmol^{-1} .

The level of sorption in Pu is fairly low compared to either PES and Phenoxy as expected. Furthermore, the resulting heats of dissolution for PES (-32.7 kJmol^{-1}) and Phenoxy (-30.1 kJmol^{-1}) were much more exothermic than for Pu. This is because both PES and Phenoxy polymers were glassy at the temperatures at which the sorption measurements were made, leading to sorption occurring in

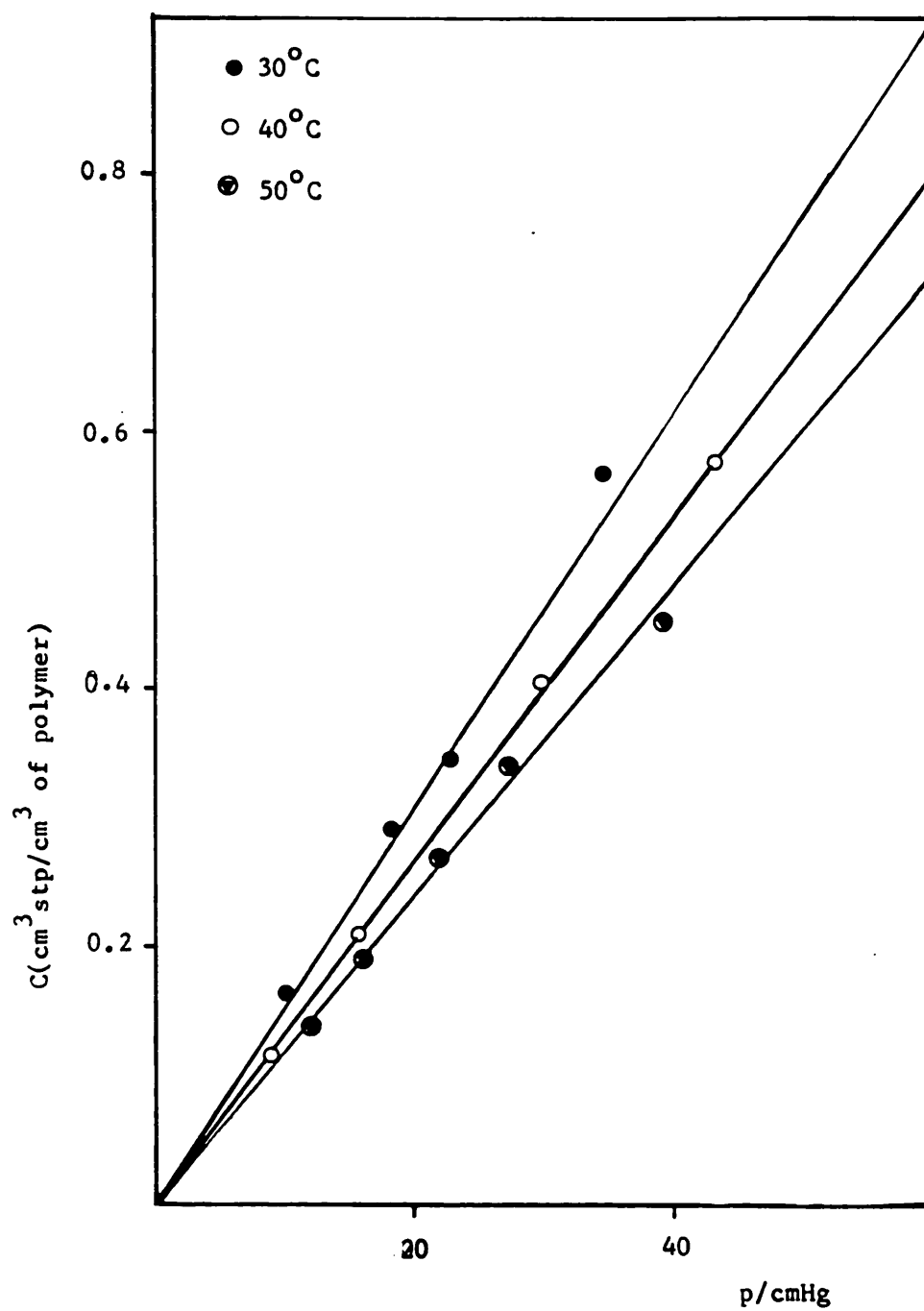


FIG. 4.19 Pu/ CO₂ SORPTION ISOTHERMS

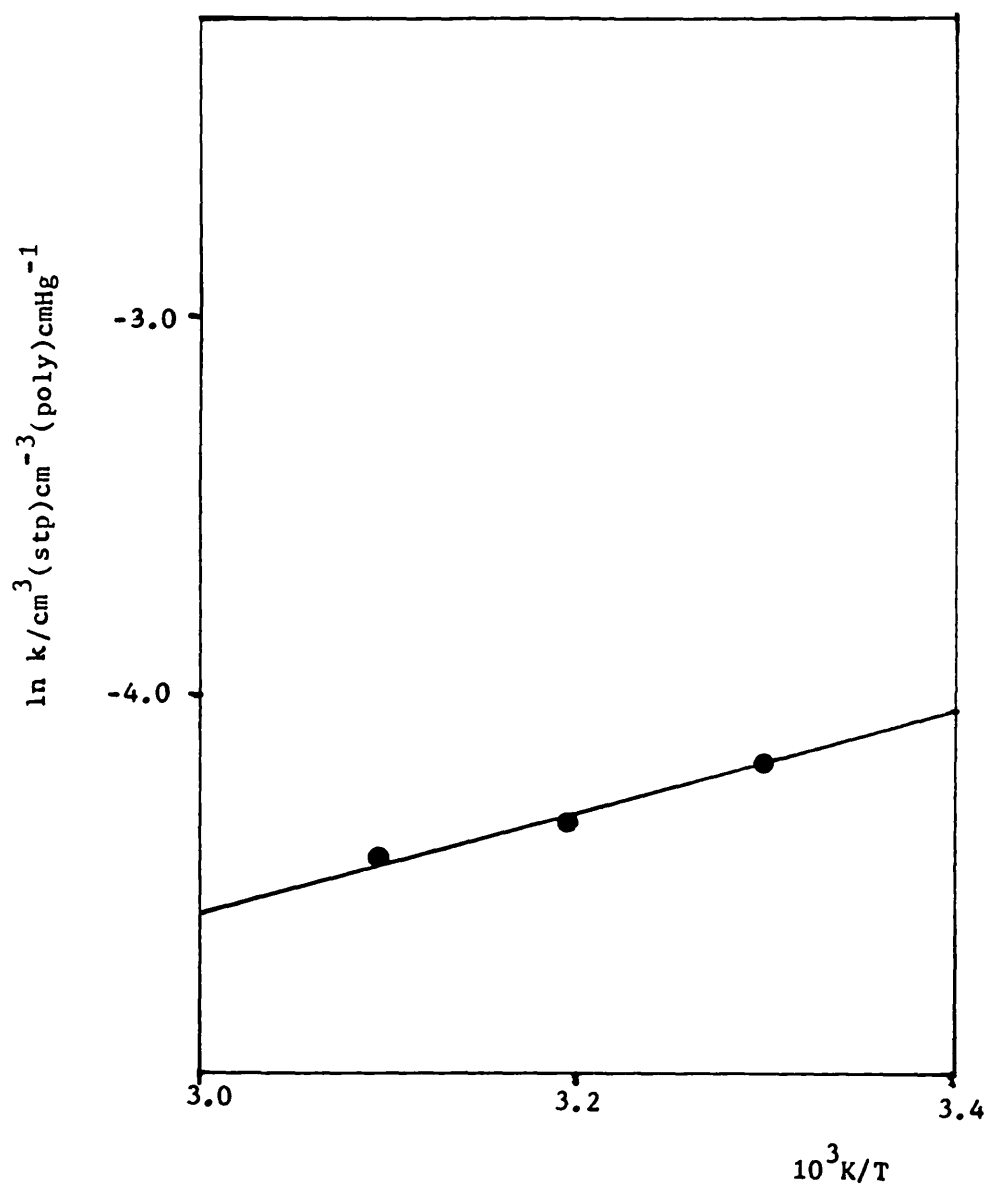


FIG. 4.20 Van't Hoff plot of CO_2 solubility in Pu

the pre - existing cavities. This resulted in a high level of sorption and greater exothermic heats of dissolution, whereas, Pu was in rubbery state and the penetrant molecule needed to create a hole to accommodate itself giving rise to less exothermic heat of dissolution. This effect has been well demonstrated by various authors. (83,85)

4.8 Permeation of CO₂ and CH₄ in Pu

The permeability of both CO₂ and CH₄ in Pu measured in the temperature range 30^o to 50^o was independent of pressure in the pressure range 0 to 25 cmHg. The values estimated from the average of 3 to 4 measurements are collected in table (4.16).

Table (4.16) : Permeability Coefficients for CO₂ and CH₄ in Pu.

$$P : 10^{-10} / \text{cm}^3 (\text{stp}) \text{ cm cm}^{-2} \text{s}^{-1} \text{ cmHg}^{-1}$$

T/ ^o C	P(CO ₂)	P(CH ₄)
30	25	0.86
40	40	1.82
50	56	2.97

The temperature dependence of P obeyed the Arrhenius relationship, $P = P_0 \exp (-E_p/RT)$, shown in figure (4.21) from which the activation energy of permeation was estimated to be 35.1 kJmol⁻¹ and 50 kJ, mol⁻¹ for CO₂ and CH₄ respectively.

4.9 Diffusion Coefficients for CO₂ in Pu

The diffusion coefficients for CO₂ determined from the

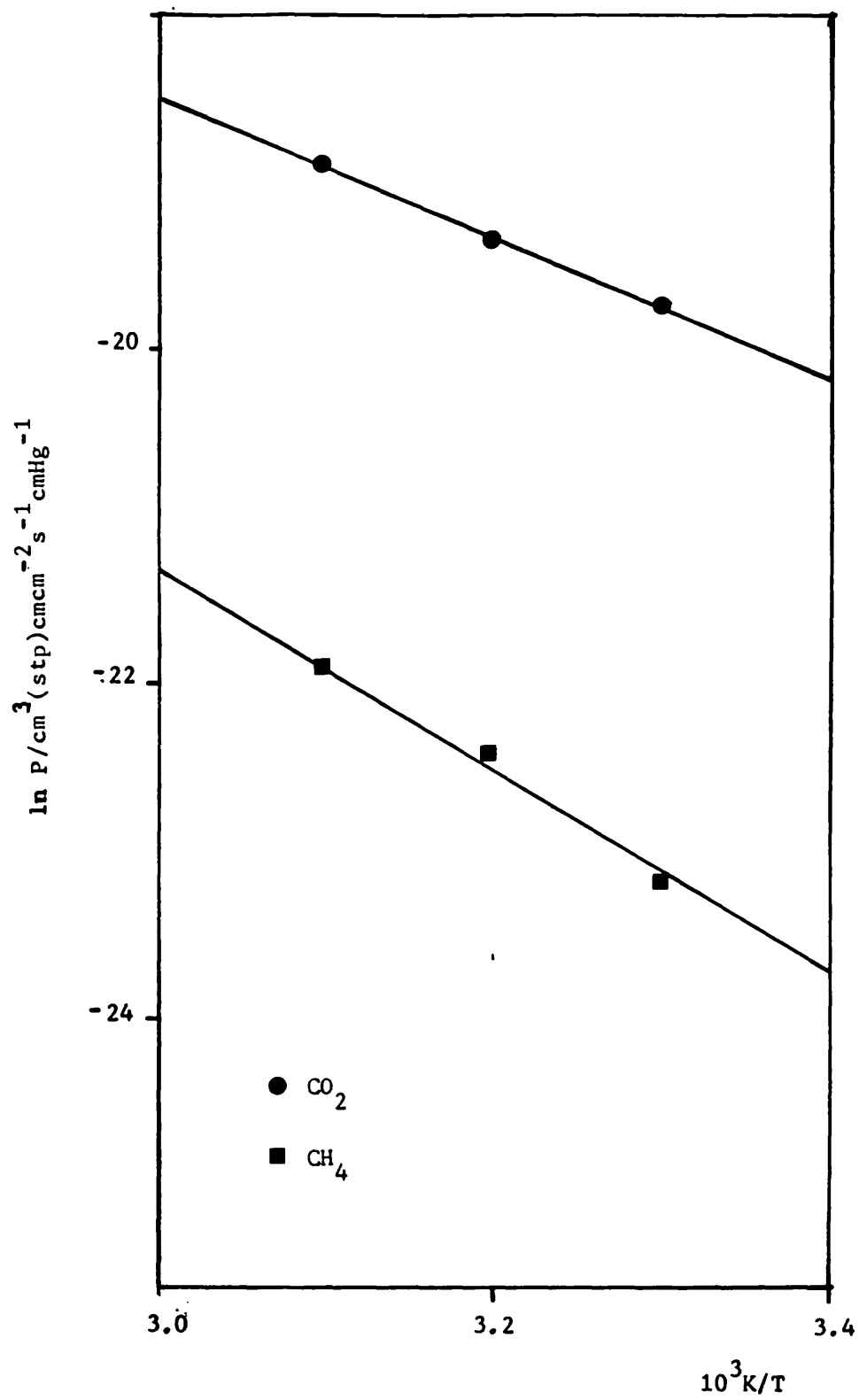


FIG. 4.21 Arrhenius plots of CO_2 and CH_4 Permeability

steady state using $P = Dk$ are collected in table (4.17). It was not possible to measure diffusion coefficients from sorption and desorption kinetics due to a rapid sorption rate.

Table (4.17) : Diffusion Coefficients for CO_2 in Pu.

$$D : 10^{-9} / \text{cm}^2 \text{s}^{-1}$$

$T/^{\circ}\text{C}$	$D(\text{CO}_2)$
30	170
40	307
50	466

The diffusion coefficient for CH_4 could not be estimated since the solubility data was not available.

The steady state diffusion coefficients were plotted according to the Arrhenius equation, $D = D_0 \exp (E_0/RT)$. The plot was linear over the entire temperature range as shown in figure (4.22) from which the activation energy of diffusion was estimated to be 42.5 kJmol^{-1} .

4.10 Separation Factors

The separation factors were obtained from the ratio of $P(\text{CO}_2)/P(\text{CH}_4)$. However, the mobility and solubility selectivities could not be obtained since the required data was not available for CH_4 gas. Table (4.18) contains the separation factors at all three temperatures.

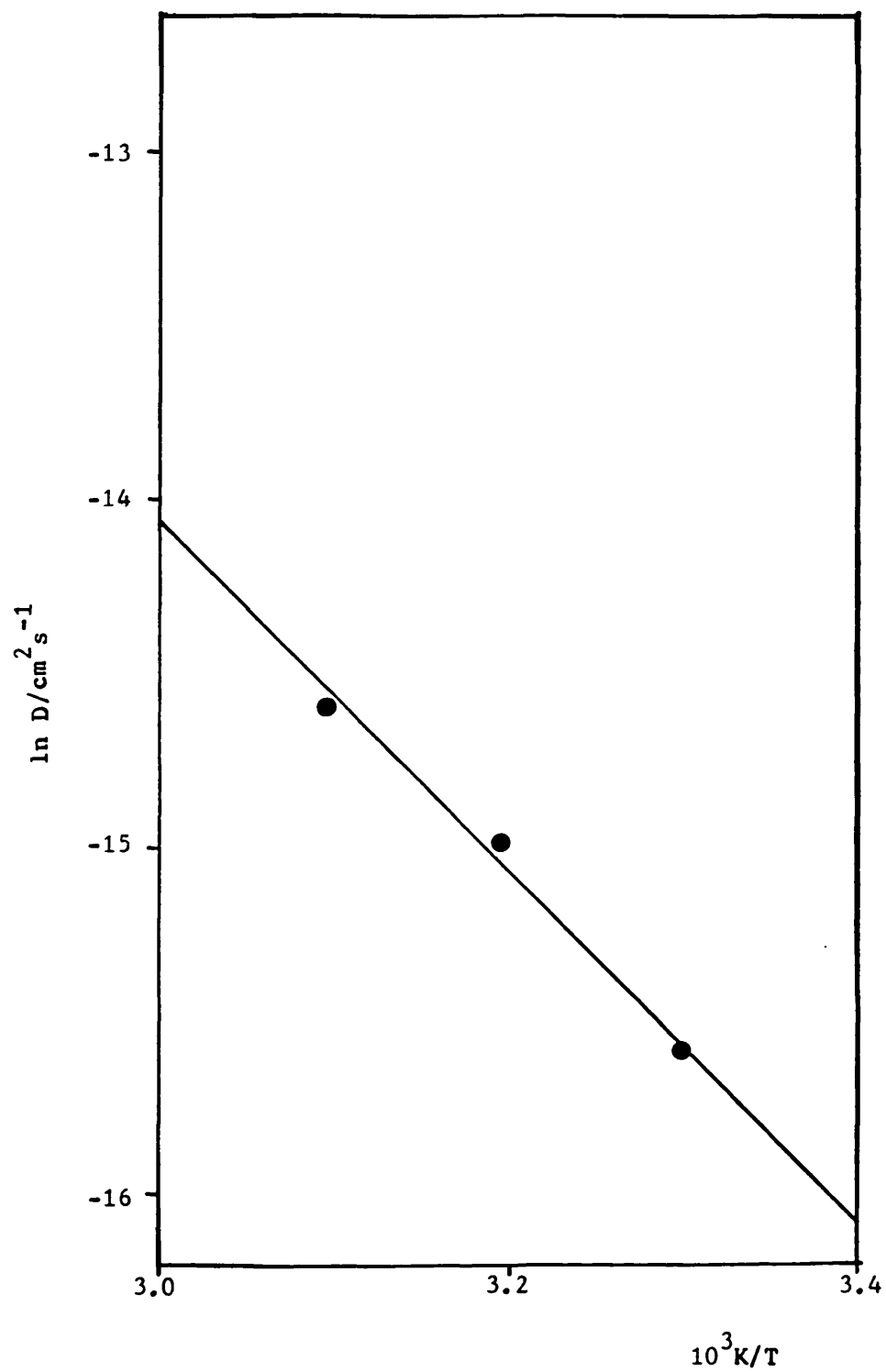


FIG. 4.22 Arrhenius plot for Diffusivity of CO_2

Table (4.18) : Ideal Separation Factors for CH₄ in

T/°C	α
30	29.1
40	21.9
50	18.8

The separation ability of Pu elastomer does not change greatly with temperature, however, a better separation is achieved at low temperature as observed in the case for PES and Phenoxy. Furthermore, the separation factor falls in the same range as those observed for PES and Phenoxy.

4.11 Conclusion

Sorption of CO_2 by both PES and Phenoxy showed typical features expected for glassy polymers since both polymers were glassy at the temperature of measurement. However, the curvature in the isotherms was relatively weak to allow for accurate evaluation of the dual mode sorption parameters. The equilibrium sorption isotherms for CH_4 obeyed Henry's law due to the very low uptake of CH_4 and it is anticipated that at sufficiently high pressures the usual curvature would be observed. Sorption of CO_2 by Pu elastomer obeyed Henry's law as expected for rubbery polymers. The amount of gas sorbed by these polymers increases in the order of Pu, Phenoxy and PES. The relatively high solubility for of PES is partly a consequence of its high T_g .

The permeabilities of CO_2 and CH_4 in PES, Phenoxy and Pu were independent of the ingoing pressures. The permeability of PES to both gases was approximately an order of magnitude greater than that for phenoxy.

The diffusion coefficients for CO_2 were slightly concentration dependent and were of similar magnitude in both PES and Phenoxy. The high permeability of PES is therefore largely a reflection of the high solubility of this gas. However, the diffusion of CO_2 in Pu was much faster than for both PES and Phenoxy.

Finally, the separation ability of all the polymers does not differ greatly; however a better separation was achieved at lower temperature and pressures.

CHAPTER 5

RESULTS AND DISCUSSION

PES-PHENOXY BLENDS

5.1 Introduction

The related materials polyethersulphone (PES) and polysulphone (PSn) are important engineering plastics. In addition coated asymmetric hollow fibres of PSn are the basis of the Monsanto Prism[®] separation unit which is used as a membrane for commercial applications. From the point of view of gas separations, the behaviour of miscible blends comprising PES or PSn as a component are of interest if improved separation membranes can be developed.

It has been shown that PES but not PSn is miscible with phenoxy polymer over the entire composition range at ambient temperatures. The cloud point curve is shown in figure (1.2) with a minimum at 180°C around 50% PES. Also the glass transition temperature of both polymers are well above ambient temperatures so that the blends are glassy at all compositions.

There appear to be no previously reported studies of gas sorption and transport in blends of PES and Phenoxy polymers and a detailed investigation of this system has now been made.

5.2 Film Characterization

Singh and Walsh⁽¹⁹⁾ using light scattering techniques obtained the cloud point - composition curve for this system and showed that it exhibited a lower critical solution temperature

(LCST) at around 180°C and 50 wt% PES, (Fig. (1.2)). They also determined the glass transition temperature, T_g , as a function of blend composition using both Dynamic Mechanical Thermal Analysis (DMTA) and Differential Scanning Calorimetry (DSC). The results were in good agreement with the Gordon-Taylor expression.

$$T_g = \frac{w_1 T_{g1} + Kw_2 T_{g2}}{w_1 + Kw_2} \quad (1.17)$$

Where K is constant which gives an indication of the strength of the interaction between the two polymers. A plot of $(T_g - T_{g1})$ against $w_2 (T_{g2} - T_g)/w_1$ gave a slope of $K = 1 \pm 0.04$ indicating that PES, Phenoxy interactions are not strong.

In this study thin transparent films of PES and Phenoxy blends were prepared by the solution casting technique. DMF was used as solvent. Singh and Walsh used dimethyl sulphoxide (DMSO) as solvent as some haziness was observed with DMF solvent cast films which they attributed to solvent induced phase separation. The DMF may not have been completely dried in their study that caused the films to be hazy. The films were characterized using differential scanning calorimetry (DSC) and typical traces are shown in figure (5.1). Each blend exhibited a single glass transition temperature, T_g , lying between that of PES and Phenoxy polymer. In figure (5.2) the dependence of T_g on overall blend composition is compared to the Fox equation⁽²²⁾

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (1.15)$$

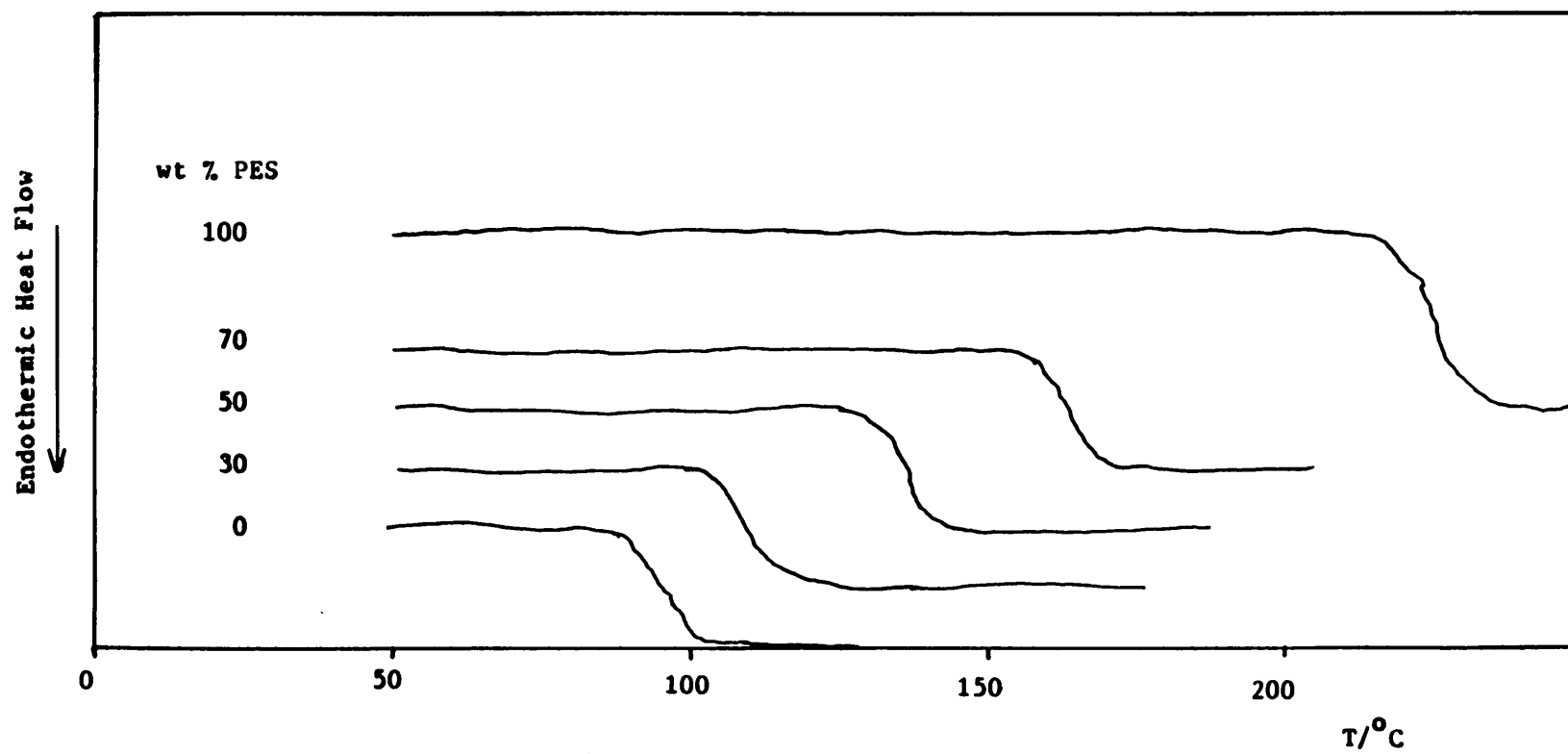


FIG. 5.1 DSC for PES - PHENOXY BLENDS CAST FROM DMF SOLUTION

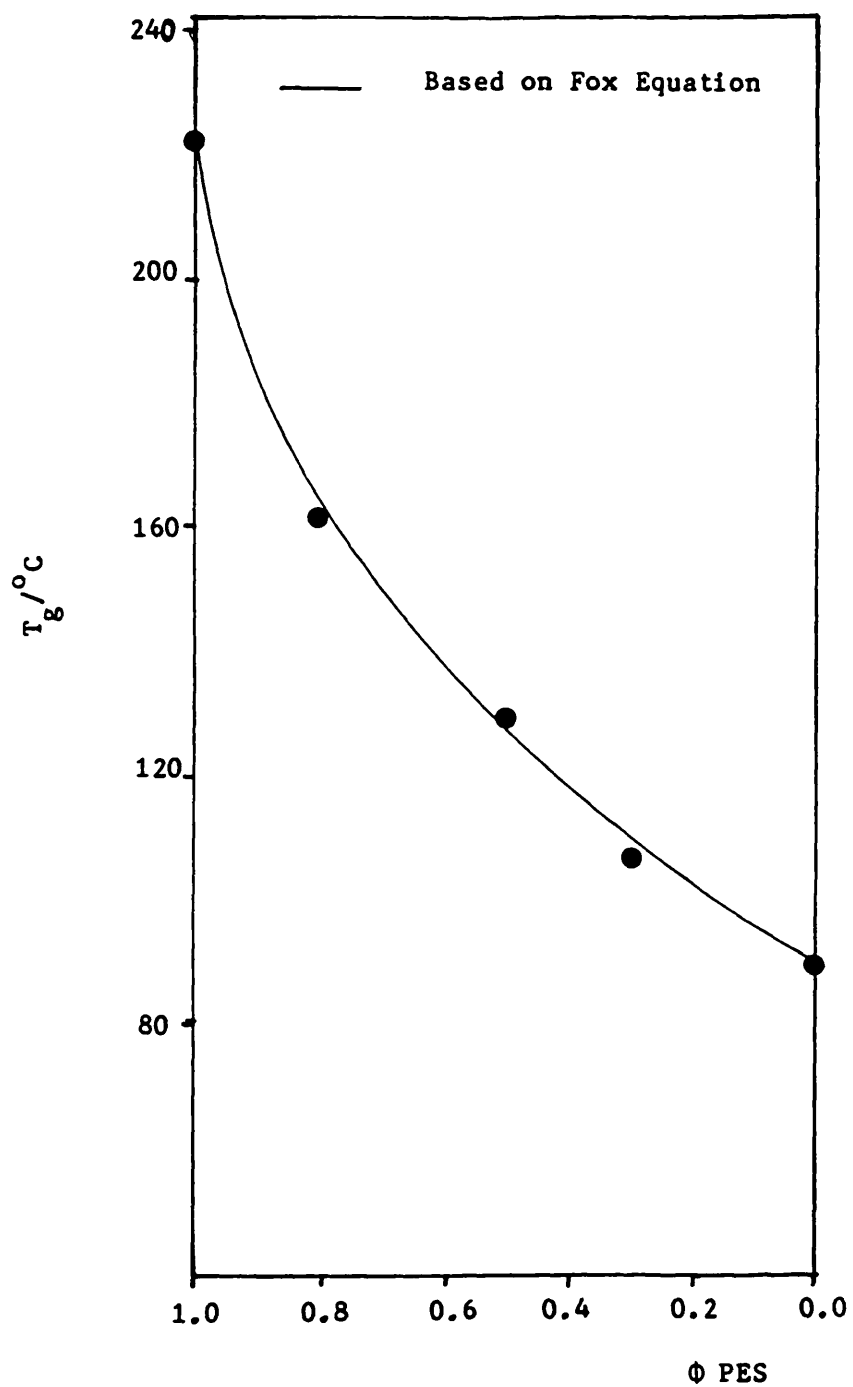


FIG. 5.2 Glass Transition Behaviour of
PES - Phenoxy Blends

Where w_1 and w_2 are the weight fractions and T_{g1} and T_{g2} the glass transition temperatures respectively of the two pure components. The experimental data are in good agreement with the Fox equation.

Phase separation, of course, occurs when the temperature is raised so that the system lies above the cloudpoint. A film of 50/50 blend was heated to 200°C in a vacuum oven for 12 hours. The sample was then quenched in liquid nitrogen and was found to exhibit two T_g 's at ~ 92 and 220°C corresponding to a phenoxy and PES rich phase respectively.

Singh and Walsh also observed the above behaviour while heating the blend on hot plate, by optical microscopy and also by DSC measurements. For example a 70/30 PES/Phenoxy blend showed a single T_g at 188°C for a homogeneous blend and two T_g 's at 135°C and 218°C for a sample which had been phase separated by heating to 230°C. Their result suggested that complete phase separation did not take place since the T_g 's were shifted inwards from those of the pure components.

The densities of PES, Phenoxy and their blends were measured by the water displacement technique at 25°C and are collected in Table (5.1) together with the volume fraction and the theoretical values for the densities calculated using the relation based on additivity of volumes

$$\frac{1}{\rho} = \frac{w_1}{\rho_1} + \frac{w_2}{\rho_2} \quad (5.1)$$

Figure (5.3), shows the specific volume plotted against the weight fraction of PES and good agreement with equation (5.1) is observed. Previous studies of miscible blends show that the

Table: 5.1 Weight Fraction, Volume Fraction and Densities of PES - Phenoxy Blends

wt % _{PES}	ϕ_{PES}	$\rho_{exp}/\text{gcm}^{-3}$	$\rho_{add}/\text{gcm}^{-3}$
100	1.0	1.375	1.375
80	0.78	1.338	1.337
70	0.67	1.311	1.316
50	0.48	1.274	1.275
30	0.32	1.240	1.243
0	0.00	1.187	1.187

specific volume of the blend, V , is often less than that calculated from linear additivity, V_{ideal} ,

$$V_{ideal} = V_1 w_1 + V_2 w_2 \quad (5.2)$$

where w is the weight fraction and subscripts 1 and 2 denote the two component. This is the result of denser packing of polymer chains due to the favourable interaction between component polymers that promotes miscibility. Since the specific volume closely follows the additive rule, it follows that the volume contraction on mixing is insignificant and that the interaction between PES-Phenoxy must be relatively weak. Similar behaviour

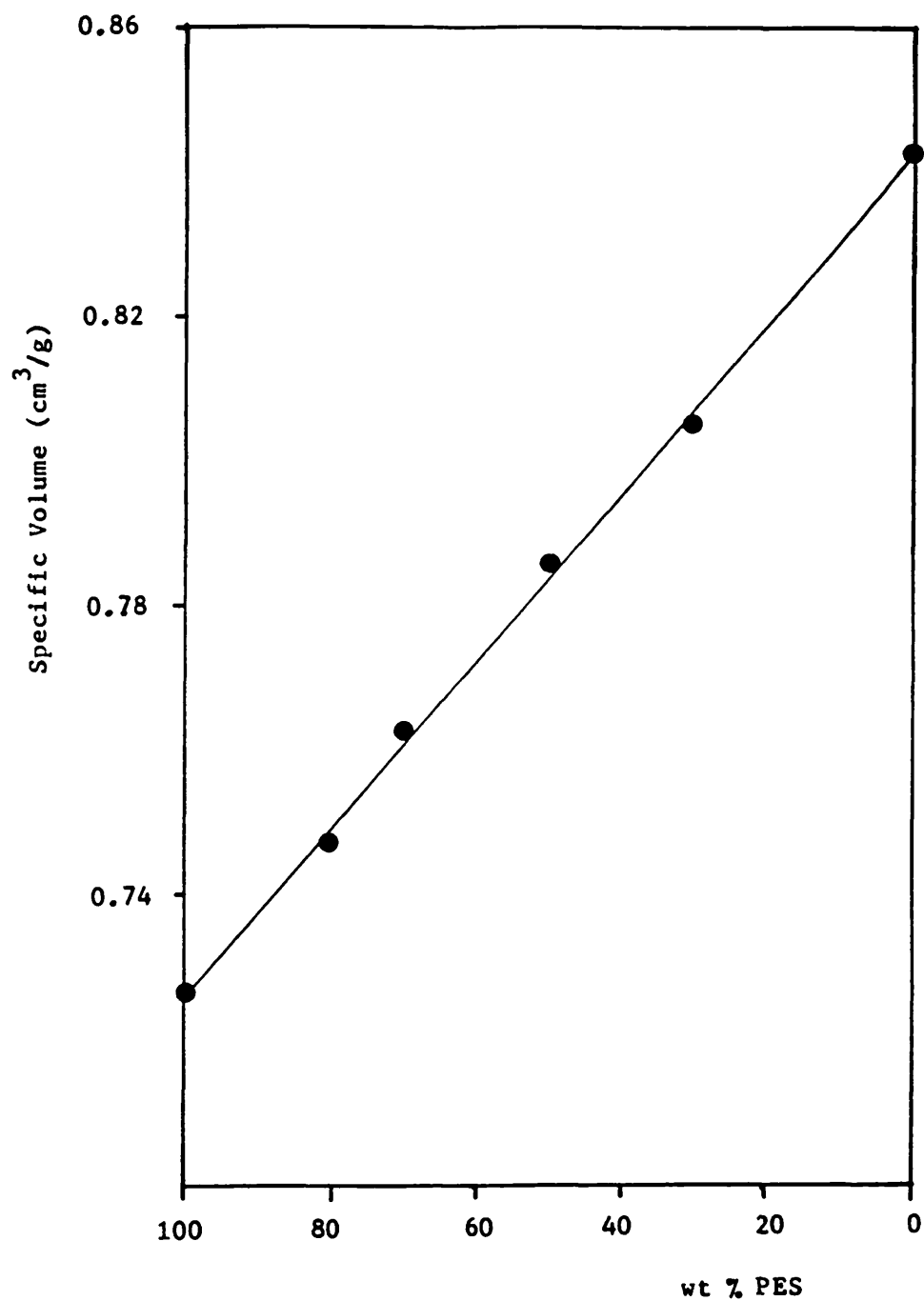


FIG. 5.3 Specific volume of PES - PHENOXY Blends

has been reported by Chiou et al for blends of poly(methyl methacrylate), PMMA and bisphenol chloral polycarbonate, BCPC⁽¹⁹³⁾ and poly(epichlorohydrine), PECH and poly(methylacrylate), PMA.

Further evidence for miscibility of the PES - Phenoxy system was provided by the variation of the frequency of hydrogen bonded hydroxy groups with blend composition. Figure (5.4) shows the infra - red spectra in the 3000 to 3800cm^{-1} region of pure phenoxy and PES-Phenoxy blends containing 30,50,70, & 80 weight percent PES, all recorded at room temperature. As mentioned previously, the spectrum in this region of pure phenoxy may be considered to be composed of two components: a broad band centered at 3450cm^{-1} attributed to hydrogen - bonded hydroxyl groups (self - associated) and a relatively narrow band at 3570cm^{-1} assigned to free (unassociated) hydroxyl groups. Upon mixing with PES, the broad hydrogen bonded hydroxyl band of the phenoxy is observed to shift to a higher frequencies as a function of increasing PES concentration. Figure (5.5) shows a plot of width at half height versus weight percent PES. The variation, proves the extent to which the hydroxyl peak of phenoxy is affected by blending with PES. Similar results have been reported on other blends containing phenoxy polymer.⁽²¹⁵⁻²¹⁷⁾ Furthermore, the relative broadness of the hydrogen bonded hydroxyl band decreases with increasing PES. The broad distribution of hydrogen bond bands in pure phenoxy would be expected due to the steric effect created by the bulky benzene rings. A similar trend was reported by Farentoltz and Kwei in

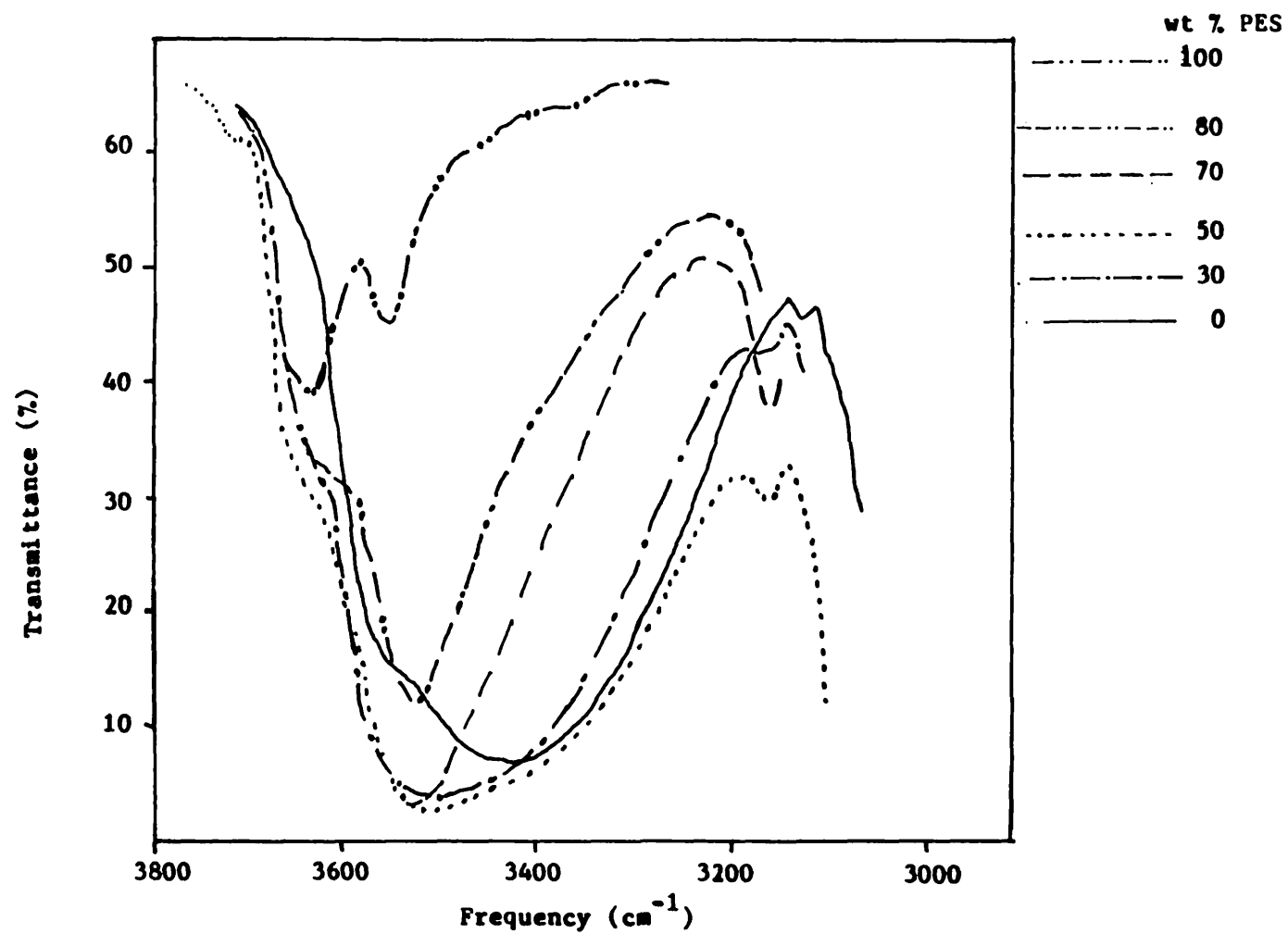


FIG. 5.4 FTIR spectra of PES - Phenoxy blends recorded at room temperature

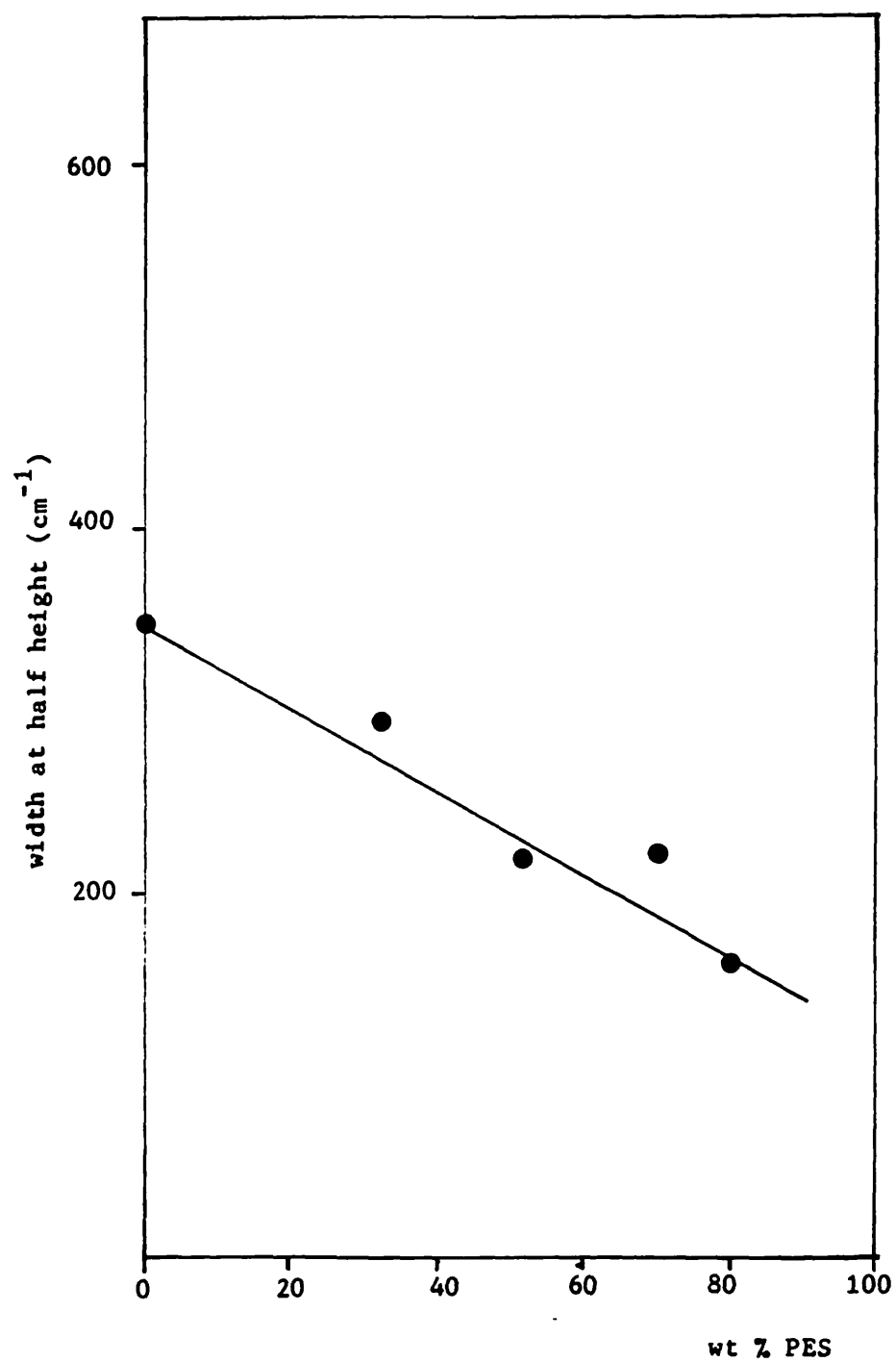


FIG. 5.5 Plot of the width at half-height versus wt.% PES

their studies of blends containing novolac resins⁽²¹⁸⁾.

5.3 Equilibrium Sorption

The solubility of CO₂ has been measured at temperatures of 30, 40 and 50°C and at penetrant pressures up to 50cmHg. The level of sorption of CO₂ in PES is larger than in Phenoxy which is the result of the difference in their glass transition temperatures and also the extensive hydrogen bonding in Phenoxy as discussed in Chap.(4). The sorption curve for the blends lie intermediate between those for the pure components as shown in figure (5.6), (5.7) and (5.8). The high pressure isotherm for CO₂/50/50/Phenox-PES blend measured at pressures up to 6 atmospheres is shown in Figure (5.9). Each curve has the characteristic shape expected for gas sorption in a glassy polymer and is well described by equation (2.23). However at high temperatures and high Phenox content, the isotherms are almost linear. The limiting solubility coefficient for CO₂ estimated from the initial slope of the isotherms, are listed in table (5.2).

The correlation between the solubility coefficient and the blend composition is shown in Figure (5.10) for all the temperatures. It is clear that the solubility increases with increasing PES composition which is as expected. The solid line through the data is predicted by,

$$\ln k = \phi_1 \ln k_1 + \phi_2 \ln k_2 \quad (5.3)$$

Where k_1 and k_2 are the solubilities for the pure component and ϕ_1 and ϕ_2 are their respective volume fractions. This data

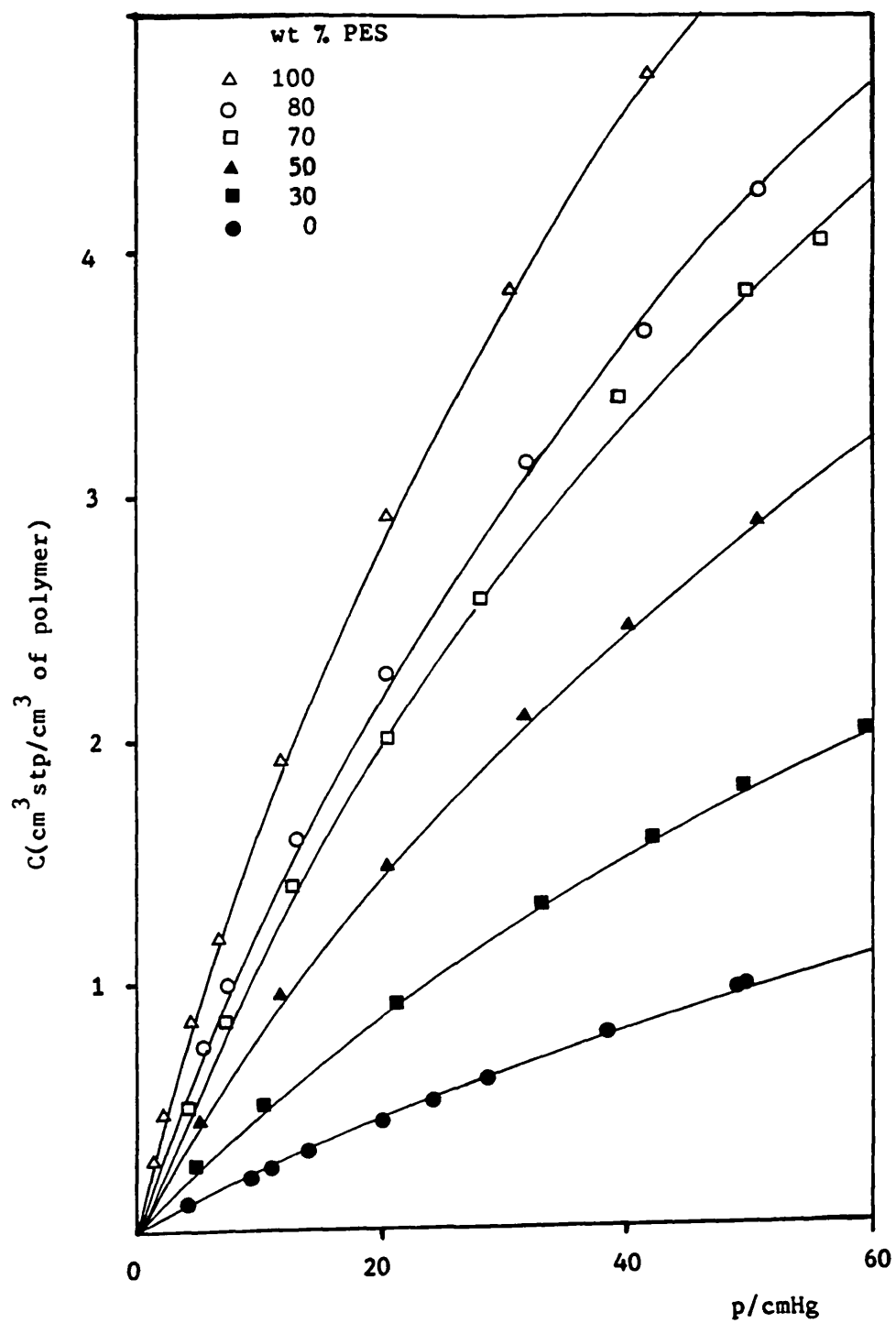


FIG. 5.6 SORPTION ISOTHERMS OF CO_2 AT 30°C

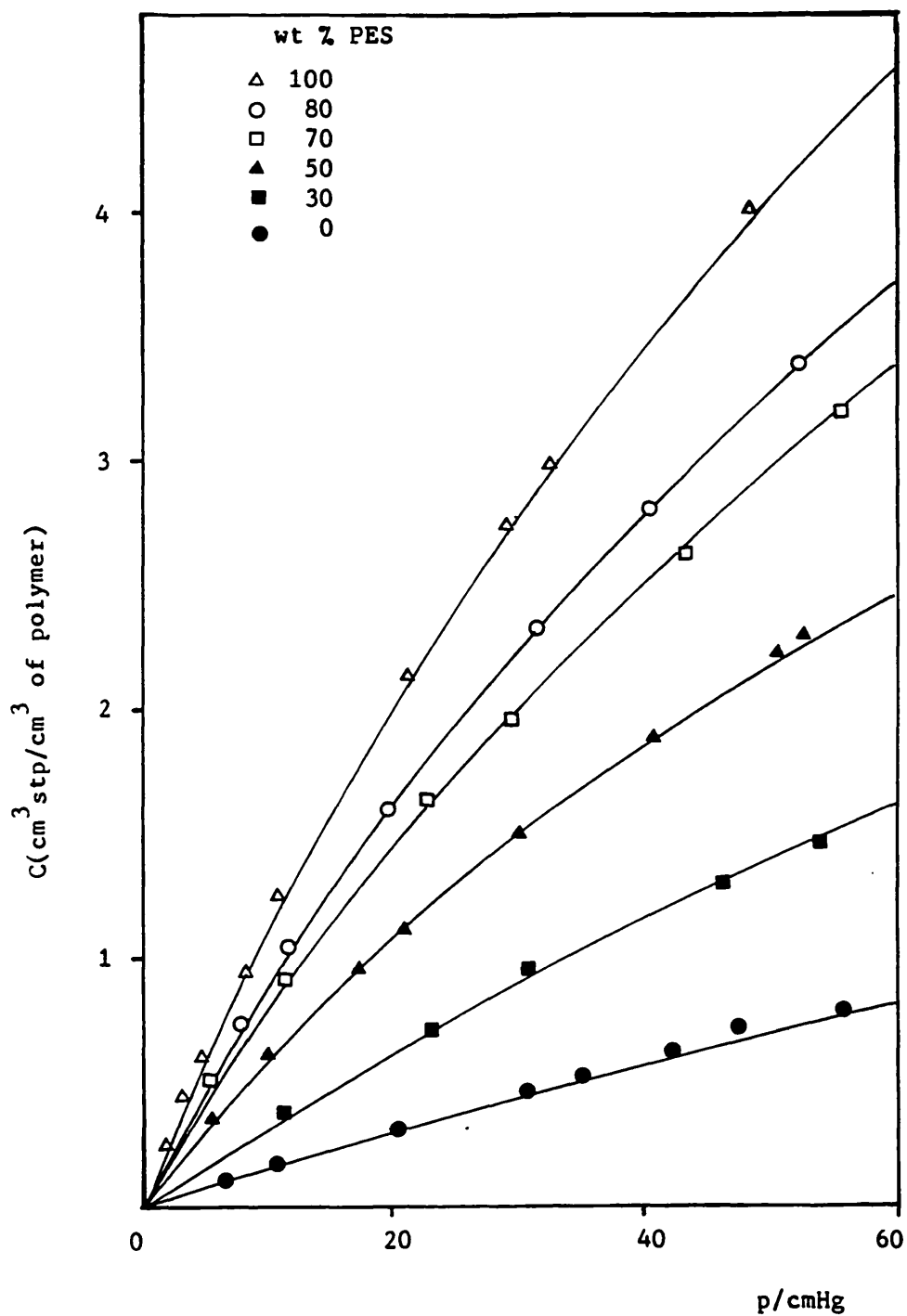


FIG. 5.7 SORPTION ISOTHERMS OF CO_2 AT 40°C

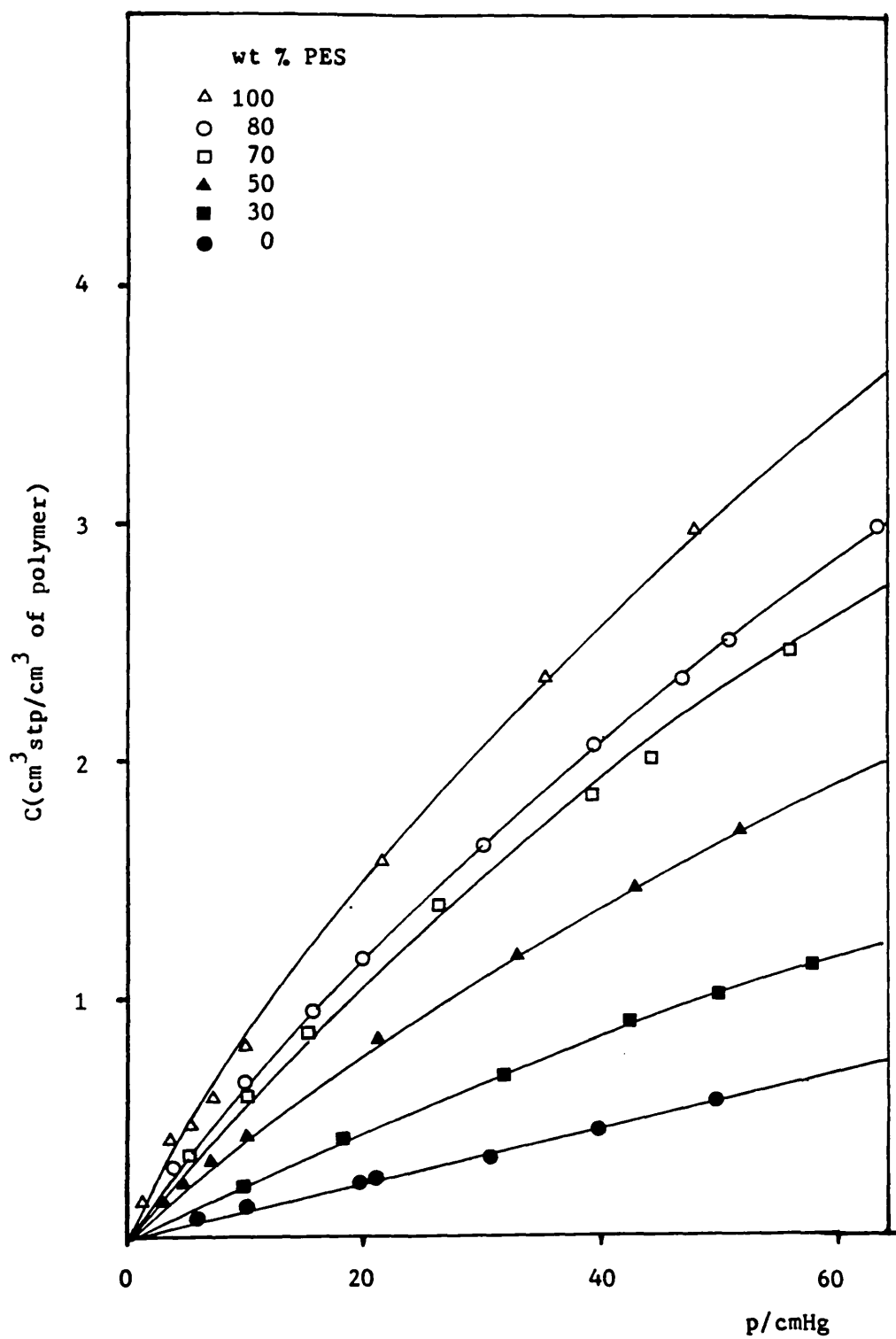


FIG. 5.8 SORPTION ISOTHERMS OF CO_2 AT 50°C

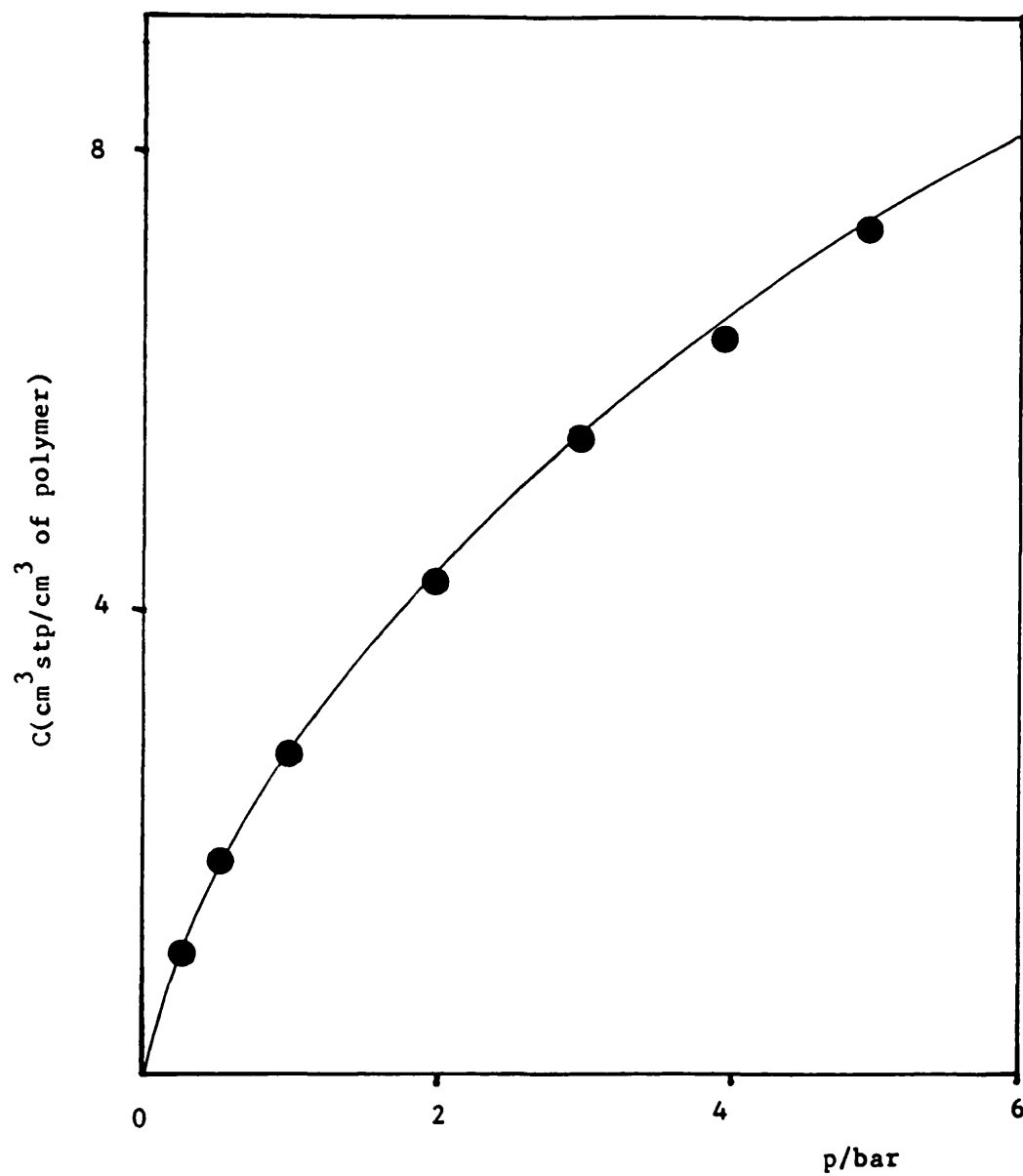


FIG. 5. 9 50% PES/CO₂ Sorption Isotherm

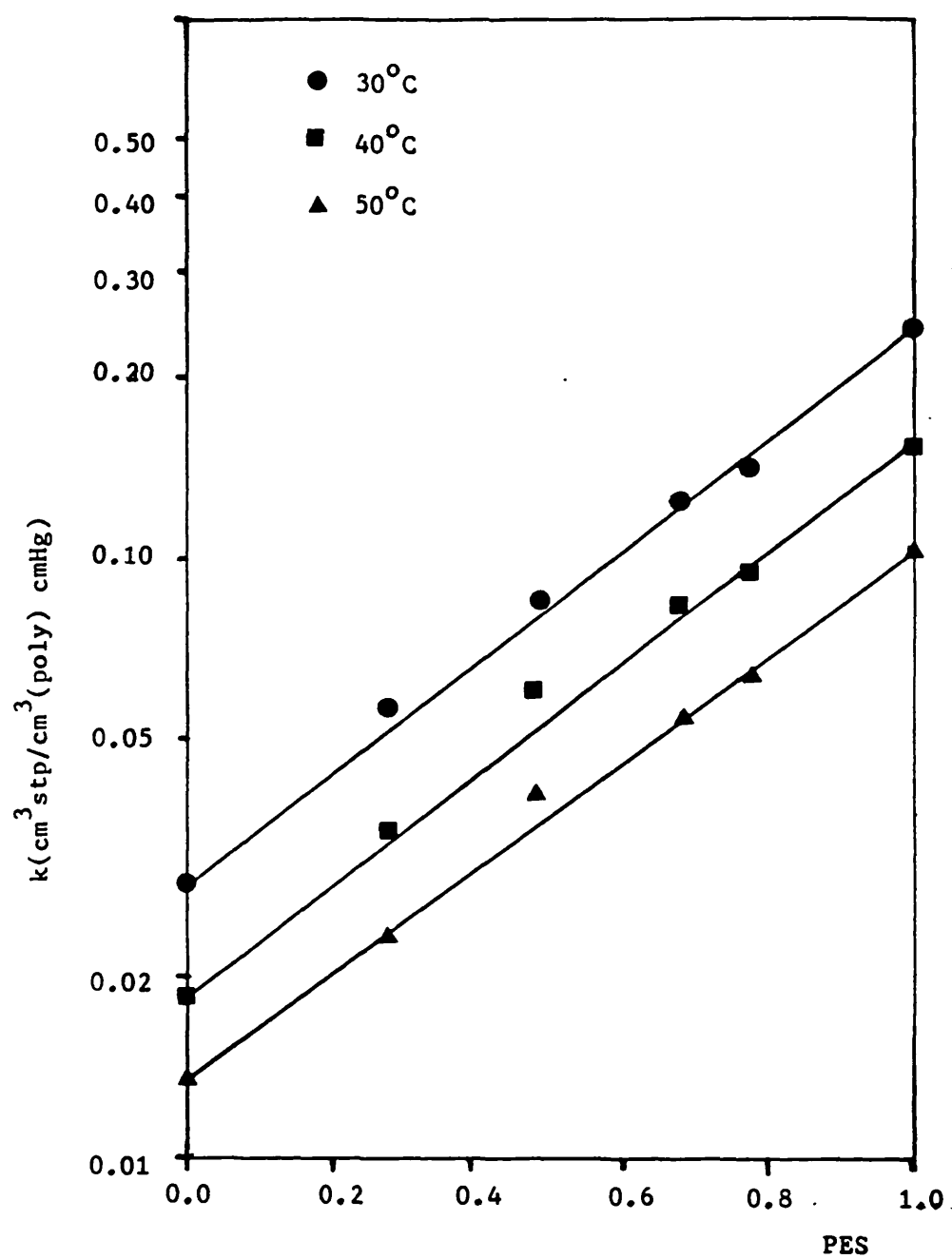


FIG 5.10 SOLUBILITY OF CO₂

indicates that the interaction parameter (χ'_{12}) in PES-Phenoxy blends is approaching zero according to equation (1.33). In

Table: 5.2 Solubility Coefficient, k of Carbon Dioxide in Blends of PES - Phenoxy

wt.% PES	$T/^{\circ}\text{C}$	$(k/\text{cm}^3 \text{ (stp)} \text{ cm}^{-3} \text{ (poly)} \text{ cmHg}^{-1})$		
		30	40	50
100		0.245	0.155	0.105
80		0.132	0.095	0.660
70		0.124	0.084	0.055
50		0.086	0.061	0.041
30		0.056	0.0353	0.0235
0		0.0286	0.0185	0.0132

general for miscible blends when the interaction between components is large, a negative deviation is observed.

The agreement of the solubility coefficient data with equation (5.3) is probably fortuitous as the expression is developed from solution theory and so only accounts for the dissolution mode of sorption in glassy polymers. Strictly a comparison should be made with k_D of the dual-mode sorption model.

The dual mode sorption parameters k_D , C'_H , and b were determined by fitting these isotherms to equation (2.23) and are

presented in table (5.3) together with the limiting Henry's law solubility coefficient = $(k = k_H + C_H' b)$. The uncertainty in these parameters was large, particularly at high temperatures and high Phenoxy content where the uncertainty was found to be greater than 100%. No percentage error has been quoted in such cases. The derived value of k will have an uncertainty considerably less than 100%. With few exceptions these parameters reveal the expected trend and decrease with increasing temperatures. Despite the large uncertainties in some of these parameters, some general conclusions can be drawn concerning the effect of blend composition on these parameters.

The Henry's law parameter k_D also shows a linear variation with blend composition as shown by figure (5.11). The Henry's law parameter, k_D is related to the equilibrium polymer-gas interaction and a rule of mixture for k_D in the blend has been developed from the Flory-Huggins theory for ternary systems, (28,29,50,56-58) which takes the following form:-

$$\ln k = \phi_1 \ln k_1 + \phi_2 \ln k_2 + \phi_1 \phi_2 \chi_{12}'$$

This relationship predicts that $\ln k$ will be a linear function of blend volume fraction when $\chi_{12}' = 0$, but will deviate above or below this line for finite interaction, depending on the sign of χ_{12}' . However, for miscible blends a negative deviation is to be expected. Since for this study the variation is linear one may assume the interaction between the two component polymer is rather weak. This has been shown by the variation of specific

TABLE: 5.3 THE DUAL MODE SORPTION PARAMETERS

wt. % PES	T/°C	$10^2 k_D$	C'_H	$10^2 b$	$k_D + C'_H b$	$C'_H b$
100	30	5.87(+49)	3.33(+90)	4.96(+66)	0.224	0.17
	40	5.47(+28)	1.92(+88)	5.03(+72)	0.151	0.09
	50	3.28	2.78	2.14	0.0922	0.06
80	30	1.01	7.25	1.99	0.154	0.14
	40	--	--	--	--	--
	50	3.00(+18)	1.84(+52)	2.31(+41)	0.073	0.04
70	30	--	16.3	0.95	--	--
	40	3.16(+11)	2.20(+21)	3.03(+20)	0.098	0.07
	50	2.49(+36)	1.87(+92)	2.29(+59)	0.068	0.04
50	30	2.89(+16)	2.18(+26)	3.43(+24)	0.164	0.07
	40*	2.74	1.30	3.49(+70)	0.07	0.05
	40*	1.03	4.06	1.32	0.06	0.05
	50	1.85(+18)	1.40(+37)	2.71(+29)	0.049	0.03
30	30	2.45	0.77	5.28	0.065	0.04
	40	1.53	1.21	1.95	0.039	0.02
	50	--	--	--	--	--
0	30	0.89	1.96	0.78	0.024	0.02
	40*	1.07	0.63	0.93	0.0166	--
	40*	0.62	1.73	0.72	0.0186	0.01
	50	1.10	0.04	2.16	0.0119	--

* Values estimated for isotherms measured at high pressure

 k_D : [cm^3 (stp) cm^{-3} (poly) cmHg^{-1}] C'_H : [cm^3 (stp) cm^{-3} (poly)] b : [cmHg^{-1}] k : [cm^3 (stp) cm^{-3} (poly) cmHg^{-1}]

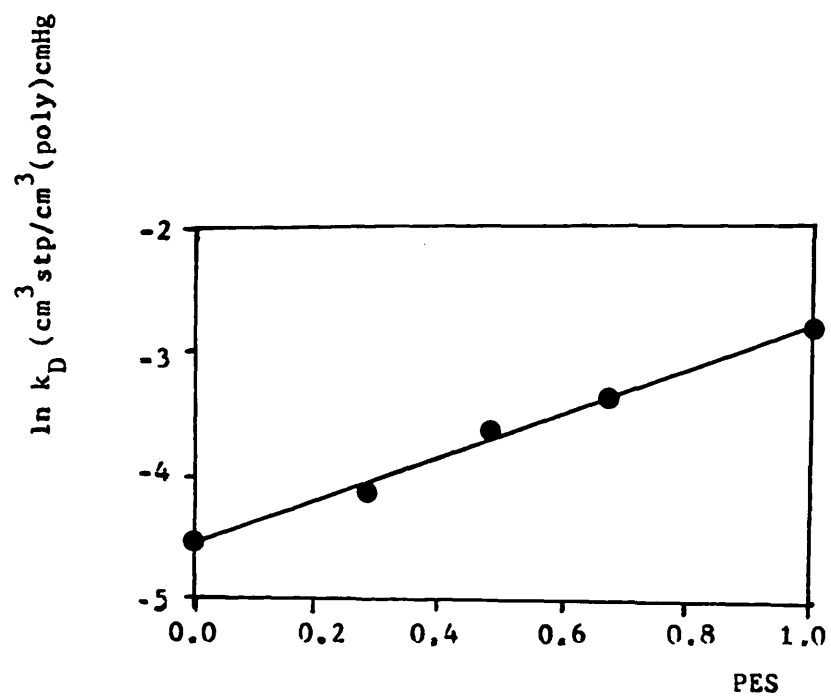


FIG. 5,11 Henry Law parameter for CO_2
in blends of PES - Phenoxy

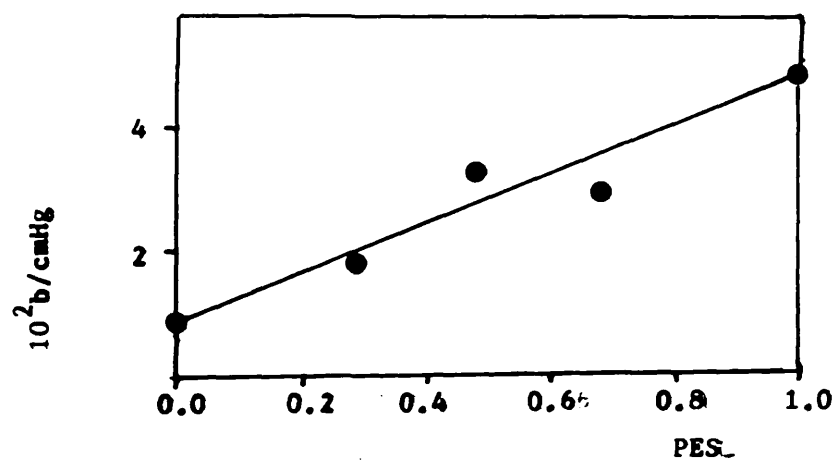


FIG. 5.12 Hole affinity parameters

volume with blend composition.

The affinity parameter, b , shows a linear variation with blend composition figure (5.12).

Figure (5.13) shows the variation of C'_H (the Langmuir capacity parameter) as a function of blend composition. The parameter increases rather smoothly with increasing PES content in the blend owing to the high T_g of PES. This behaviour have also been observed in several other glassy systems. (192,197,198,199) It has been proposed (91,133,184,201) that C'_H arises from the non-equilibrium nature of the glassy state and is related to the excess volume, $V_g - V_l$ by the following relationship:

$$C'_H = \frac{22,414}{V_{CO_2}} \frac{V_g - V_l}{V_g} \quad (5.4)$$

and that the Langmuir sorption mode stems from filling the excess volume with CO_2 in a liquid-like state, which has a molar volume V_{CO_2} of $55\text{cm}^3/\text{mole}$.

The excess volume can be computed from thermal expansion coefficients in the liquid and glassy state of the polymers using:-

$$\frac{V_g - V_l}{V_g} = (\alpha_l - \alpha_g) (T - T_g) \quad (5.5)$$

However, for most glassy polymers, the difference in thermal

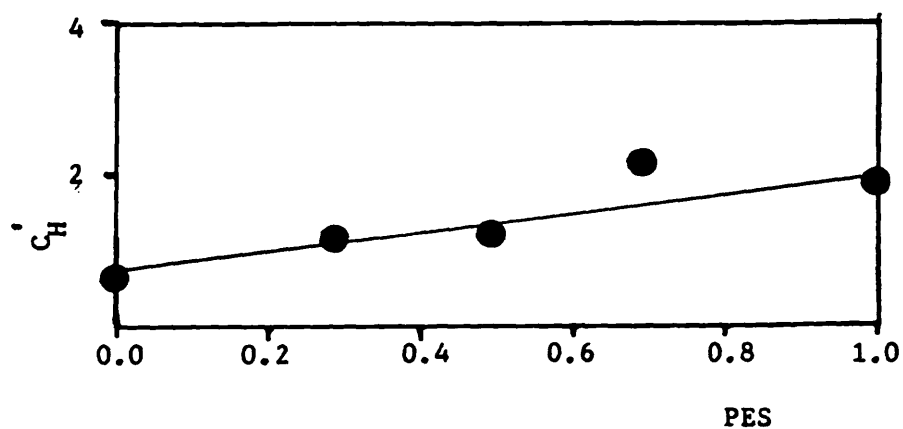


FIG. 5.13 Langmuir capacity parameter for CO_2

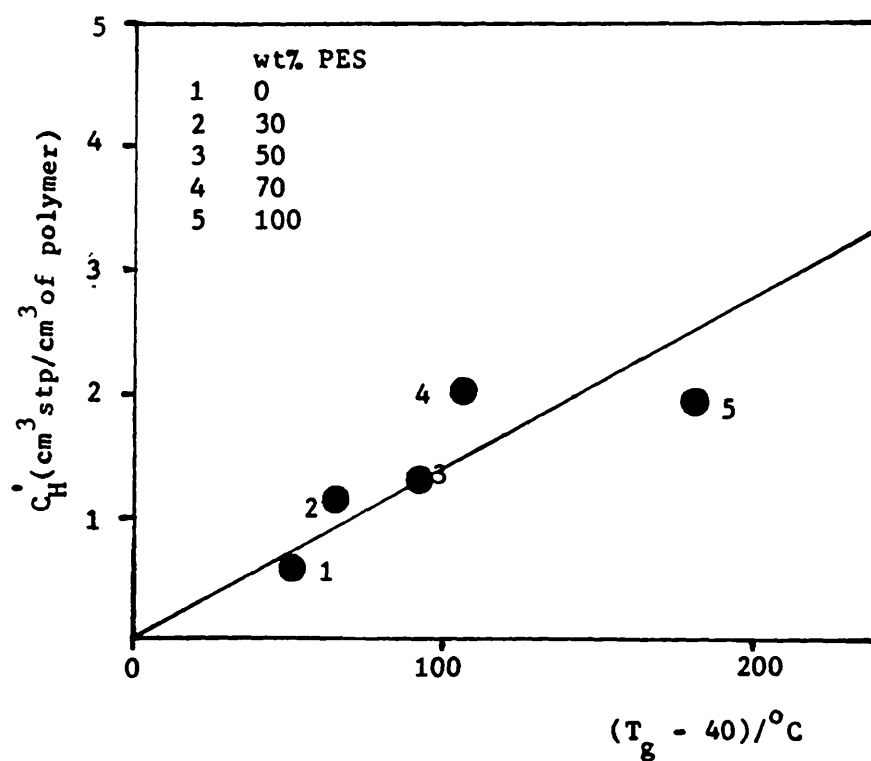


FIG. 5.14 Correlation of measured C_H^* versus $(T_g - 40^\circ\text{C})$ for various blends

expansion coefficient does not vary widely⁽²²³⁾ with temperature hence C'_H generally varies linearly with $(T_g - T)$, although exceptions have been found.⁽¹⁹⁸⁾ A plot of C'_H versus $(T_g - T)$ is shown in figure (5.14) in various blend compositions.

The solubilities decrease with increasing temperature and the solubility is plotted according to equation (2.20) in figure (5.15) from which the heats of solution estimated for each blend are given in Table (5.4).

Table: 5.4 The Heat of solution, $\Delta\bar{H}_s$, of CO_2 in Blends of
PES - Phenoxy

Vol. Fraction PES	$\Delta\bar{H}_s / \text{kJmol}^{-1}$
1.0	-32.7
0.775	-32.2
0.680	-34.5
0.475	-30.3
0.28	-34.5
0.00	-30.1

The enthalpy of solution is practically independent of the blend composition.

The corresponding isosteric heat of sorption $\Delta\bar{H}_s$ was calculated using equation (4.1) and is given in table (5.5) for all the blends.

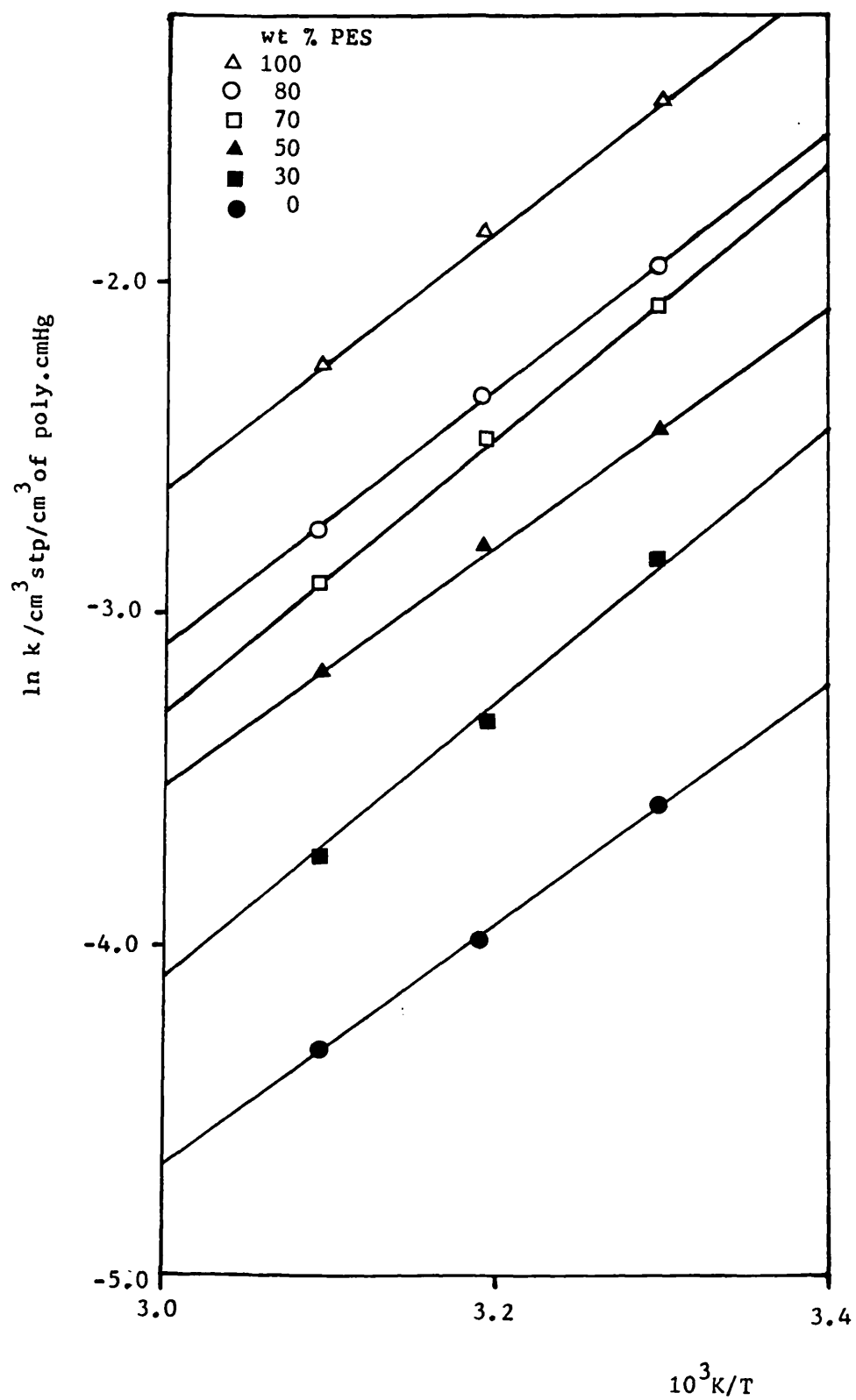


FIG. 5.15 Van't Hoff plots of CO₂ solubility in PES - Phenoxy blends

Table: 5.5 Isosteric Heat of Sorption of CO₂ in PES - Phenoxy Blends

Wt. % PES	$c/\text{cm}^3(\text{stp})\text{cm}^{-3}(\text{poly})$	$-\Delta\bar{H}_s/\text{kJmol}^{-1}$
100	1.0	36.71
	1.5	28.49
	2.5	34.50
	3.0	33.67
	3.5	29.93
70	1.5	30.35
	2.0	31.18
	2.5	36.99
50	0.8	32.42
	1.2	30.35
	1.6	31.59
30	0.4	33.62
	0.6	31.17
	1.0	28.69
	1.2	29.10
0	0.1	29.69
	0.3	25.78
	0.5	26.60
	0.6	28.26
	0.7	25.36

The CH_4 equilibrium sorption isotherms for CH_4 in PES/Phenoxy mixture are shown in figures (5.16), (5.17) and (5.18). Although there is slight scatter in the data, it is obvious that Henry's law is followed. This may be due to the very low uptake of CH_4 , and it is anticipated that at sufficiently high pressures, the usual curvature would be observed. The sorption of CH_4 in the 50/50 PES-Phenoxy blend was measured at 40°C in the pressure range of 0 - 6 atmosphere. As can be seen from figure (5.19), a weak but distinct negative deviation was observed. The solubility coefficient estimated from the initial slope of the isotherm shows excellent agreement with the value obtained from the low pressure isotherm. Dual mode sorption analysis could not be carried out since the isotherm was relatively weak. The solubility coefficients estimated from the best fit straight line, constrained, to pass through the origin are given in table (5.6).

Due to large scatter in the data, the variation of solubility with blend composition is only shown for 30°C (Figure (5.20)). Once again the deviation from the tie line is fairly small, considering the uptake was low. The temperature dependence of the solubility coefficient is shown in the form of a Van't Hoff plot (equation (2.20)) in figure (5.21) from which the heat of solutions were determined and are collected in table (5.7).

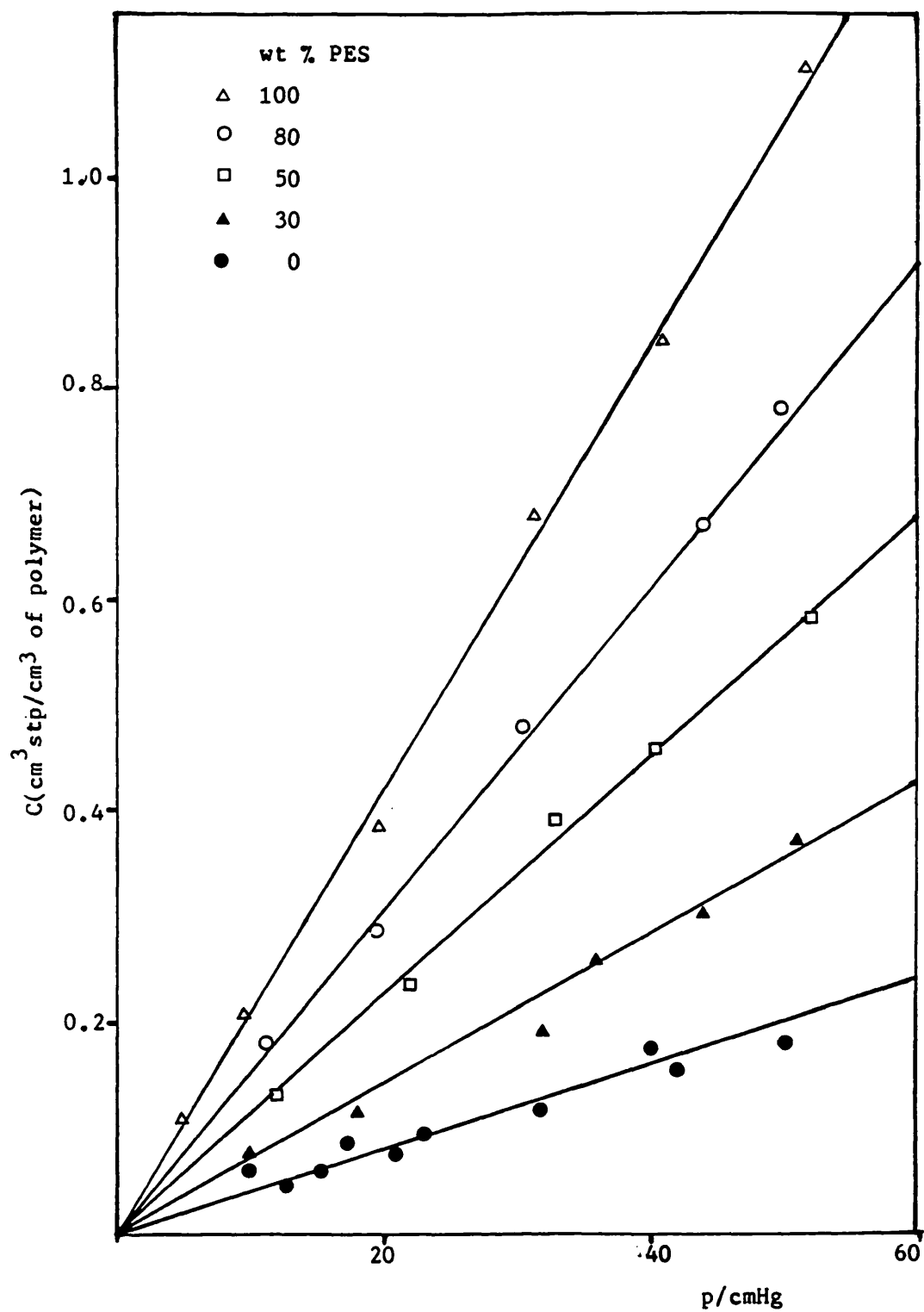


FIG. 5.16 SORPTION ISOTHERMS OF CH_4 AT 30°C

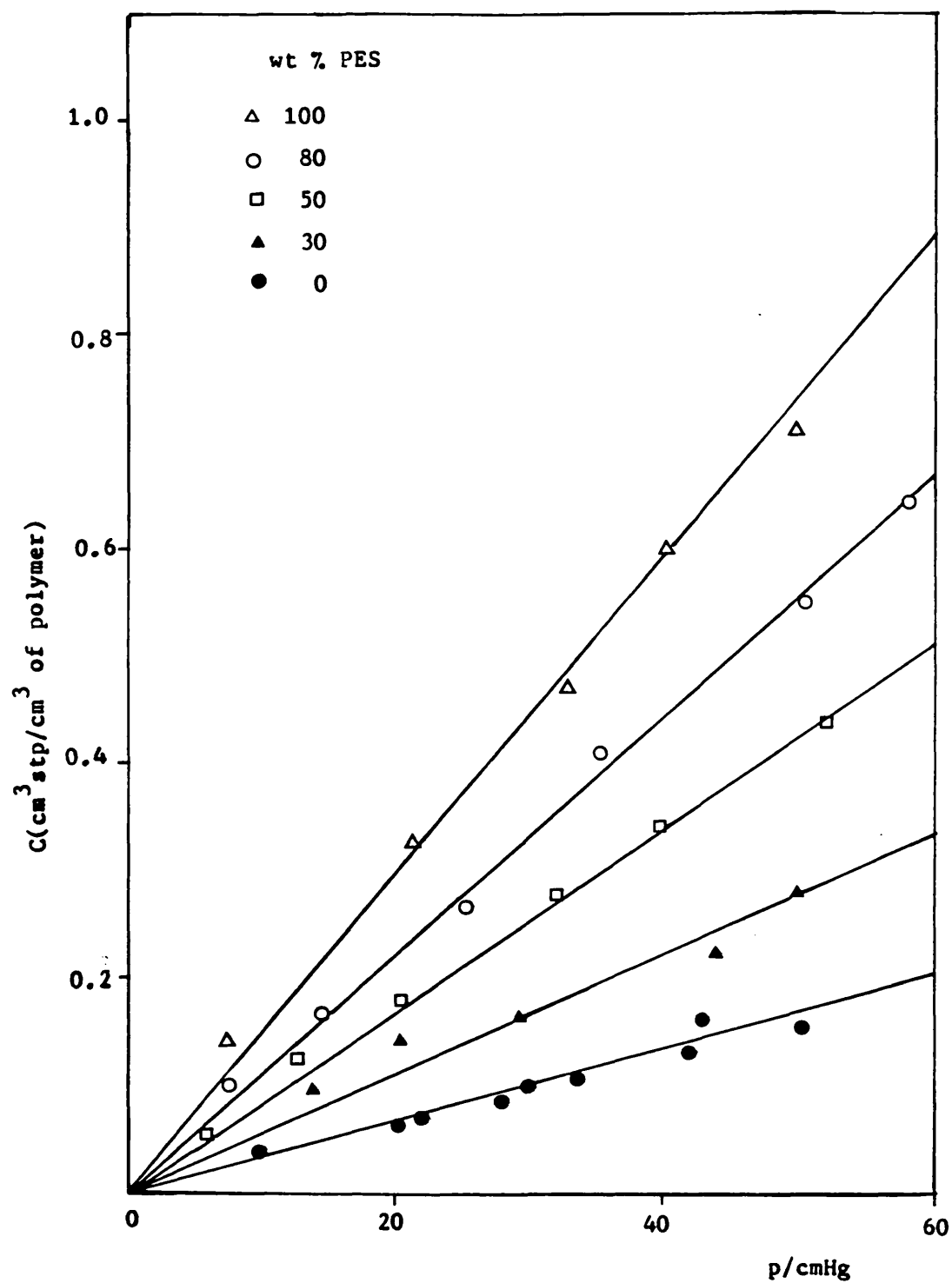


FIG. 5.17 SORPTION ISOTHERMS OF CH_4 AT 40°C

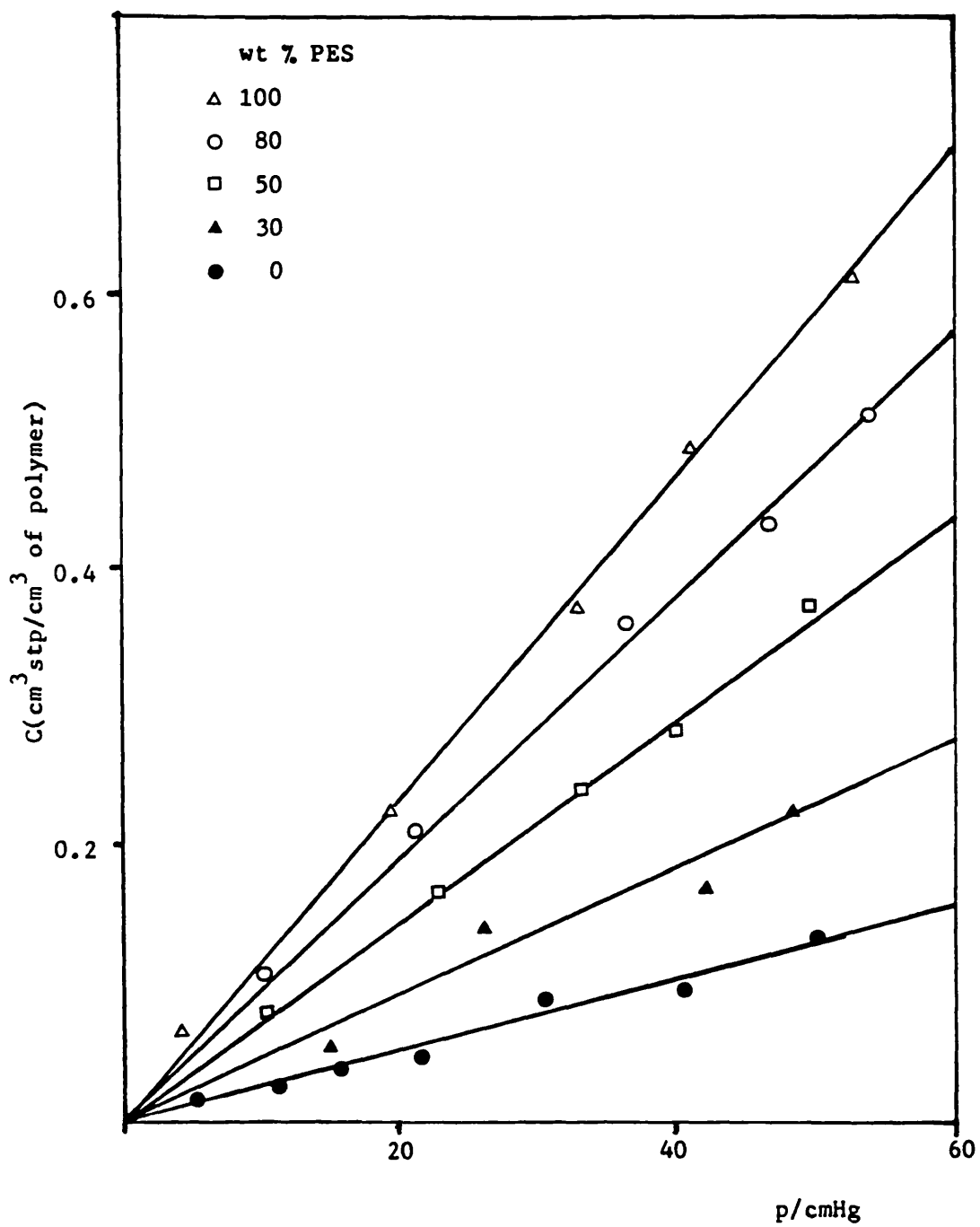


FIG. 5.18 SORPTION ISOTHERMS OF CH_4 AT 50°C

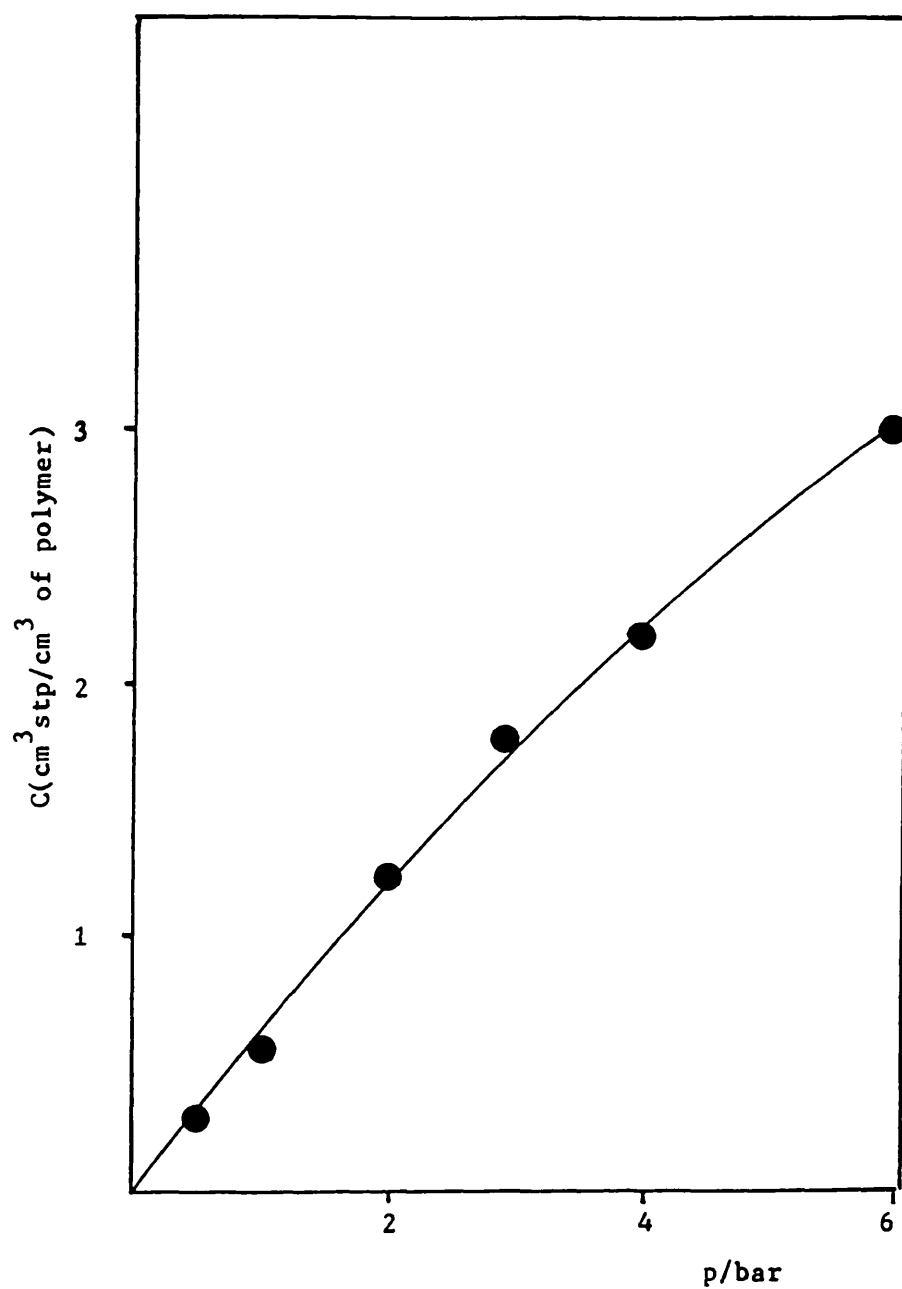


FIG. 5.19 50% PES/CH₄ Sorption Isotherm at 40°C

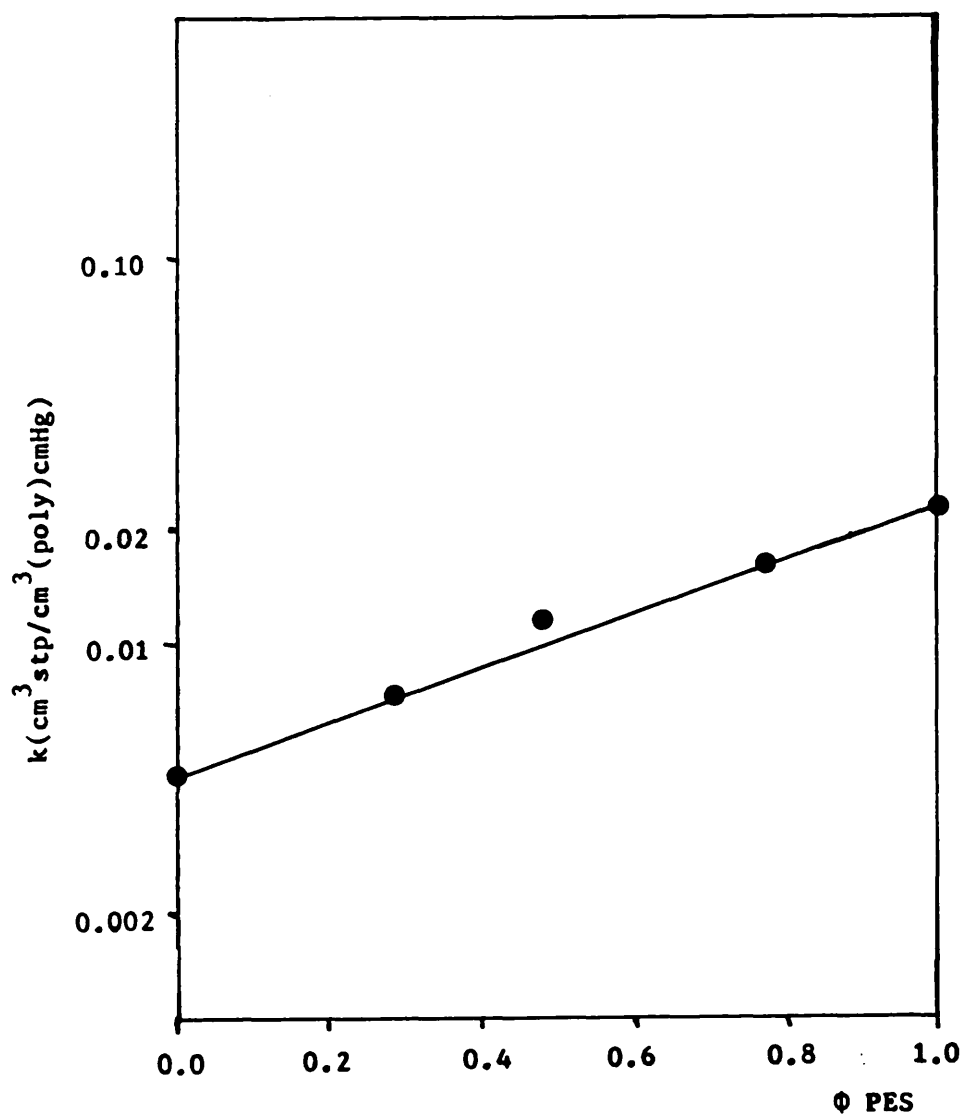


FIG. 5.20 SOLUBILITY OF CH_4

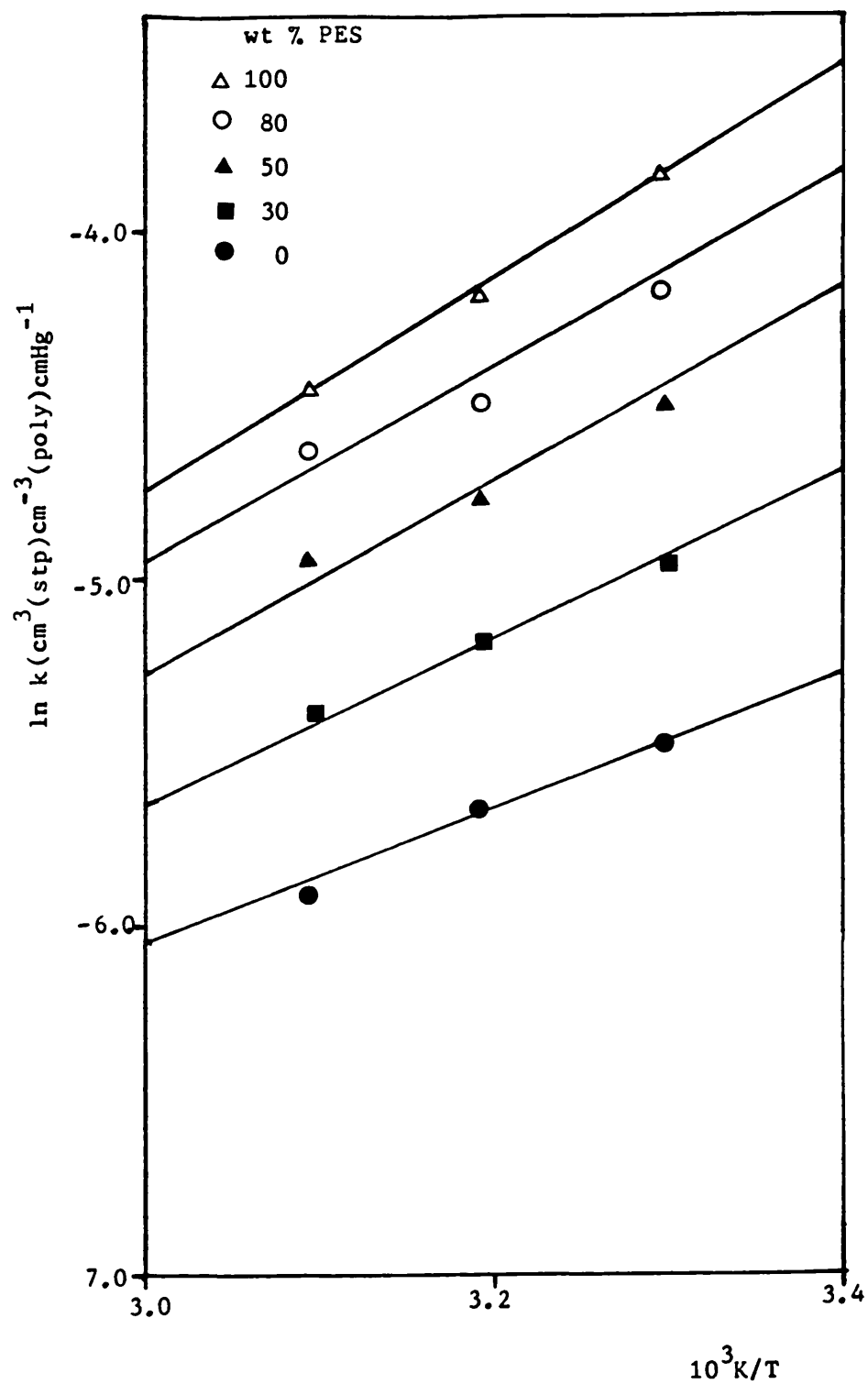


FIG. 5.21 Van't Hoff plots of CH_4 solubility in PES - Phenoxy blends

TABLE: 5.6 HENRY'S LAW SOLUBILITY COEFFICIENT, k , FOR CH_4 IN
PES - PHENOXY BLENDS.

Wt % PES	$T/^{\circ}\text{C}$	$(k/\text{cm}^3(\text{stp}) \text{ cm}^{-3}(\text{poly}) \text{ cmHg}^{-1})$		
		30	40	50
100		0.0210	0.0149	0.0119
80		0.0152	0.0112	0.0095
50		0.0111	0.0085* 0.0082	0.0078
30		0.0072	0.0056	0.0046
0		0.0041	0.0035	0.0027

* Solubility coefficient estimated from high pressure isotherm

TABLE: 5.7 HEATS OF SOLUTION OF CH_4 IN PES - PHENOXY BLENDS

Vol. Fraction PES	$\Delta \bar{H}_s / \text{kJmol}^{-1}$
1.0	-28.84
0.775	-23.38
0.475	-23.38
0.280	-20.01
0.000	-15.85

The heat of solution increased with increasing phenoxy composition. This may be due to the large difference in their

glass transition temperatures which reflect on the dual mode sorption mechanism. The existence of hydrogen bonding in phenoxy as mentioned previously, makes the polymer chain more rigid and may also contribute to this behaviour.

5.4 Steady State Permeation

Permeabilities for CO₂ measured in the range 30^o to 50^oC are summarized in Table (5.8). The permeabilites were independent of the ingoing pressure in the range 0 - 25 cmHg and the values in Table (5.8) are the average of 3 to 4 measurements made over a wide pressure range. Detailed results are given in Appendix (2).

Table (5.8) Permeability Coefficient for CO₂ in PES - Phenoxy Blends

	T/ ^o C	(10 ¹⁰ P/cm ³ (STP) cm cm ⁻² s ⁻¹ cmHg ⁻¹)	
Wt % PES	30	40	50
100	5.33	5.92	6.25
80	2.16	2.54	2.96
70	1.84	2.16	2.50
50	1.11	1.32	1.56
30	0.66	0.84	1.11
0	0.52	0.73	0.93

However, as mentioned in Chapter (4), for most glassy polymers a decrease in permeability with increasing penetrant pressure is observed^(126,127,162,200,209-212) at higher

pressures. Permeation of CO₂ with pressures up to 6 atmospheres in 50/50 blend of PES/Phenoxy measured at 40°C showed a decrease in permeability as shown in Figure (5.22). This decrease is very small and the value for the permeability coefficient is in good agreement with that obtained from the low pressure measurements.

There is a marked decrease in permeability as the phenoxy content is increased as expected for the reasons mentioned in chapter (4). Figure (5.23) shows the variation of permeability plotted semi-logarithmically against volume fraction of PES at 30°C. As discussed in chapter (3), for miscible blends, when the interaction between component polymers is weak⁽¹⁶¹⁾ a linear variation of log permeability with blend composition is described by the following equation (2.57).

$$\ln P = \phi_1 \ln P_1 + \phi_2 \ln P_2 \quad (2.57)$$

Where ϕ represents the volume fractions and subscripts 1 and 2 refer to the two component polymers. As can be seen, gas permeabilities for the blends are lower than those calculated from equation (2.57), represented by the solid line in Figure (5.23). Similar results have been reported for other miscible blend systems.^(193,197) These systems possessed a moderate interaction between the component polymers. In cases where the interaction is relatively strong, permeabilities of the blends are significantly lower than those of the two component polymers. Whereas, on-the other hand for systems where interactions appear to be very weak, for example random co-polymers of methacrylonitrile and styrene⁽¹⁷⁷⁾, and poly (methyl

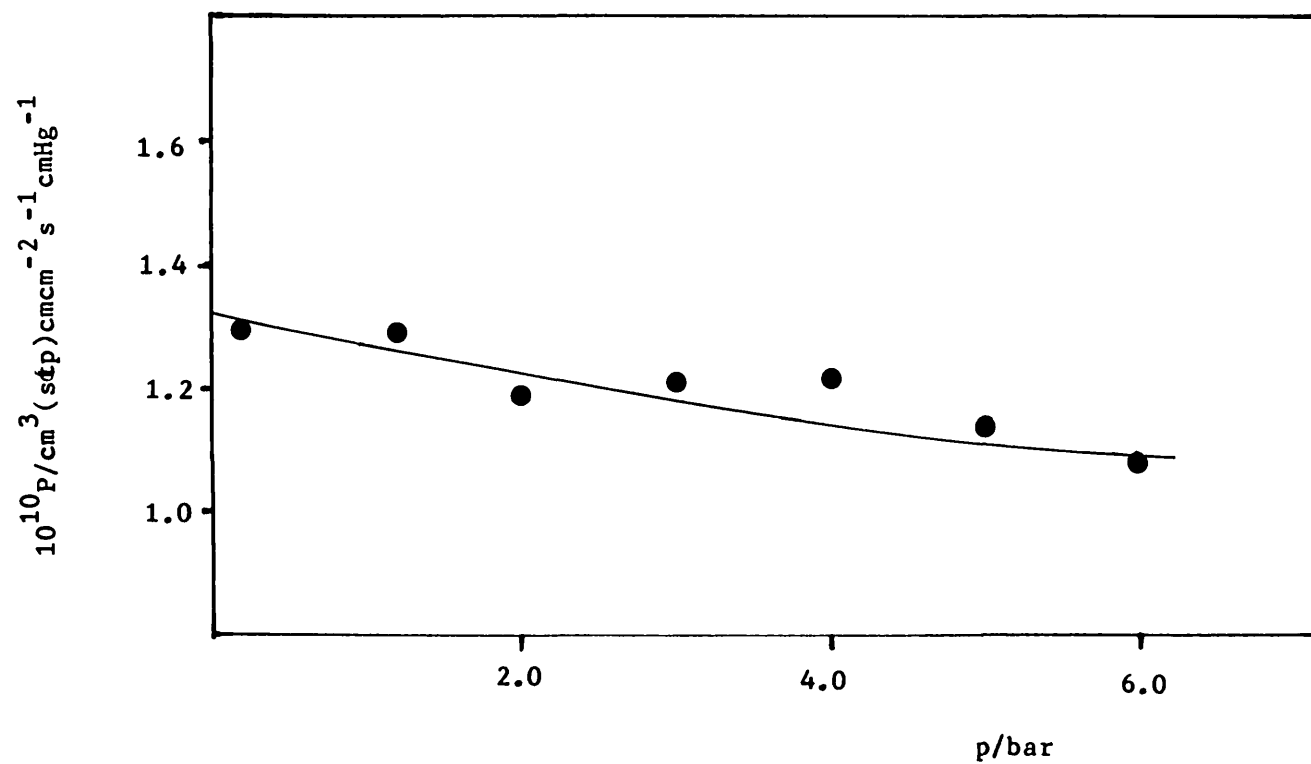


FIG. 5.22 Pressure dependence of CO_2 permeability of 50/50 blend of PES - Phenoxy at 40°C

methacrylate), styrene - acrylonitrile co-polymer blends^(170,171), the permeability coefficients are higher than those predicted by equation (2.57). This suggests that the interaction between the components in this study may be moderate. However, the solubility data and the specific volume show a relatively weaker interaction. The permeabilities predicted by the free volume theory equation (2.64) proposed by Lee^(166,167) are also shown in Figure (5.23), represented by the dashed line.

$$\ln(P/A) = \left[\frac{\phi_1}{\ln(P/A)} + \frac{\phi_2}{\ln(P/A)} \right]^{-1} \quad (2.64)$$

Where A is a gas constant, in this case a value of $6. \times 10^{-6} \text{ cm}^3$ (stp) $\text{cm/cm}^2 \text{ s}^1 \text{ cmHg}$ was used for CO_2 . Once again the experimental permeabilities are lower than those calculated from equation (2.64). A similar effect was reported for gas permeation in miscible blends of Poly (methyl methacrylate) with bisphenol Chloral Polycarbonate⁽¹⁹³⁾. It has been known that if there is a significant volume contraction for the blend on mixing, then the permeability will be lower than predicted by equation (2.64). Since the permeabilities are lower than those calculated, one may assume that there is some volume contraction during mixing. However, from the variation of specific volume this contraction is not significant enough to need a correction which would enable the values of the experimental permeabilites to become closer to the theoretical values based on equation (2.64). Furthermore, according to equation (2.64), which assumes additivity of free volume, the gas permeability of the blend will

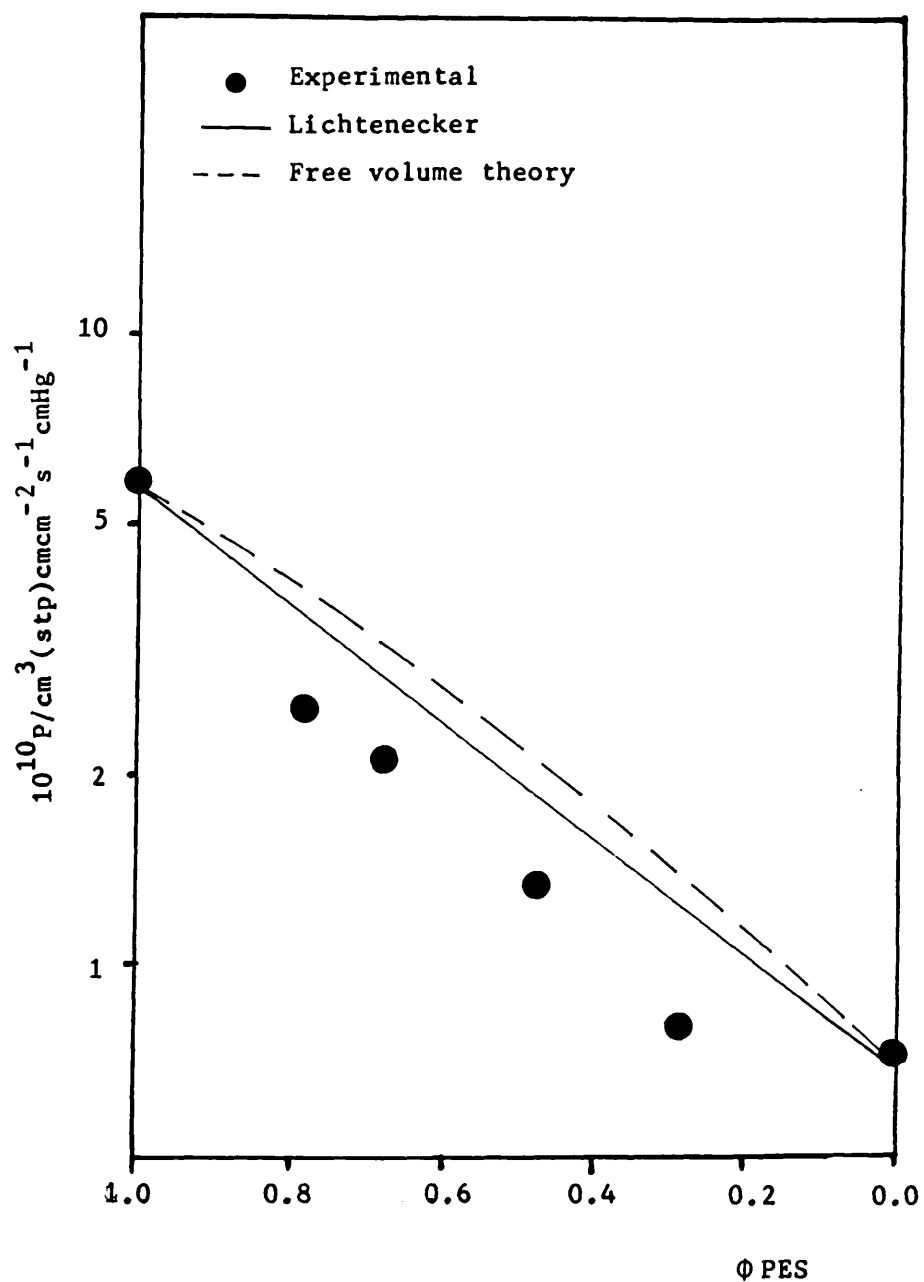


FIG. 5.23 Permeability of CO_2 at 30°C -
Comparison with Homogeneous models

be higher than that calculated from equation (2.57) provided P_1 and P_2 are different. In this case the permeabilities calculated using equation (2.64) are higher than those from equation (2.57). However, the difference in P_1 and P_2 differ only by a factor of 10 which results in the values predicted by equation (2.64) and (2.57) being fairly close. Chiou et al have shown that when P_1 and P_2 only differ by a factor of 10 equation (2.64) reduces to eqn (2.57).

Although it is established that the PES/Phenoxy blends are miscible it is of interest nevertheless to compare the permeability with that for a heterogenous blend. In figure (5.24) comparison is made with the Maxwell, Higuchi and Bottcher expressions. Clearly they do not represent the experimental data.

The lines show the prediction of the models for the case when $P_c \gg P_d$, the equations reducing to the following forms:-

$$\text{Maxwell} \quad P_m = P_c \frac{2\phi_c}{2 + \phi_d}$$

$$\text{Böttcher} \quad P_m = P_c (\phi_c)^{3/2}$$

$$\text{Higuchi} \quad P_m = P_c \frac{1.61 \phi_c}{1.61 + 1.39 \phi_c}$$

In this case PES was considered as the continuous phase and phenoxy as the disperse. Maxwell model was also tested for phenoxy representing the continuous phase.

The permeabilities of PES Phenoxy blends to CH_4 , measured in

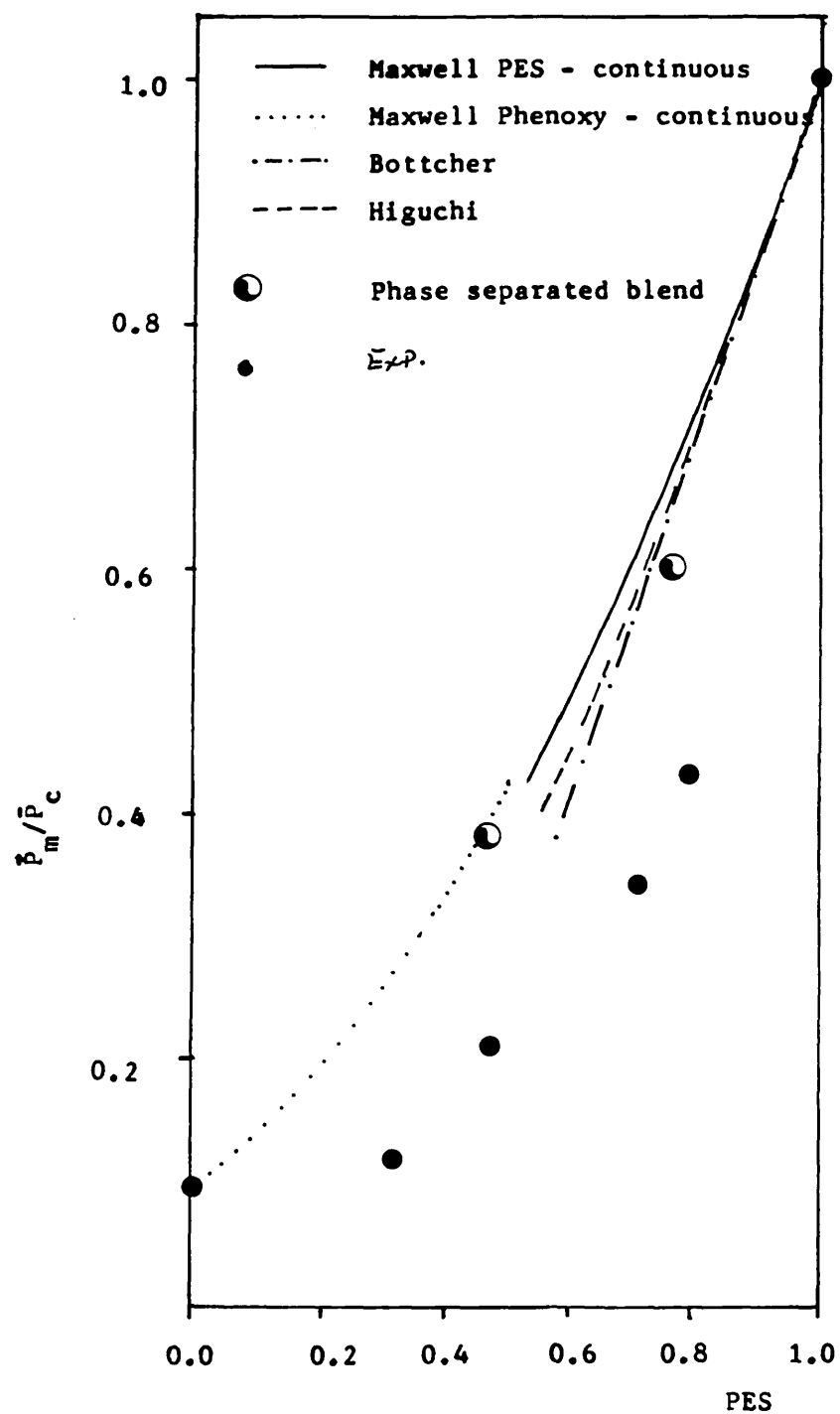


FIG. 5.24 Permeability of CO_2 at 30°C
- Comparison with Heterogeneous
models with PES as the continuous
phase

the same temperature and pressure range were independent of the ingoing pressures.

Table (5.9) Permeability Coefficient for CH₄
in PES - Phenoxy Blends

Wt%PES	$(10^{11} \text{P/cm}^3 (\text{STP}) \text{cm cm}^{-2} \text{s}^{-1} \text{cm Hg}^{-1})$		
	T°/C		
	30	40	50
100	1.1	1.61	2.38
80	0.58	0.80	1.17
70	0.47	0.71	1.08
50	0.29	0.42	0.83
30	0.21	0.33	0.49
0	0.14	0.24	0.41

The variation of permeability coefficients, estimated from the average of 3-4 measurements, made over a range of pressures, at three different temperatures is shown table (5.10) and in figure (5.25).

Once again the permeability increases monotonically with increasing PES content in the blend, since the overall rate of permeation in PES is high compared to Phenoxy.

The temperature dependence of the permeability for both gases is shown in the form of Arrhenius plots in figure (5.26) and (5.27). The respective activation energies for permeation calculated from these linear plots are given in Table (5.10).

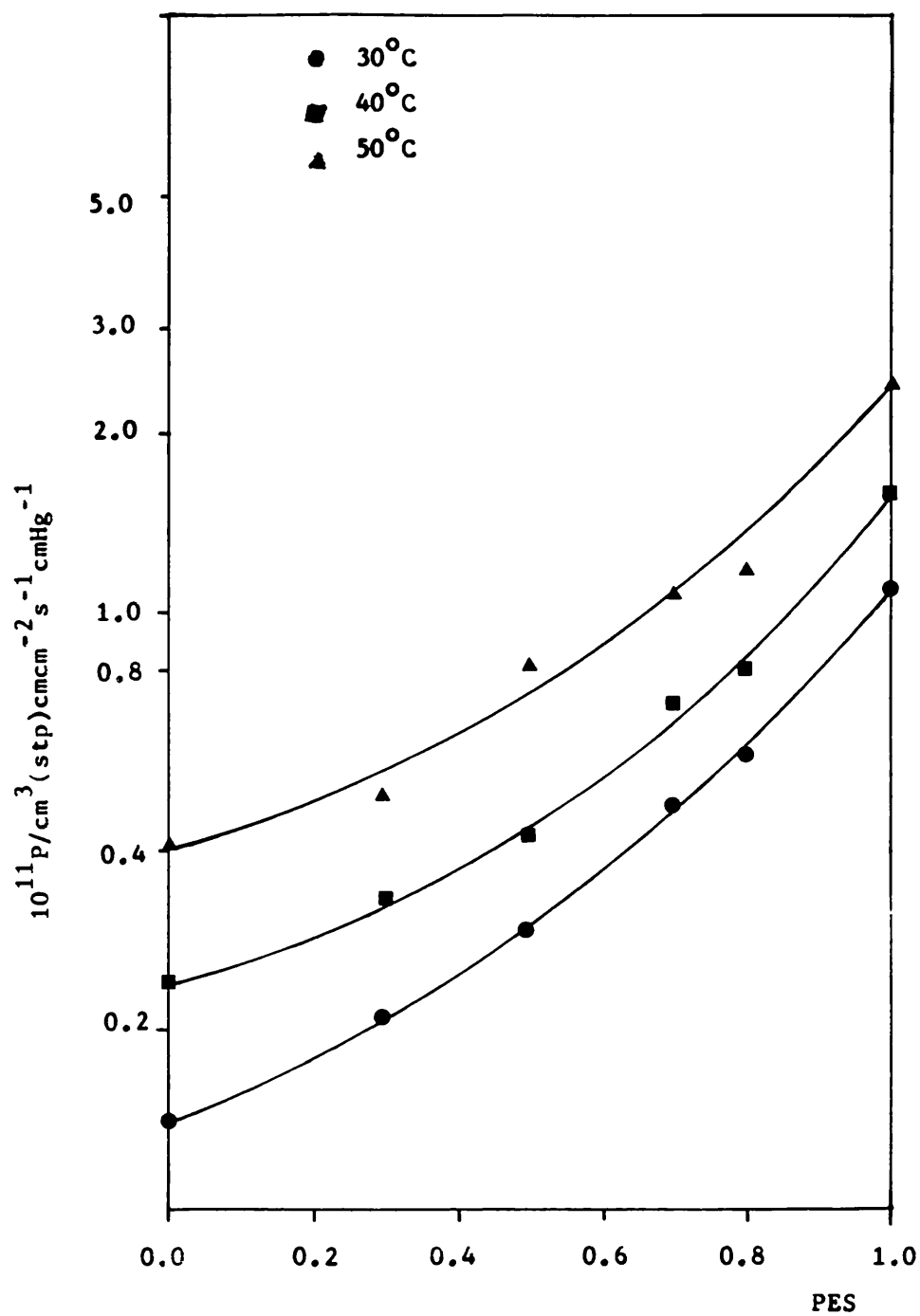


FIG. 5.25 Permeability of CH_4 in blends of PES - PHENOXY

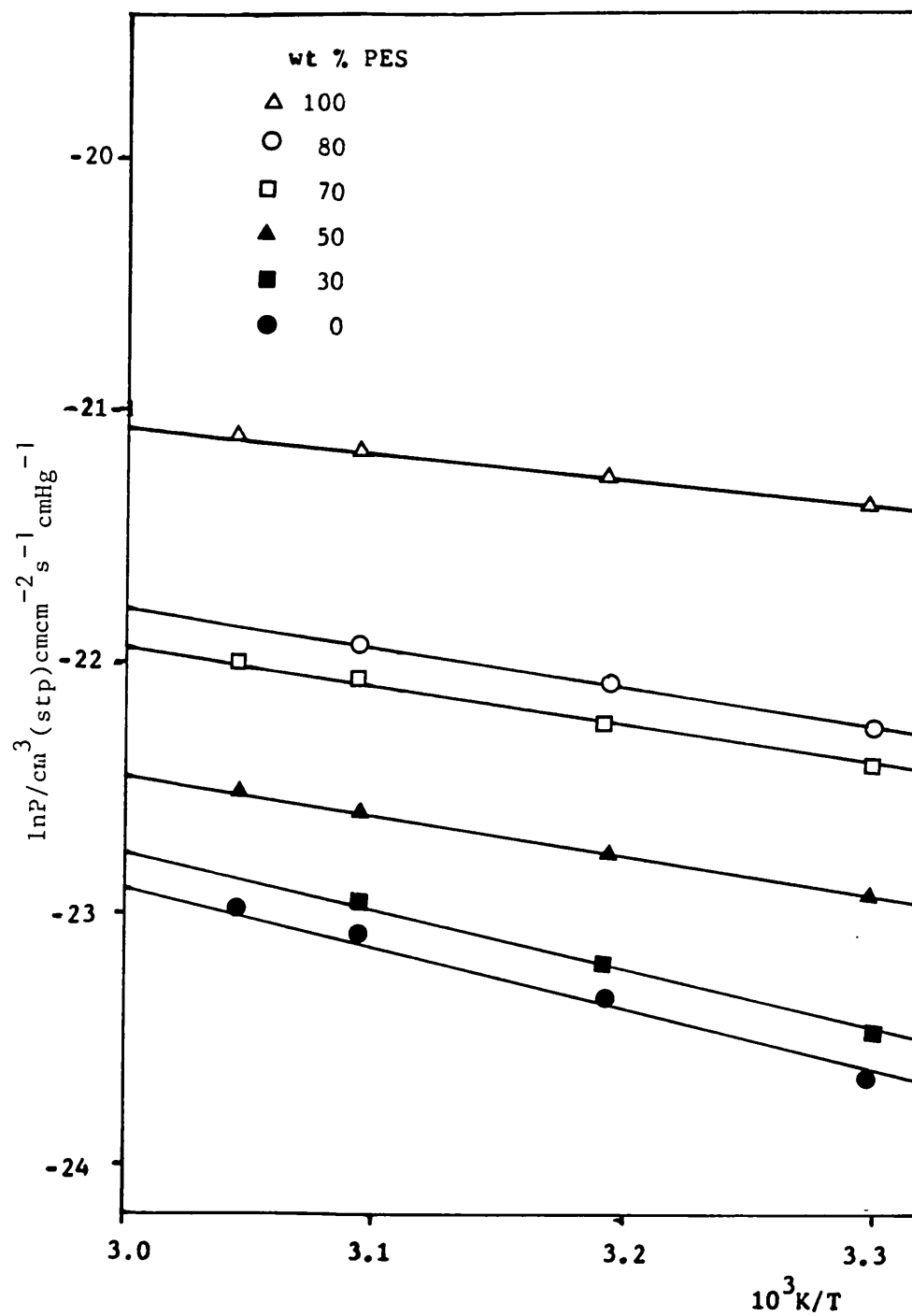


FIG. 5.26 Arrhenius plots of CO_2 Permeability

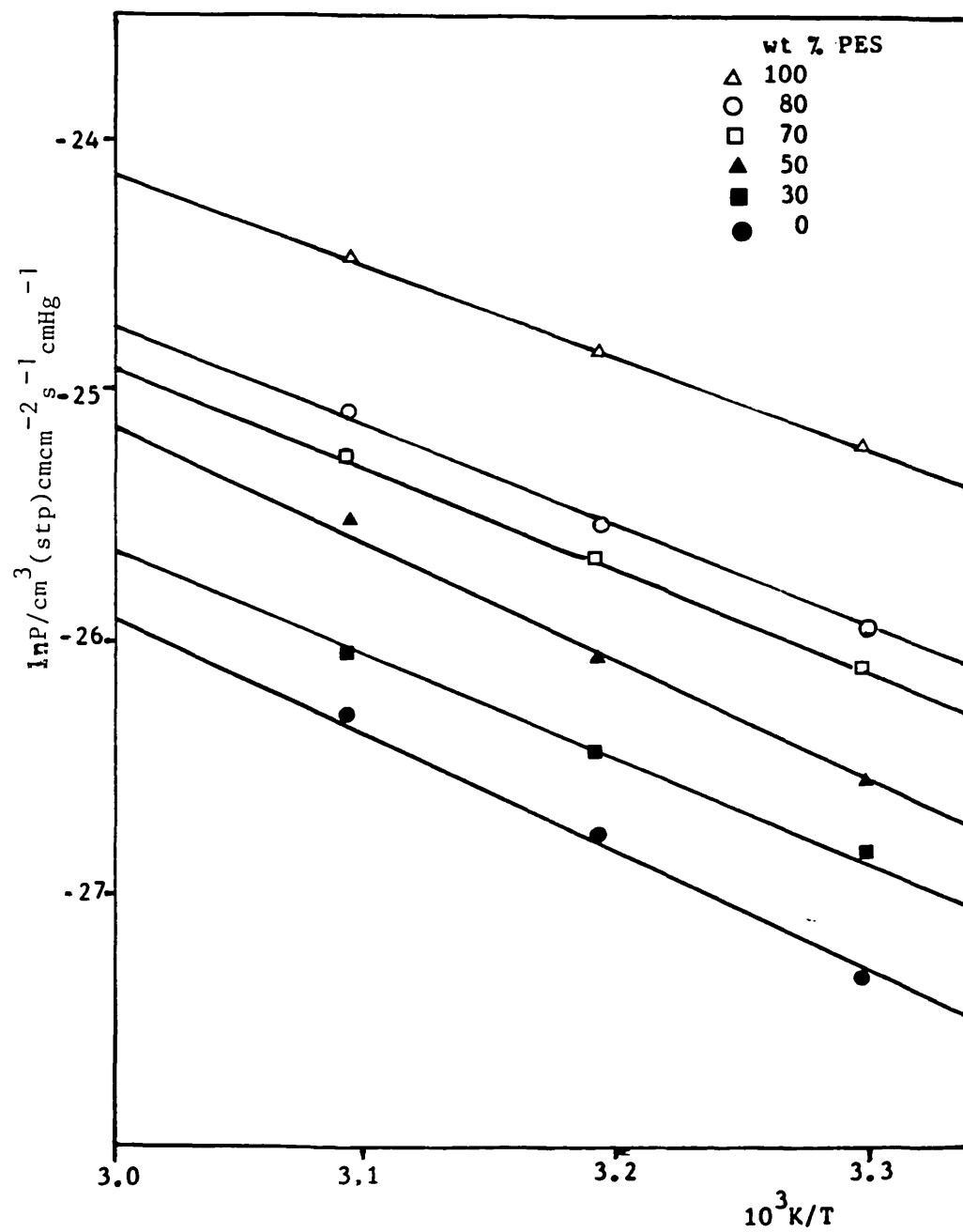


FIG. 5.27 Arrhenius plots of CH_4 Permeability

Table (5.10) Activation Energies for Permeation of
CO₂ and CH₄ (kJmol⁻¹)

Wt IPES Blend	E _{pCO2}	E _{pCH4}
100	11.4	31.6
80	12.5	35.3
70	13.5	37.6
50	15.0	42.6
30	20.2	38.8
0	22.6	42.3

Clearly the activation energies for CH₄ are much higher compared to CO₂ since CH₄ is a larger molecule as already mentioned in chapter (4). The variation of the activation energies of CO₂ as a function of blend composition are presented in figure (5.28). The linear variation along the additivity line (represented by solid line) is again consistent with miscibility of the two homopolymers. Figure (5.28), also includes activation energies for the phase separated blends represented by filled symbols.

5.5 Diffusion Coefficients

As mentioned in chapter (4) although the permeabilities were independent of ingoing pressure, the non-linear isotherms obtained for CO₂ in these blends indicated that the measured

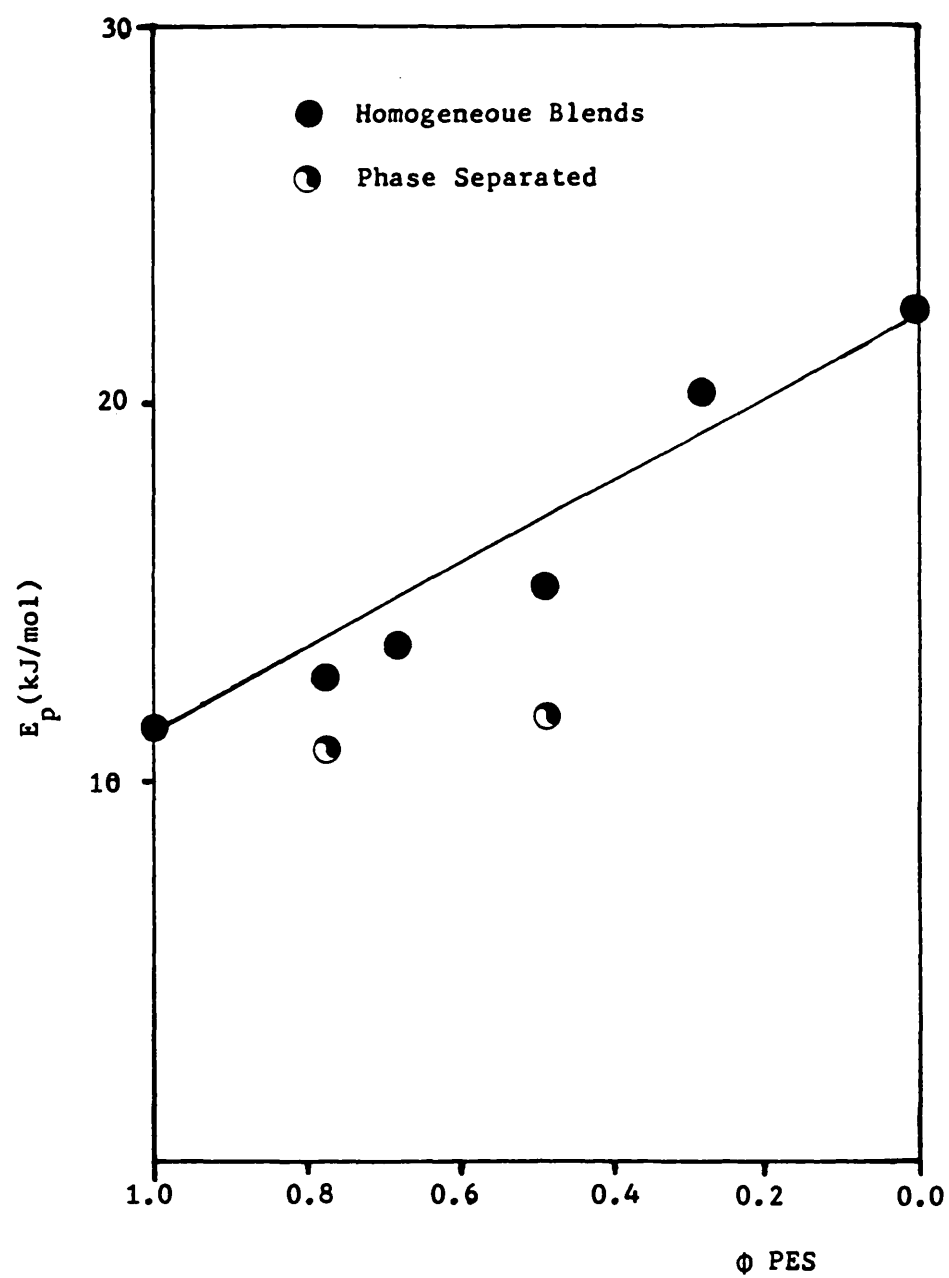


FIG. 5.28 Activation Energies for Permeation of CO_2

diffusion coefficients are concentration dependent. The average diffusion coefficient ($\bar{D}$) was determined as a function of concentration from the relation $\bar{P} = \bar{D} \bar{k}$.

Experimental plots of $\bar{D}$ vs c were constructed at each temperature. Each curve was fitted with a polynomial and the differential diffusion coefficients (D) were thus established. The variation of $\bar{D}$ and D with concentration is shown in figure (5.29) for selected blends at 30°C. However, detailed results are given in appendix (2).

Extrapolation of $\bar{D}$ and D to $c=0$ gave the same values for $D_{c=0}$ which are given in Table (5.11) for all three temperatures.

Figure (5.30) shows the variation of $D_{c=0}$ with blend composition. It is interesting to note that the diffusion coefficient goes through a minimum around 50/50 PES/Phenoxy blend composition, while the solubility and the permeability increases with increasing PES composition. A similar trend has been observed for diffusion coefficients estimated from the time lag method, i.e. $\theta = l^2/6D$, where l is the thickness of the membrane and θ is the time lag. However the time-lag values (given in brackets) are higher than those obtained from steady state as can be seen in table (5.11).

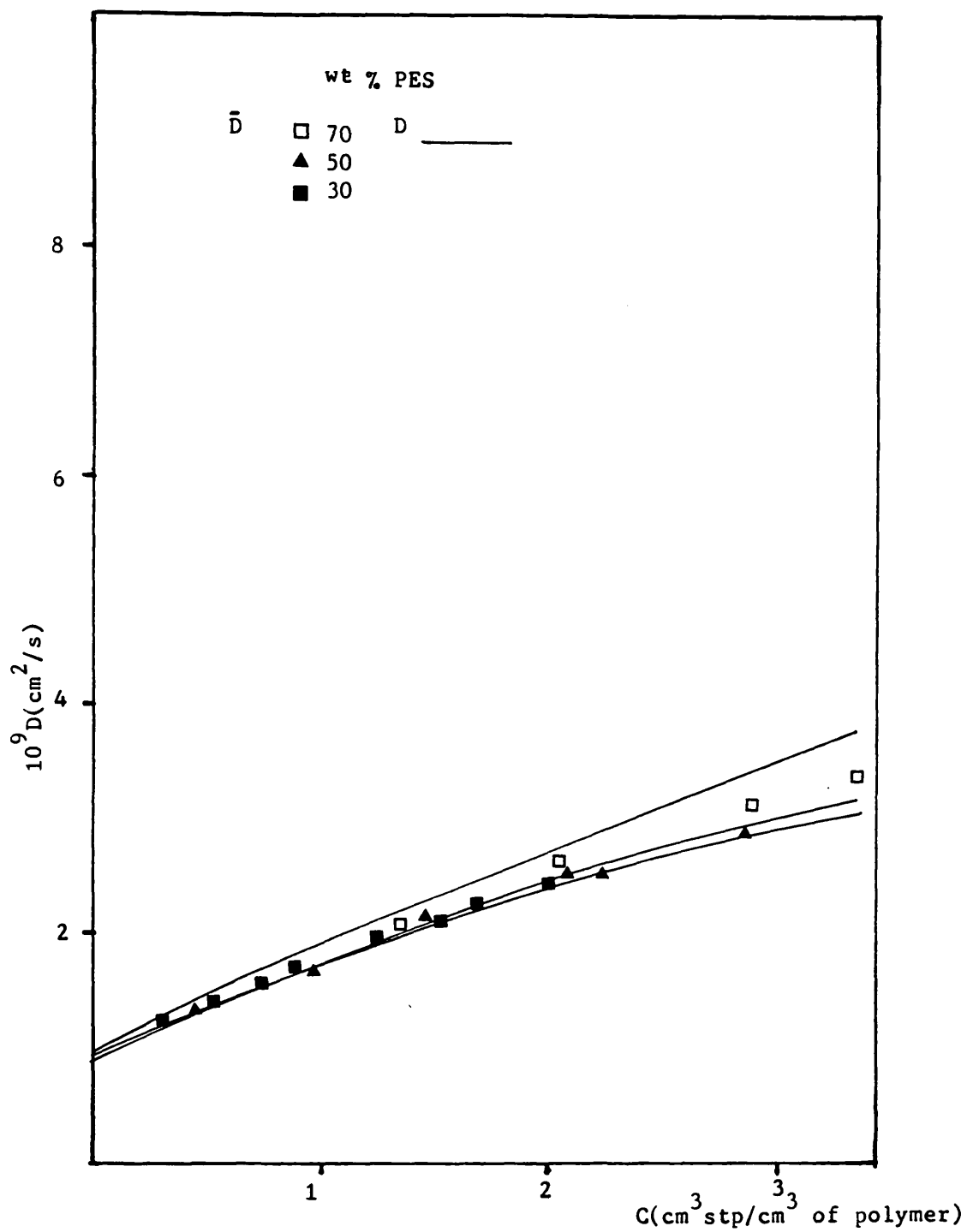


FIG. 5.29 Concentration dependence of $\bar{D}$ and D at 30°C for CO_2

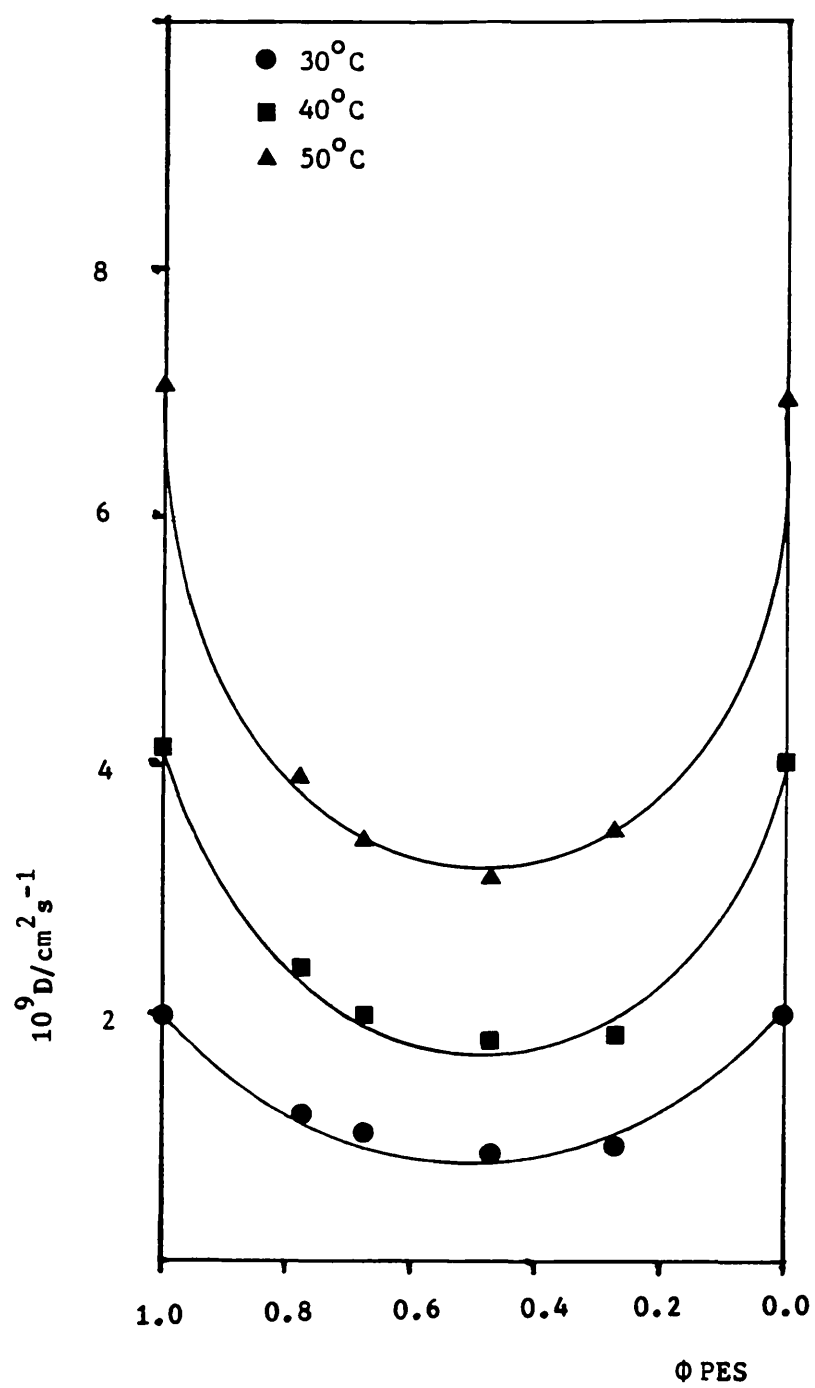


FIG. 5.30 Steady State Diffusion Coefficients
for CO_2

Table (5.11) Diffusion Coefficient ($D_{c=0}$) for CO_2 in PES/Phenoxy Blends ($10^9 D/cm^2 s^{-1}$)

Wt % PES	T/°C		
	30	40	50
100	2.0 (3.92)	4.15	7.10
80	1.25 (1.44)	2.48	3.99
70	1.08 (1.44)	2.15	3.60
50	1.00 (1.66)	1.98	3.46
30	1.10 (1.26)	2.11	3.79
0	2.10 (2.40)	4.35	6.96

Stalling et al.⁽¹⁹⁵⁾ also observed a minimum at 50/50 Polypropylene-oxide/Polystyrene (PPO/PS) for diffusion of Neon, Argon and Krypton. Their explanation of this behaviour was that either the system was not really homogeneous, or that since both polymers were glassy, the nature of the dual mode sorption mechanism may have been responsible for it. Paul⁽¹⁶²⁾ found that the diffusion coefficient for the dissolved (Henry's law) and Langmuir species, D_D and D_H respectively, exhibited a distinct minimum when plotted against composition. Smaller departures from linearity were also observed for D_D and D_H in the poly-(carbonate)/copolyester⁽¹⁷⁵⁾ system which had been shown by ternary solution method to have a smaller interaction parameter. In this case the glass transition temperature and other evidence⁽¹⁹⁾ have shown the PES/Phenoxy system to be completely

compatible over the entire composition range. Since both polymers are in the glassy state the resultant diffusion coefficient dependence on blend composition will be complex and contain components from D_D and D_H , the dissolution and microcavity contributions to D arising from dual mode transport.

The steady state diffusion coefficients for CH_4 determined from the ratio of the permeability to the equilibrium solubility, since Henry's law was obeyed, are collected in Table (5.12).

Table (5.12) Steady State Diffusion Coefficients, for CH_4 ,
in Blends of PES/Phenoxy

Wt % PES	$T/^{\circ}\text{C}$	$10^9 D/\text{cm}^2\text{s}$		
	30	40	50	
100	0.53	1.13	1.98	
80	0.37	0.72	1.22	
50	0.26	0.55	1.07	
30	0.32	0.61	1.05	
0	0.34	0.69	1.47	

Although, Henry's law was obeyed for sorption and permeabilities were independent of ingoing pressures for all the blends, a minimum was still exhibited by the diffusion coefficient of CH_4 as shown in figure (5.31).

The activation energies of diffusion were obtained from the Arrhenius plots shown in figure (5.32) and (5.33). The activation energy is plotted as a function of blend composition in figures (5.34) and (5.35) for CO_2 and CH_4 respectively, and

shows excellent agreement with the values predicted by the simple additivity relationship. This indicates that the transport parameter ΔE_{12} in equation (2.60) must effectively be zero.

A similar behaviour has been observed for CO_2 ⁽¹⁸⁷⁾ diffusion in miscible blends of poly(methyl acrylate)-poly(epichlorohydrin). However, a small negative value for ΔE_{12} for propane diffusion in miscible blends of polystyrene and poly(vinyl methyl ether)⁽¹⁸⁵⁾ and for CO_2 diffusion in miscible blends of ethylene vinyl acetate co-polymer and chlorinated polyethylene⁽⁵⁹⁾ has been reported. However, in general positive ΔE_{12} values are expected for transport in miscible blends

5.6 Separation Factors

Chapter (4) described the basic theory involved in predicting and calculating the ideal separation factors for the homopolymers, namely PES and Phenoxy. Although, the separation ability of the two polymers did not differ greatly, a high separation factor was achieved with PES at all temperatures. Also for both the homopolymers and the blends the separation increased as the temperature was lowered.

Also of interest is the dependence of the various separation factors on blend composition.

In general, if the interaction between the two component polymers in the blend is relatively strong,^(192,193,188,224,225) then the observed separation factors are higher than predicted from the semilogarithmic additivity rule:-

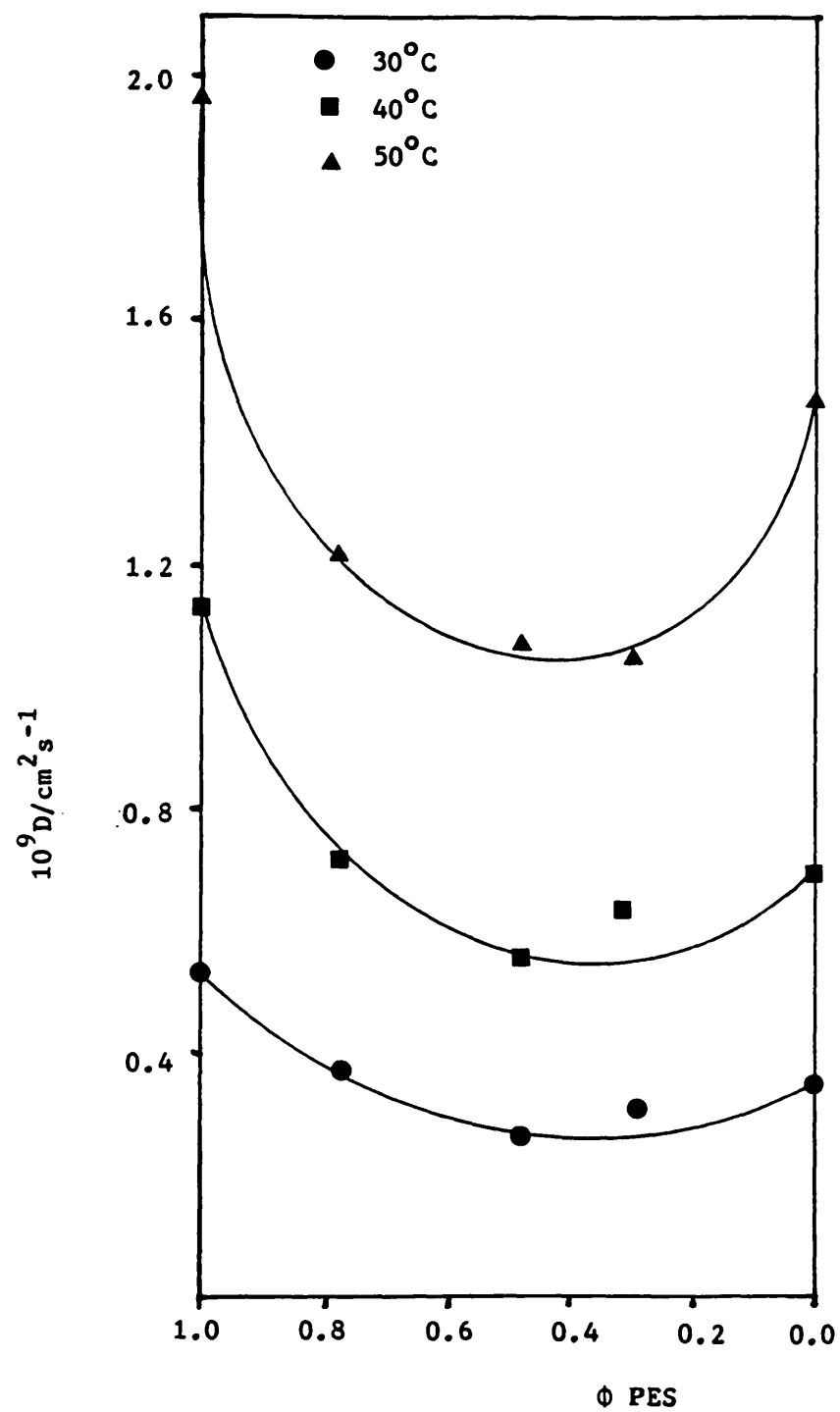


FIG. 5.31 Steady State Diffusion Coefficients for CH_4

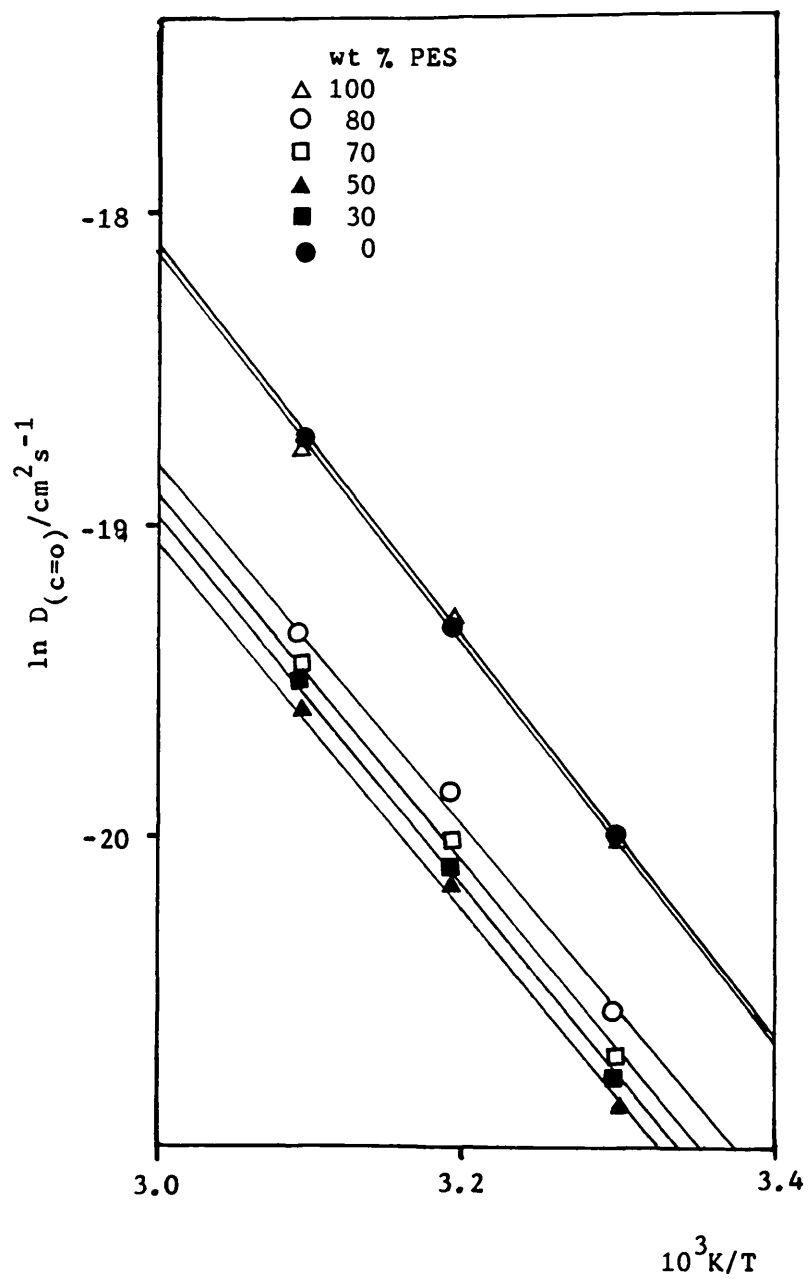


FIG. 5.32 Arrhenius plots for CO₂ Diffusivity

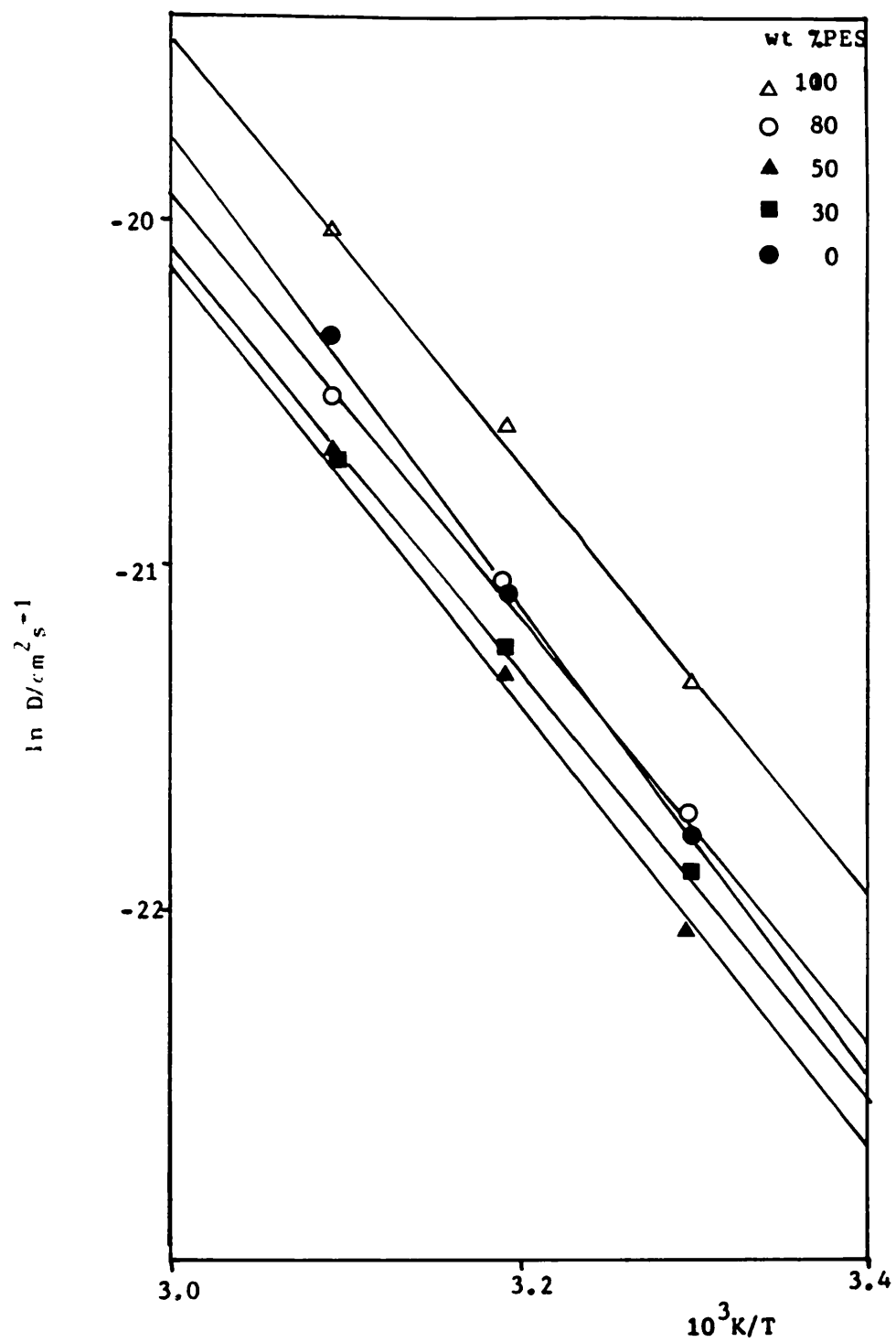


FIG. 5.33 Arrhenius plots for CH_4 diffusivity

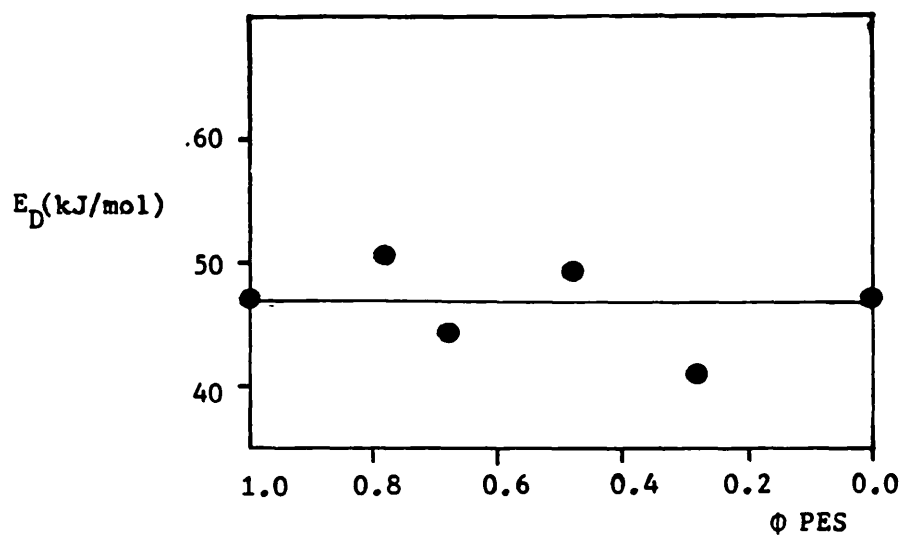


FIG. 5.34 Activation Energies for Diffusion of CO_2

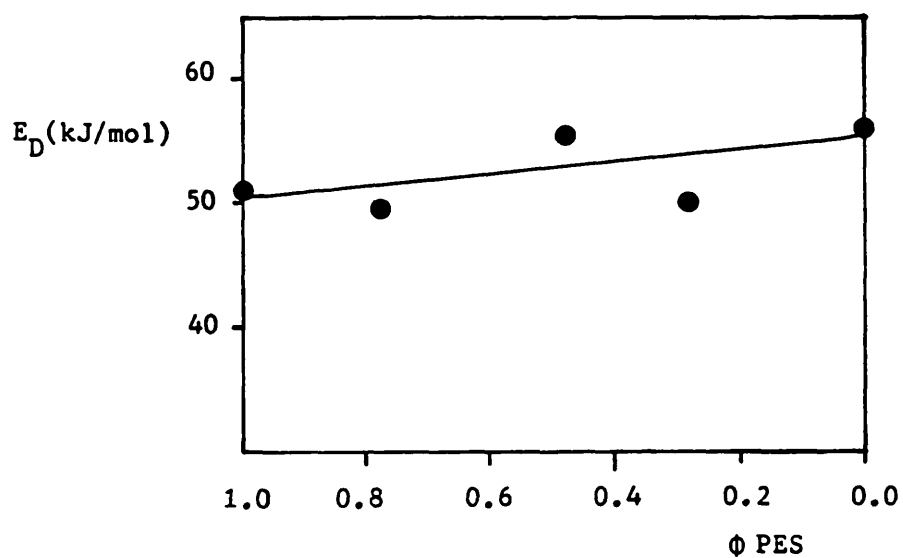


FIG. 5.35 Activation Energies for Diffusion of CH_4

$$\ln \alpha_B^A = \phi_1 \ln (\alpha_B^A)_1 + \phi_2 \ln (\alpha_B^A)_2 \quad (5.6)$$

However, Chiou et al⁽¹⁹²⁾ reported a positive deviation from the additivity rule for separation factors for CO₂/CH₄ in blends of Poly (methyl methacrylate) with Bisphenol Chloral Polycarbonate where the interaction between the homopolymers was weak.

The permeability, solubility and diffusion coefficients of CO₂ and CH₄ were determined using the same sheet of membrane, therefore any errors occurring in evaluating these parameters are reduced.

The separation factor $\alpha_{A/B}$ is shown in figure (5.36) as a function of blend composition and temperature. At all compositions α decreases as the temperature is increased. The dependence of $\alpha_{A/B}$ on blend composition is not strong and shows a small negative deviation from the line of equation (5.6). This relatively small increase in selectivity is however, accompanied by a more marked decrease in permeability. It is of interest to break down the dependence of α on blend composition to those of its component selectivities namely the solubility and diffusivity selectivities β and γ respectively.

The dependence of β on blend composition is almost linear and it increases slightly with increasing PES content. The diffusivity selectivity, γ again depends rather weakly on composition and tends to exhibit a shallow minimum. As temperature decreases β increases but γ is little affected.

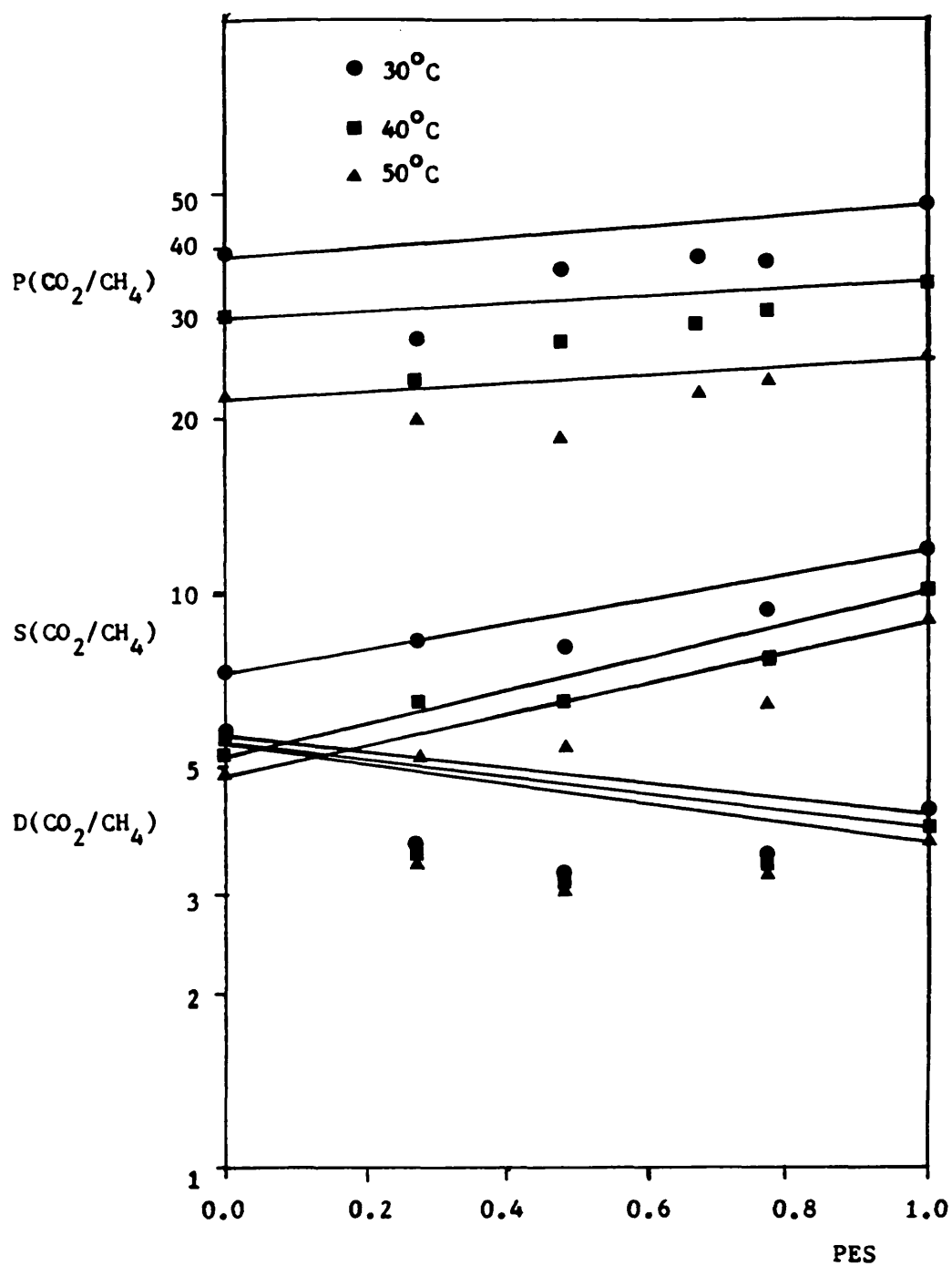


FIG. 5.36 CO₂/CH₄ Permeability , Solubility ,
and Diffusivity Ratio

Neither the solubility selectivity factor or the diffusivity selectivity factor appear to dominate.

Finally the separation factors are lower than those predicted using equation (4.2), suggesting the interaction between the two homopolymers is weak. Webb et al⁽⁵⁹⁾ and Chiou et al⁽¹⁹²⁾ reported a linear variation of separation factor with composition. In both cases a slight positive deviation of the permeability was observed from equation (5.6).

5.7 Phase - Separated Blends

As mentioned, PES/Phenoxy blends exhibit phase separation on heating, i.e exhibit a lower critical solution temperature behaviour around 180°C. Singh and Walsh have demonstrated this behaviour using a light scattering turbidimeter and also by optical microscope. In this case a film of the blend was heated in a furnace under vacuum at 200°C until it become cloudy. The film was quenched with liquid nitrogen to prevent remixing. To examine the effect of phase separation the permeability measurements were made with CO₂ only on three blends of composition 80/20, 50/50, and a new blend of 40/60 PES-Phenoxy. Measurements were made at 30, 40 and 50°C except for the 40/60 blend which was studied at 50°C only. It was not possible to phase separate blends with high phenoxy content without cracking or rupturing the membrane. The results are collected in Table (5.13) and are also shown in figure (5.37) at 50°C.

TABLE (5.13) Permeability of CO₂ Through Phase Separated Blends
of PES/Phenoxy

Blend	T ^o C	30 ^o C	40 ^o C	50 ^o C
wt.% PES		(10 ¹⁰ P(cm ³ cstp) cm cm ⁻² s ⁻¹ cmHg ⁻¹)		
80		3.21	3.62	4.37
50		1.97	2.26	2.61
40		-	-	1.61

Clearly there is a significant increase in the permeability on phase separation, giving better agreement with the Maxwell equation.

5.8 Conclusion

Blends of PES - Phenoxy were clear over the entire composition range and exhibited a single composition dependent glass transition temperature suggesting that the system was miscible. The specific volume followed the simple additivity rule indicating the interaction between the two components was weak.

The transport and sorption behaviour in miscible blends of PES - Phenoxy is similar to many other miscible blend systems. The sorption of CO₂ was sufficiently high for the isotherms to exhibit the curvature generally observed with gas sorption in glassy polymers. With CH₄ Henry's law was observed as the solubility was an order of magnitude smaller. At pressures

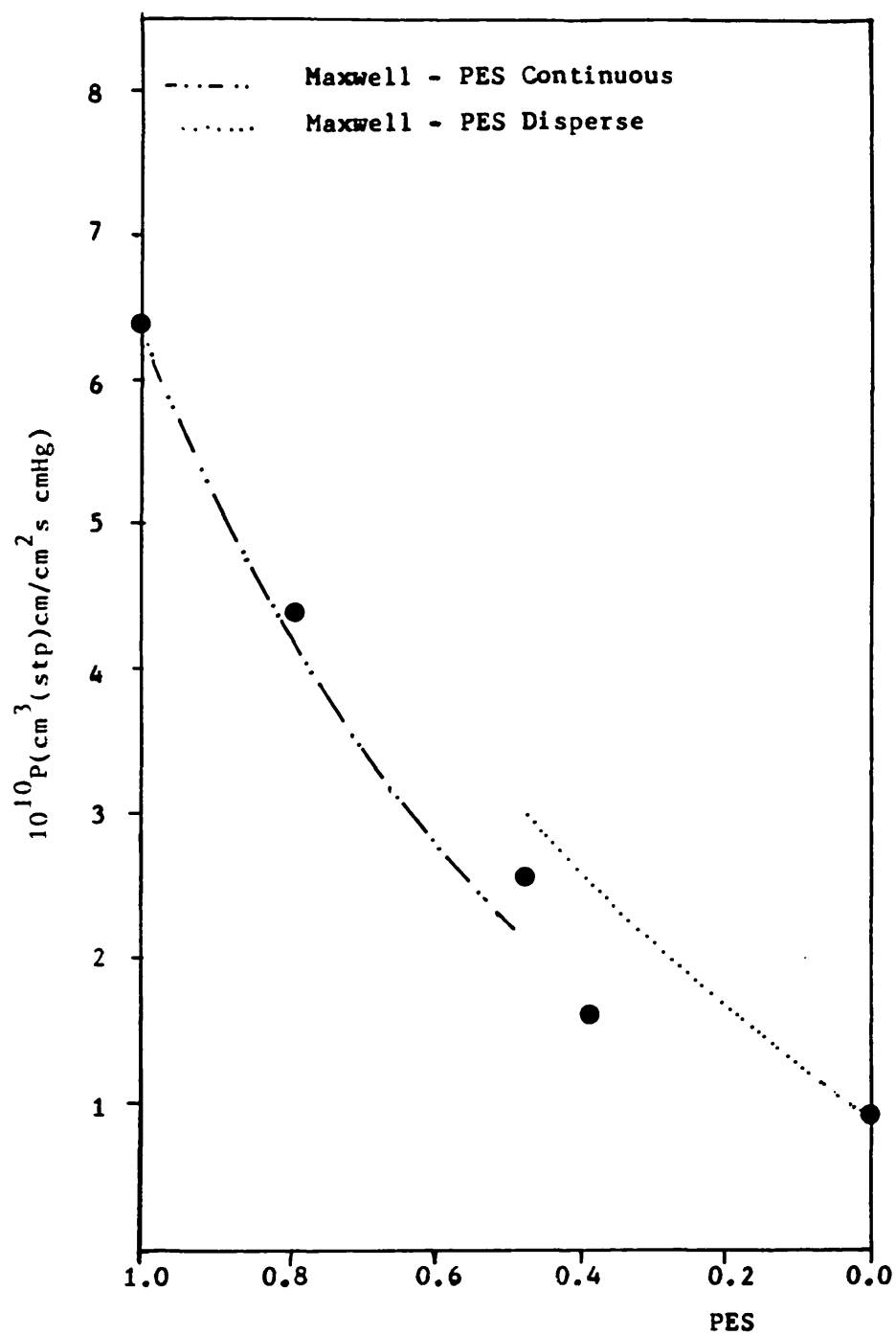


FIG. 5.37 Permeability of CO_2 at 50°C in Phase
- Separated blends of PES - Phenoxy

considerably greater than atmospheric the methane isotherm also exhibited curvature. The solubility coefficients followed the additivity rule as expected for miscible blends, again indicating the interaction to be very weak between PES-Phenoxy.

The permeabilities were independent of the ingoing pressures when studied at low pressures, but showed a slight decrease at high pressures. The dependence of the permeability on composition was relatively weak and has been compared with various models for homogeneous and heterogeneous systems. As expected the agreement is better with models for homogeneous systems. Permeation of CO₂ in phase separated blends was significantly higher and in better agreement with models for a heterogeneous system.

The diffusion coefficients for CO₂ were a weak function of concentration. Furthermore, for both gases, CO₂ and CH₄, the diffusion coefficients exhibited a minimum around 50/50 wt% PES/Phenoxy blend while the permeability and solubility decreased with increasing Phenoxy content in the blend.

The ideal separation factor $\alpha_{A/B}$ increased slightly as the PES content increased with indication of a slight minimum in the curve. Also the slight improvement in separation factors was accompanied by a significant decrease in permeability.

CHAPTER 6

RESULTS AND DISCUSSION

PES - Pu BLENDS

6.1 Introduction

Chapter (5) has described the transport and sorption of CO_2 and CH_4 in glassy polymer blends of PES - Phenoxy. Although high separation factors were achieved, the permeability was considerably lower. This is expected for glassy polymers. On the other hand, rubbery polymers provide a high rate of permeation but low separation factors. The number of diffusion studies in polyurethane is limited and concerned mainly with the effect of varying the structure and length of the soft and hard block. (220,221,222)

In this section the effect of blending a rubbery polymer (polyurethane) with a glassy polymer (PES) on the transport and sorption of CO_2 will be discussed.

6.2 Film Characterization

Blends of PES and Polyurethane (Pu) were prepared by the solution casting technique from DMF. Blends with Pu content greater than 50% were clear, whereas those with a high PES content exhibited cloudiness. Cloudiness is often an indication of two phase behaviour.

The measured densities together with the volume fractions of PES in the blends are collected in Table (6.1).

Table (6.1) also includes densities calculated from equation (5.1). The variation of specific volume with volume fraction is shown in figure (6.1). The solid line was derived from equation (5.2), based on the additivity of volumes. The data lie below the line suggesting the possibility of some degree of interaction between the PES and Pu segments.

Table (6.1) Weight Fractions, Volume Fractions and Densities
of PES/Pu Blends

Wt % _{PES}	ϕ_{PES}	ρ/gcm^{-3}	ρ/gcm^{-3}
		(exp)	(add)
0	0.000	1.251	1.251
20	0.185	1.284	1.274
50	0.477	1.328	1.310
70	0.679	1.335	1.344
100	1.000	1.375	1.375

Two principal glass transitions were observed in all samples when studied by differential scanning calorimetry using a Du Pont 990 Thermal Analyser operating at a heating rate of $10^{\circ}\text{C}/\text{min}$. The results are summarized in Table (6.2) and indicate that two independent phases are present in the blends with a small amount of mixing occurring since the highest T_g is shifted below that of PES. The transitions at T_{g1} and T_{g2} correspond to the glass transition temperature of Pu and PES rich phases respectively.

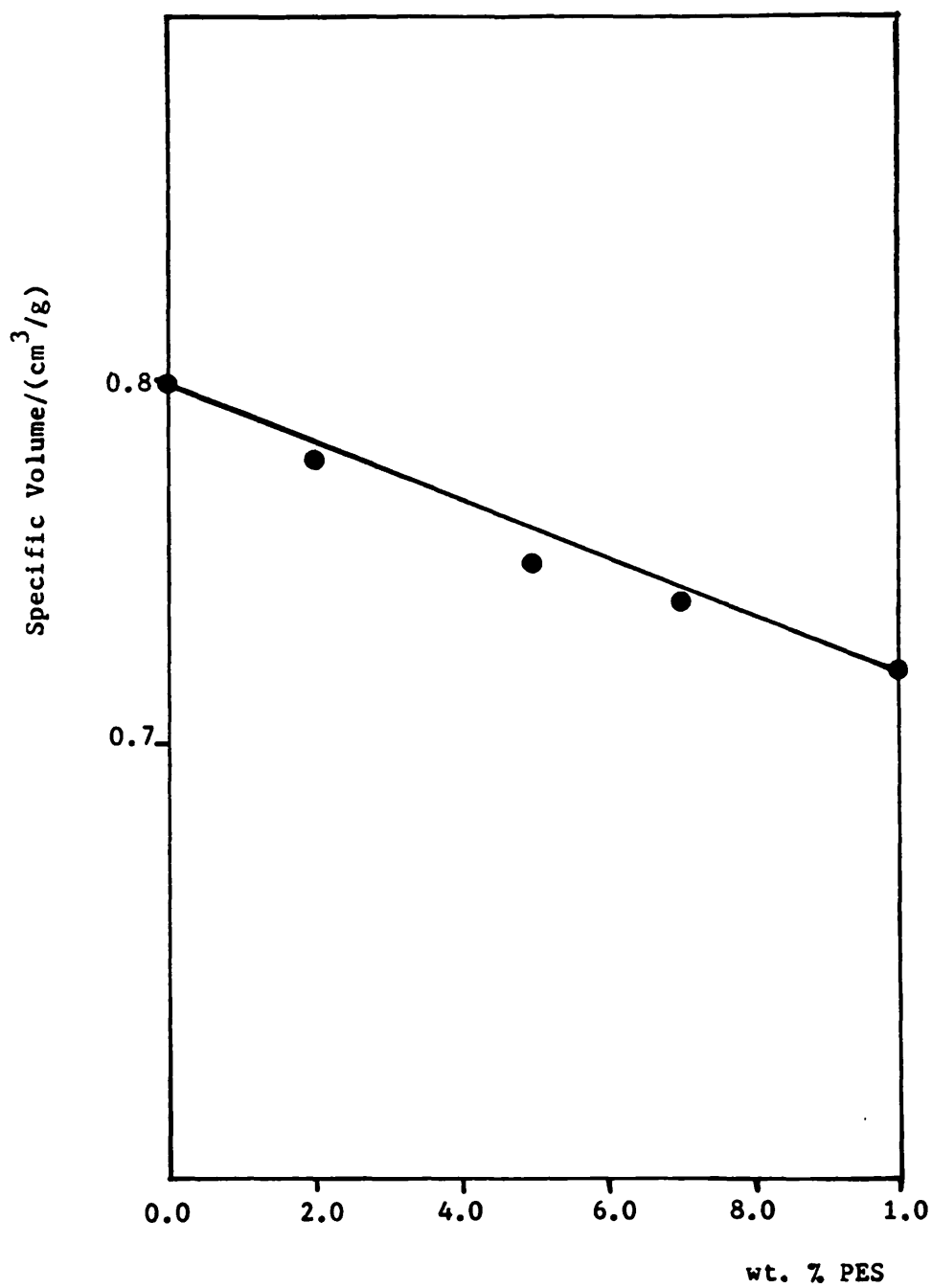


FIG. 6.1 Variation of Specific Volume with
Weight Fraction of PES

The only exception is for the blend containing 70% PES where only one transition is observed corresponding close to PES.

Table (6.2) Glass Transition Temperature ($^{\circ}\text{C}$)

Blends Wt % PES	T_{g1}	T_{g2}
0	-29	-
20	-29	212
50	-25	200
70	-	200
100	-	222

A similar effect has been reported by Ismail⁽¹⁷⁹⁾ for Pu-PMMA blend system. In his case the blend with the high Pu content showed a single T_g corresponding to the T_g of Pu. Also in his study for all compositions clear films were obtained although a slight increase in turbidity was observed in sheets containing 30% volume Pu. Allen et al⁽⁷⁹⁾ studied the same system and only low turbidity was observed for all compositions and was attributed to the small difference in refractive index between the two component polymers.

An attempt was made to measure the mechanical strength of the blends using a "Minimat" tensile testing machine. However, meaningful results were not obtained as the films were too thin and slipped during the course of the experiment.

6.3 Equilibrium Sorption

Equilibrium sorption isotherms for CO₂ were measured in the temperature range 30-50°C and a representative set of isotherms at a given temperature of 30°C is shown in figure (6.2). For PES and the blend containing 70% PES, the isotherms are concave to the pressure axis which is a typical feature for glassy polymers. Such isotherms are well described by the dual-mode sorption equation (2.23). On the other hand, the isotherms for Pu, and 80% Pu are linear and may be described by Henry's law.

The solubility coefficient estimated from the linear region of the isotherms are collected in table (6.3).

Table (6.3) Solubility for CO₂ in PES-Pu

k/cm³(stp)cm⁻³ (polymer) cmHg⁻¹

Blends wt%PES	Temp/°C		
	30	40	50
0	0.015	0.013	0.108
20	0.018	-	-
50	0.025	0.019	0.015
70	0.108	0.066	0.044
100	0.248	0.154	0.098

Dual - mode sorption analysis was not carried out on these isotherms due to the curvature being relatively weak. Clearly there is a marked decrease in solubility on addition of Pu to PES. Figure (6.3) illustrates the solubility coefficient versus

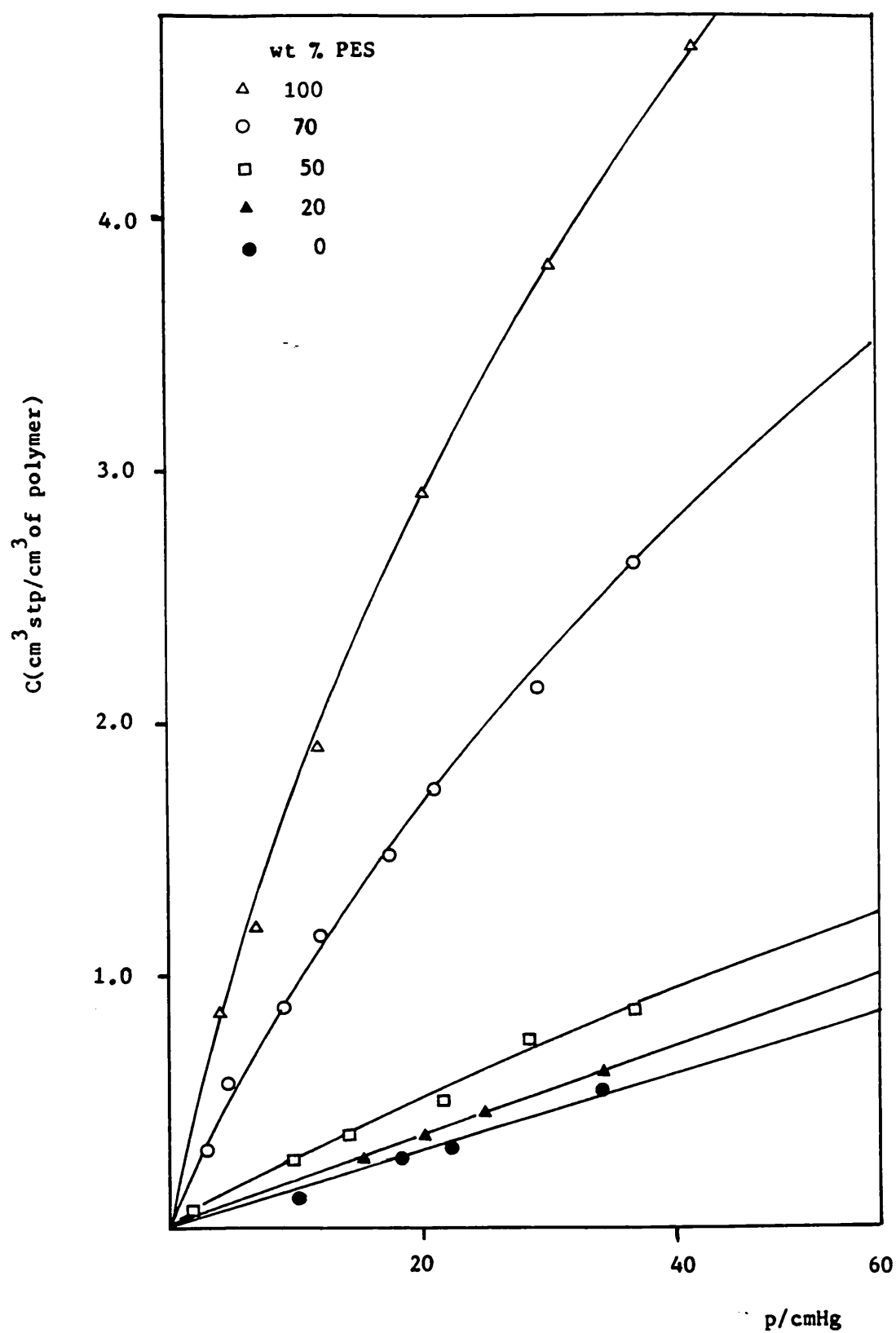


FIG. 6.2 SORPTION ISOTHERMS OF CO_2 AT 30°C

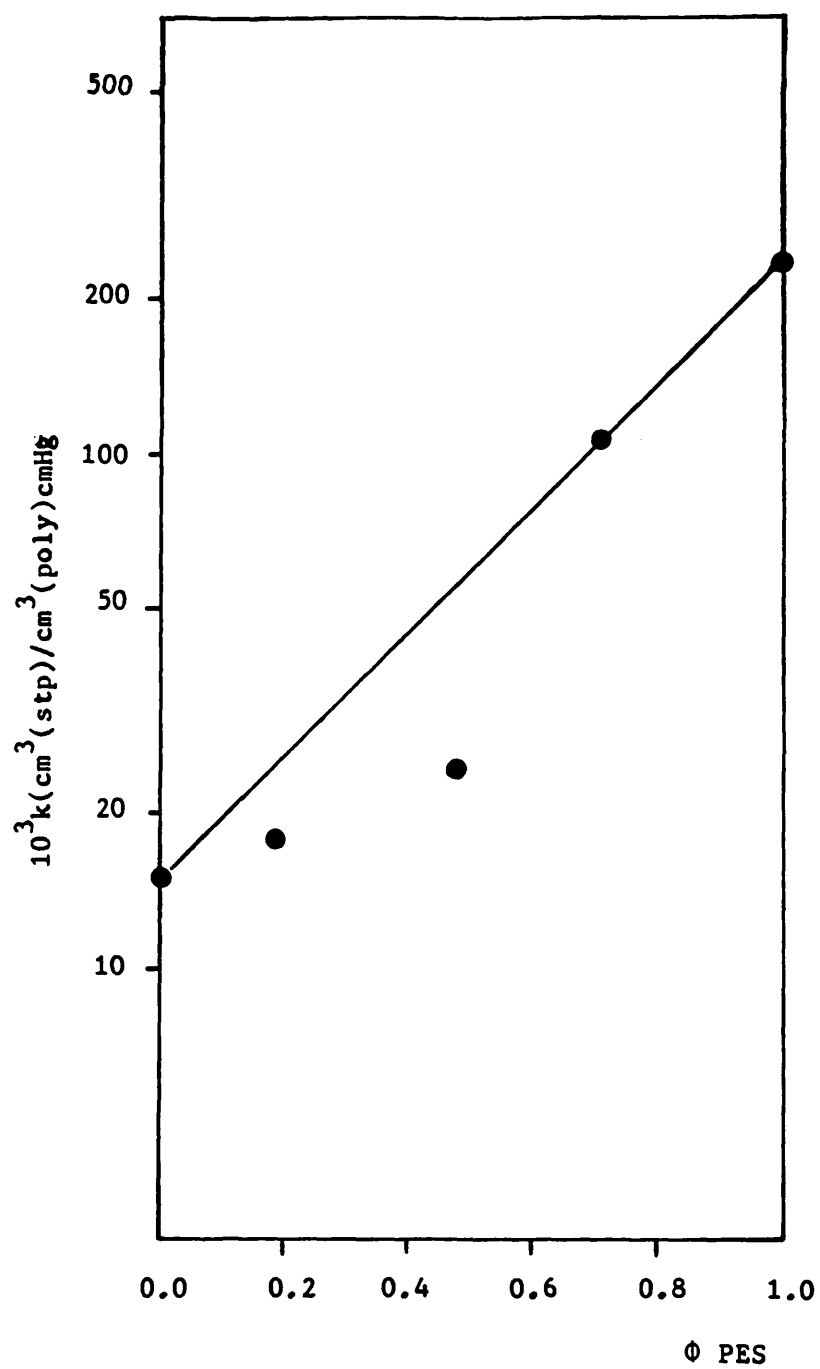


FIG. 6.3 SOLUBILITY OF CO₂

composition plot where the solid line represents the prediction by equation (5.3). The negative deviation from the tie line also indicates that there may be some interaction between PES-Pu.

The temperature dependence of the solubility coefficient is shown in figure (6.4). The heat of dissolution obtained from these plots are shown in figure (6.5) as a function of blend composition.

As expected the heat of dissolution becomes less exothermic as the Pu content in the blend is increased. This is because the blends are in the rubbery state and energy is required to move the segments of the polymer chains in order to create a hole which would accommodate the penetrant molecules. Whereas blends with high PES are glassy, and Langmuir sorption occurs in pre-existing cavities, thus giving rise to more exothermic heat of sorption. This phenomenon has been well described by Meares (83,84), Barrer et al⁽¹¹⁷⁾ and Micheal et al.^(86,87) However their measurements involved sorption above and below the glass transition temperature of the same material.

6.4 Steady State Permeation

Permeabilities measured for CO₂ in the temperature range 30^o to 50^oC were independent of the ingoing pressures. These permeabilities are summarised in Table (6.4) and figure (6.6) and are average values over at least 4 different ingoing pressures.

It is clear, that there is a marked decrease in permeability as the volume fraction of PES is increased in the blend.

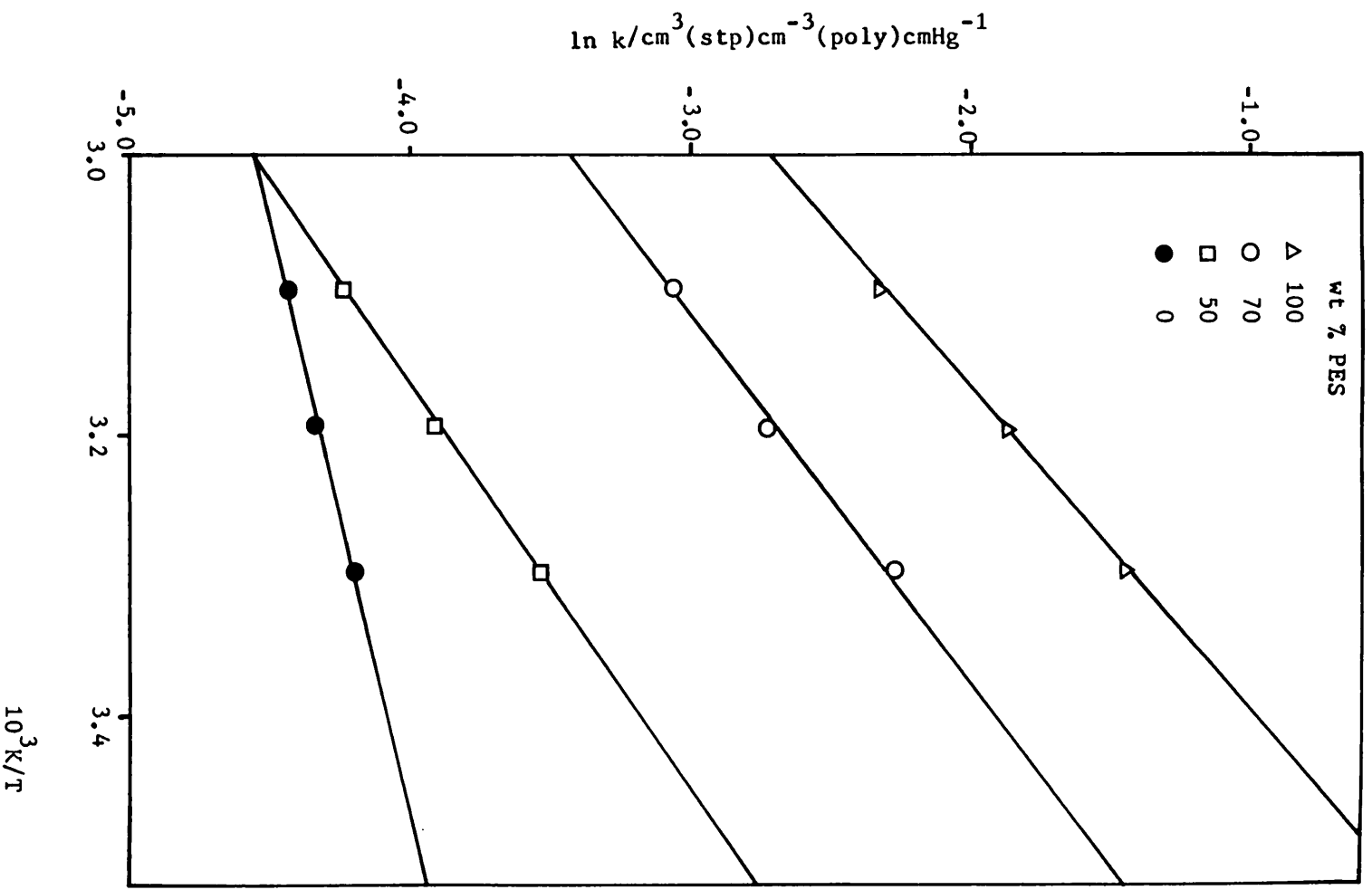


FIG. 6.4 Van't Hoff plots of CO_2 solubility in PES - Pu blends

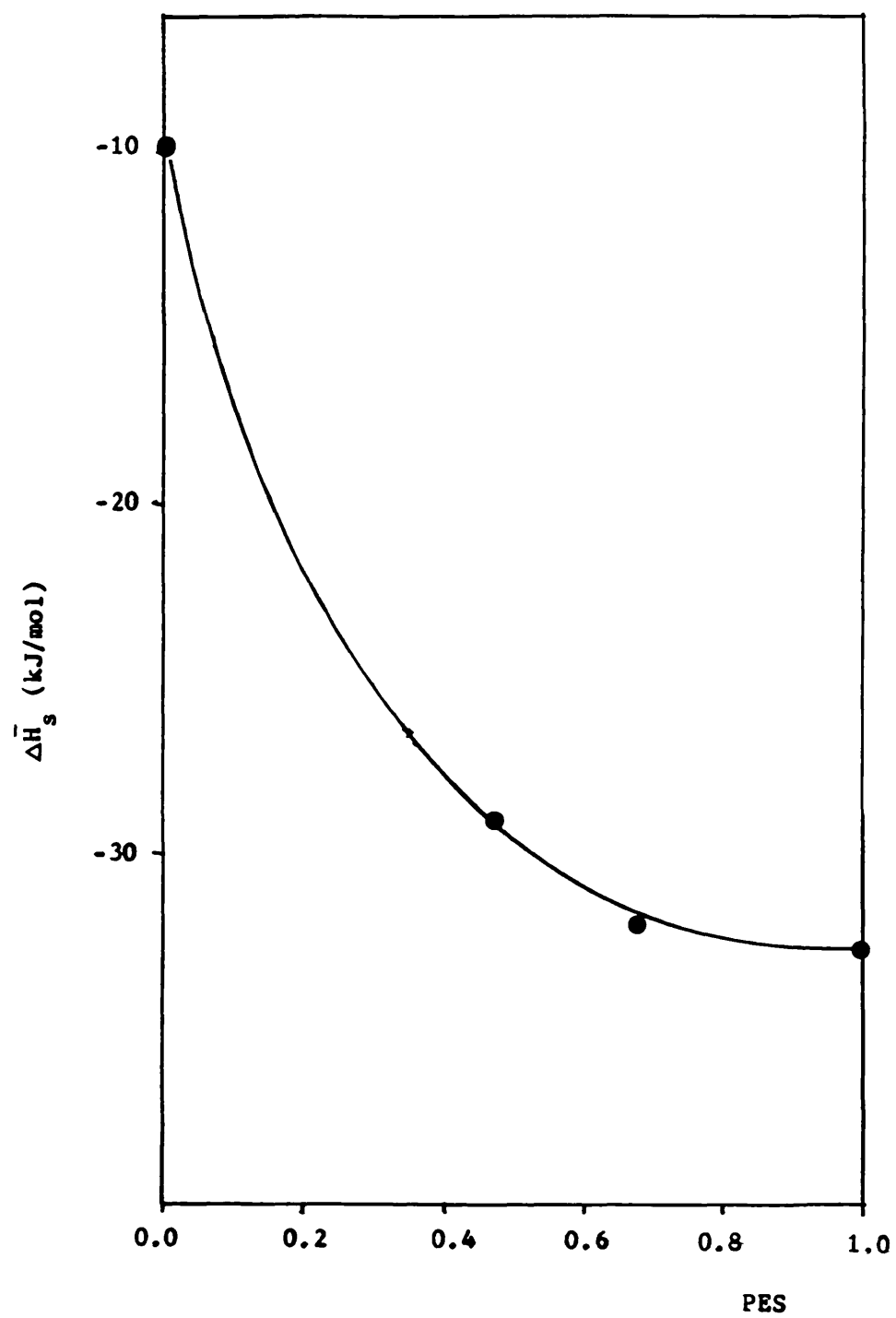


FIG. 6.5 HEATS OF SORPTION FOR CO_2

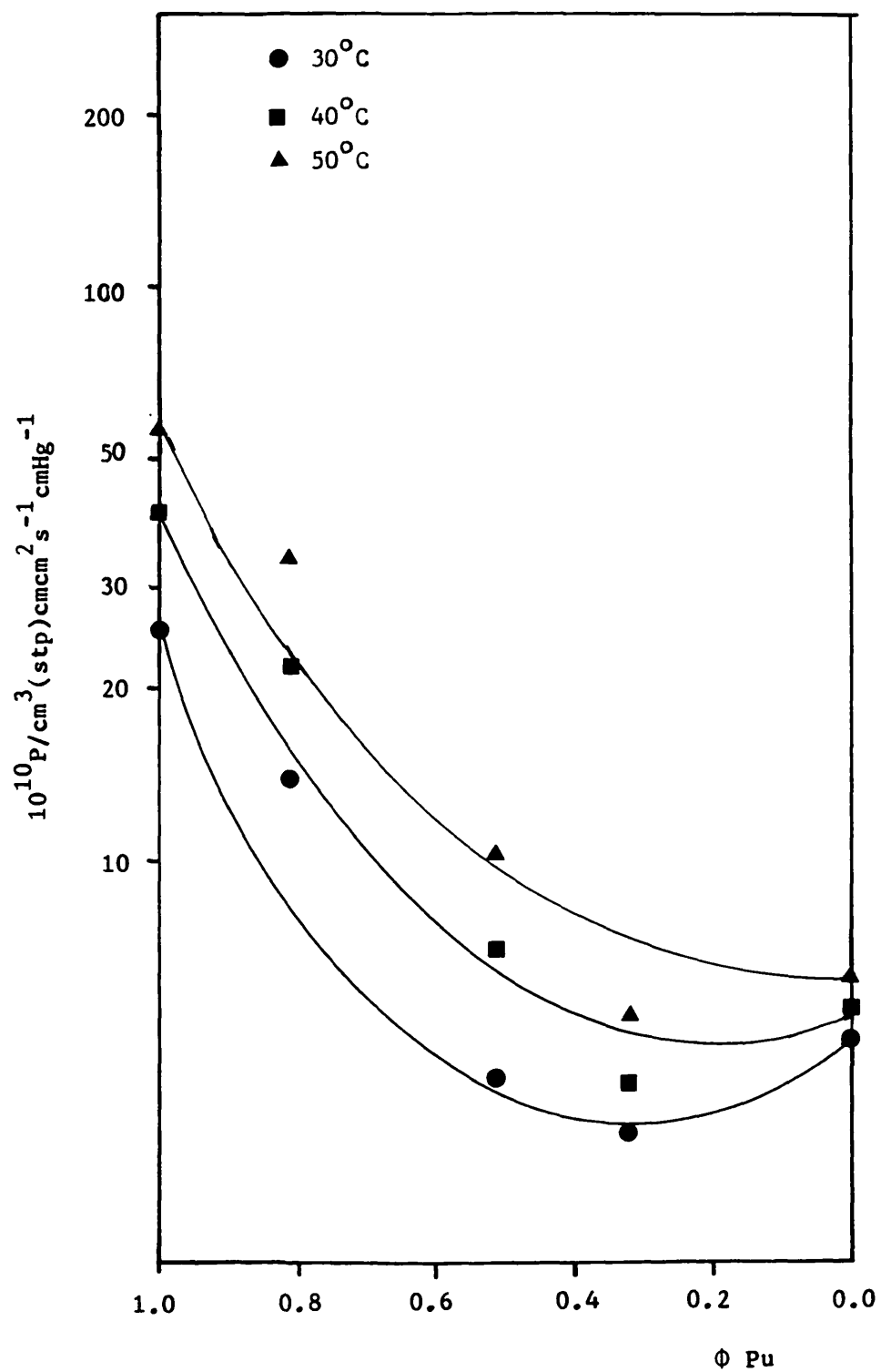


FIG. 6.6 PERMEABILITY OF CO_2 IN BLENDS OF
PES + Pu

Futhermore a minimum is observed around 70% PES. This effect was also reported by Murugenandam et al for transport of CH₄ and CO₂ in miscible blends of Tetramethyl Bisphenol Polycarbonate and Polystyrene.

Table (6.4) Carbon Dioxide Permeabilities
in PES-Pu Blends at 30, 40, and 50°C

	$10^{10} P: \text{ cm}^3 (\text{stp}) \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$		
Blend wt% PES	30	40	50
0	25.0	40.0	56.0
20	14.0	22.0	34.0
50	4.2	7.0	10.4
70	3.35	4.2	5.5
100	4.9	5.6	6.3

Figure (6.7) compares the experimental data with the simple Maxwell model for two phase systems. In general when $P_c \gg P_d$ and $P_d \gg P_c$ equation (2.48) and (2.49) may be used to predict the permeability of the blend. However in this case $P_d/P_c = 0.2$ when Pu is the continuous phase and $P_d/P_c = 5$ when PES is the continuous phase. Substituting these values into equation (2.47) for the two limiting case results:
when Pu is the continuous phase

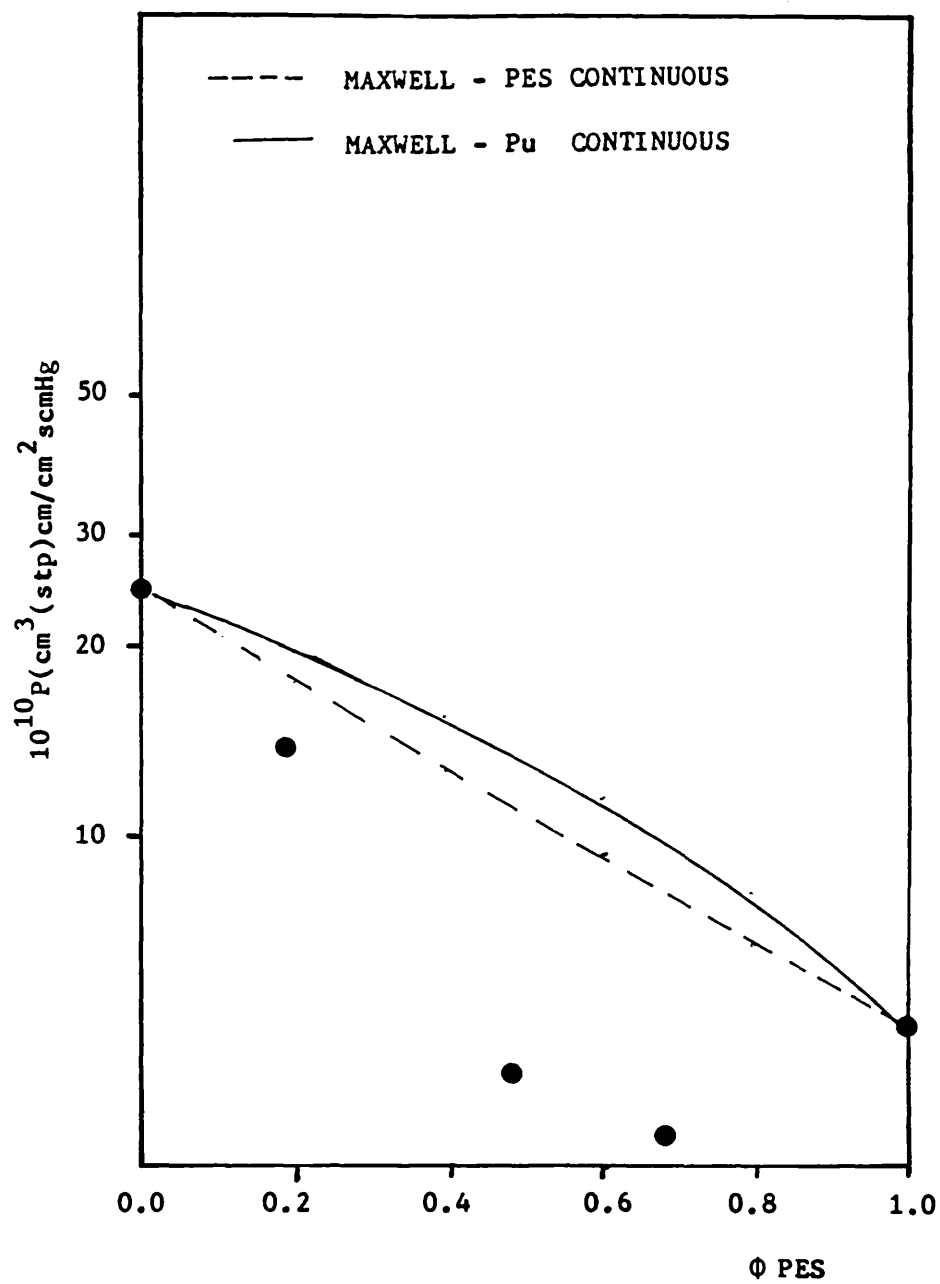


FIG. 6.7 PERMEABILITY OF CO_2 AT 30°C

$$\frac{P_m}{P_c} = \frac{2.2 - 1.6 \phi}{2.2 + 0.8 \phi} \quad (6.1)$$

and when PES is the continuous phase

$$\frac{P_m}{P_c} = \frac{7 + 8 \phi}{7 - 4 \phi} \quad (6.2)$$

It is clear from figure (6.7) that the permeabilities predicted from the equations do not show significant differences and that the experimental data is not represented in terms of two phase Maxwell model.

The experimental data lie well below the predicted values which again suggests mixing of the two component since the results indicate behaviour for miscible blends.

The temperature dependence of the permeability coefficients shown in the form of Arrhenius plots in figure (6.8) were linear over whole of the temperature range. The activation energies obtained from these plots are given in table (6.5).

E_p is close to that for the Pu sample suggesting that the continuous phase is largely responsible for the penetrant flux. However, at high PES content the value for E_p falls between those of the homopolymers suggesting that there may be greater extent of homogeneity of this blend compared to any others. On the other hand the disperse phase may be responsible for the penetrant flux for this blend. However the overall variation of the activation

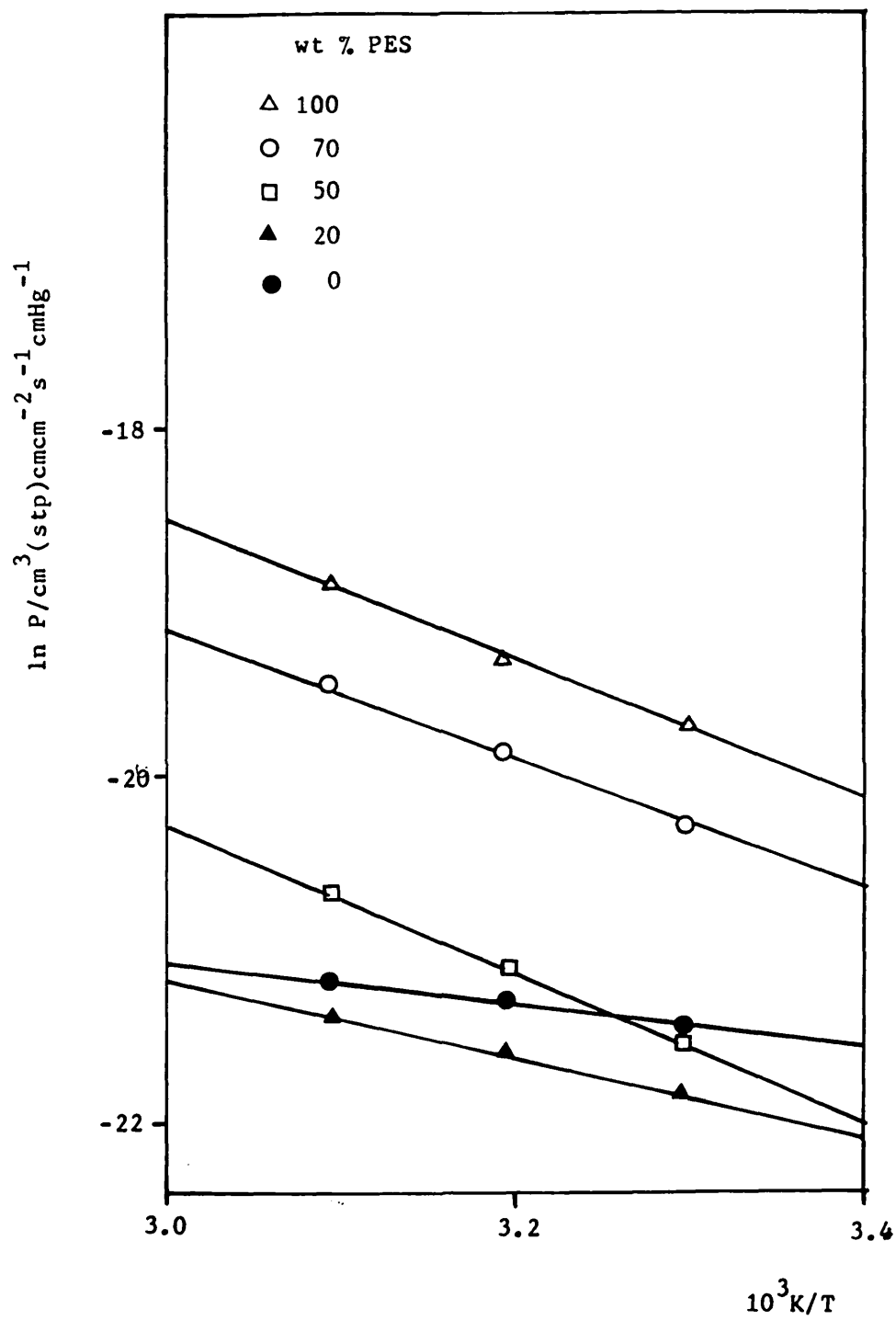


FIG. 6.8 Arrhenius plots of CO_2 Permeability

energy with blend composition again suggest that there may be some mixing.

Table:(6.5) Activation Energies Of Permeation For CO₂ In
PES-Pu Blends

Wt. %PES	E_p/kJmol^{-1}
0	33.1
20	36.6
50	32.2
70	20.0
100	11.3

6.5 Diffusion Coefficients

Average diffusion coefficients were obtained for CO₂ in the 50% and 70% PES blends since the isotherms were non-linear. average solubility, $\bar{k} = c/p$, over the entire pressure range was estimated and since P was independent of pressure, an average $\bar{D}$ was estimated from $\bar{D} = \bar{P}/\bar{k}$. Figure (6.9) and (6.10) shows the variation of $\bar{D}$ versus c for both blends. The diffusion coefficient is a very weak function of c and further analysis to obtain more accurate result as carried out for the PES-Phenoxy system (chapter (5)) is not required in this case. Table (6.6) contains the extrapolated values at $c=0$ from these plots together with the values for the homopolymers.

The values in the brackets are the diffusion coefficients

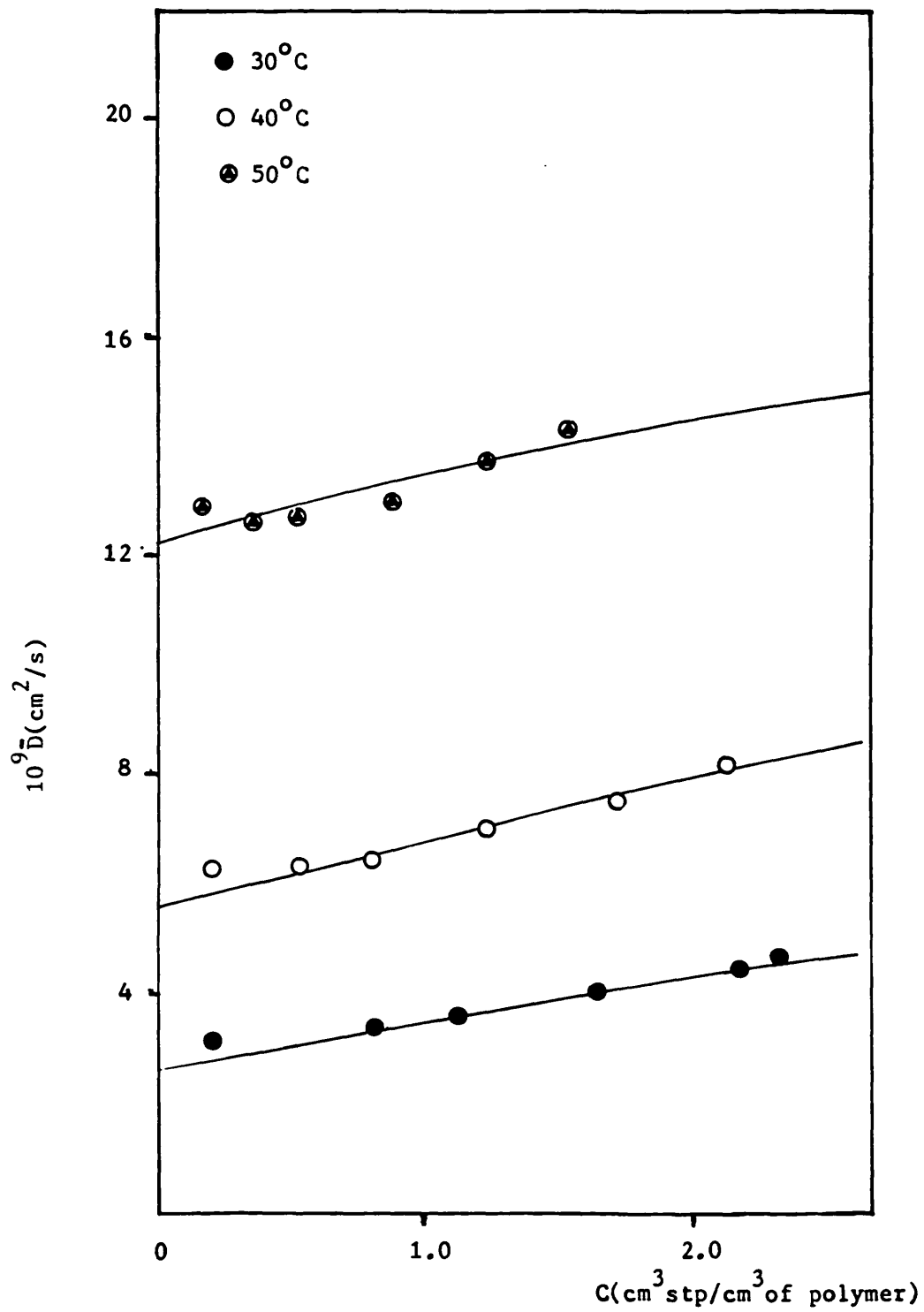


FIG. 6.9 80% PES Blend/CO₂ concentration dependence of $\bar{D}$

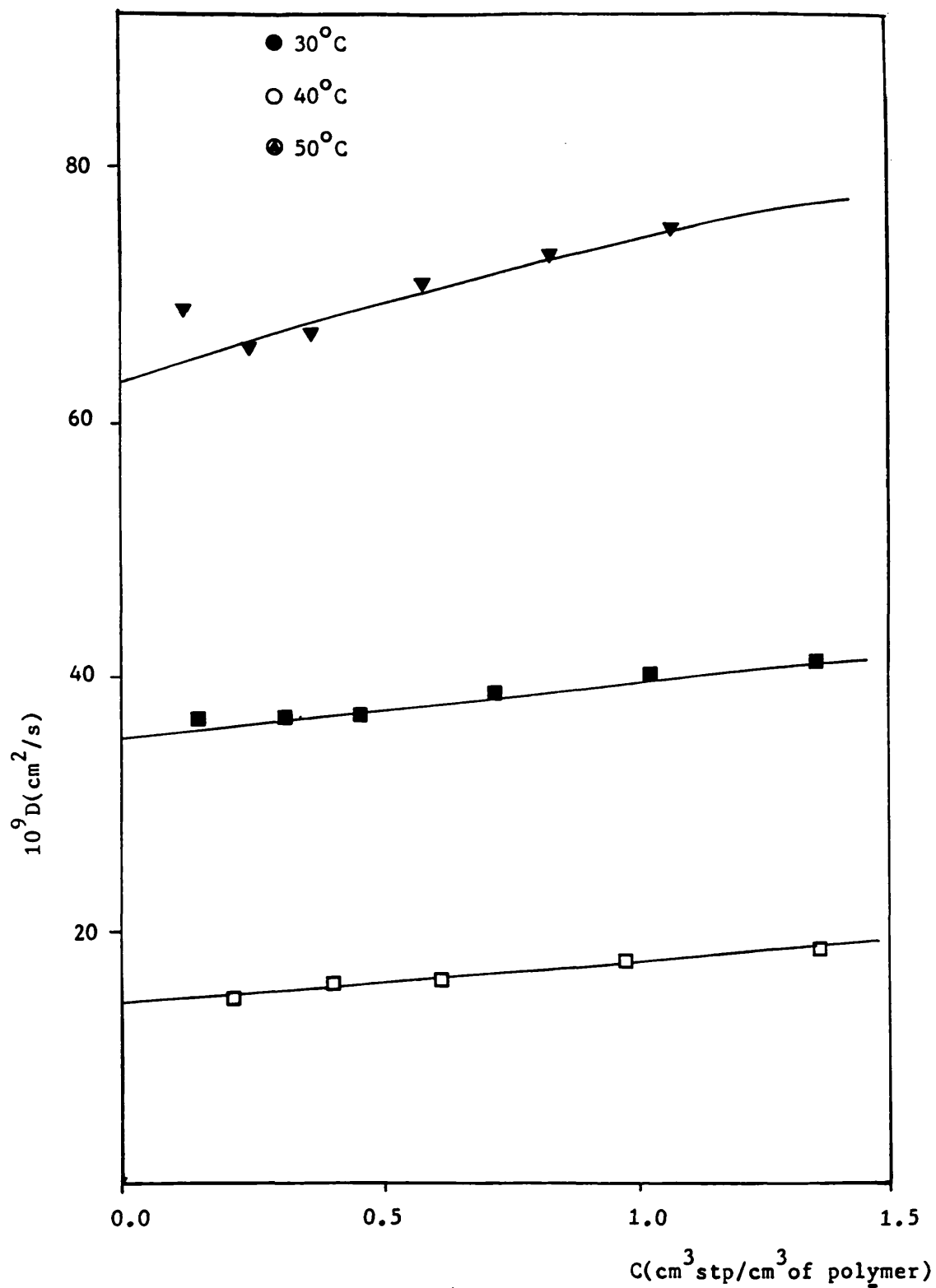


FIG. 6.10 50% PES Blend/ CO_2 concentration dependence of $\bar{D}$

obtained from the time - lag, using, $\theta = l^2/6D$. After allowing for edge effects, the excellent agreement between the two sets of data suggest that the diffusion coefficients are almost concentration independent. The excellent agreement between two sets of diffusion coefficient also confirms the steady state permeability and solubility results which seem to indicate some degree of interaction in the system.

Table (6.6) Diffusion Coefficients For CO_2 In PES - Pu Blends
 $10^9 D/\text{cm}^2 \text{ s}^{-1}$

Wt. % PES	30	40	50
0	170	307	466
20	77.8	-	-
50	14.4 (15.0)	36.0 (33.0)	64 (70.0)
80	2.8 (3.2)	5.9 (6.2)	12.3 (12.0)
100	2.0	4.01	6.95

The variation of D with volume fraction of PU at 30°C is shown in figure (6.11). The half filled circles represents the diffusion coefficients estimated from the time lag method. The diffusion coefficients were plotted in terms of equation (2.19), shown in Figure (6.12) from which the activation energies for diffusion, E_D were estimated and are collected in table (6.7).

It is evident that E_D is practically independent of blend composition.

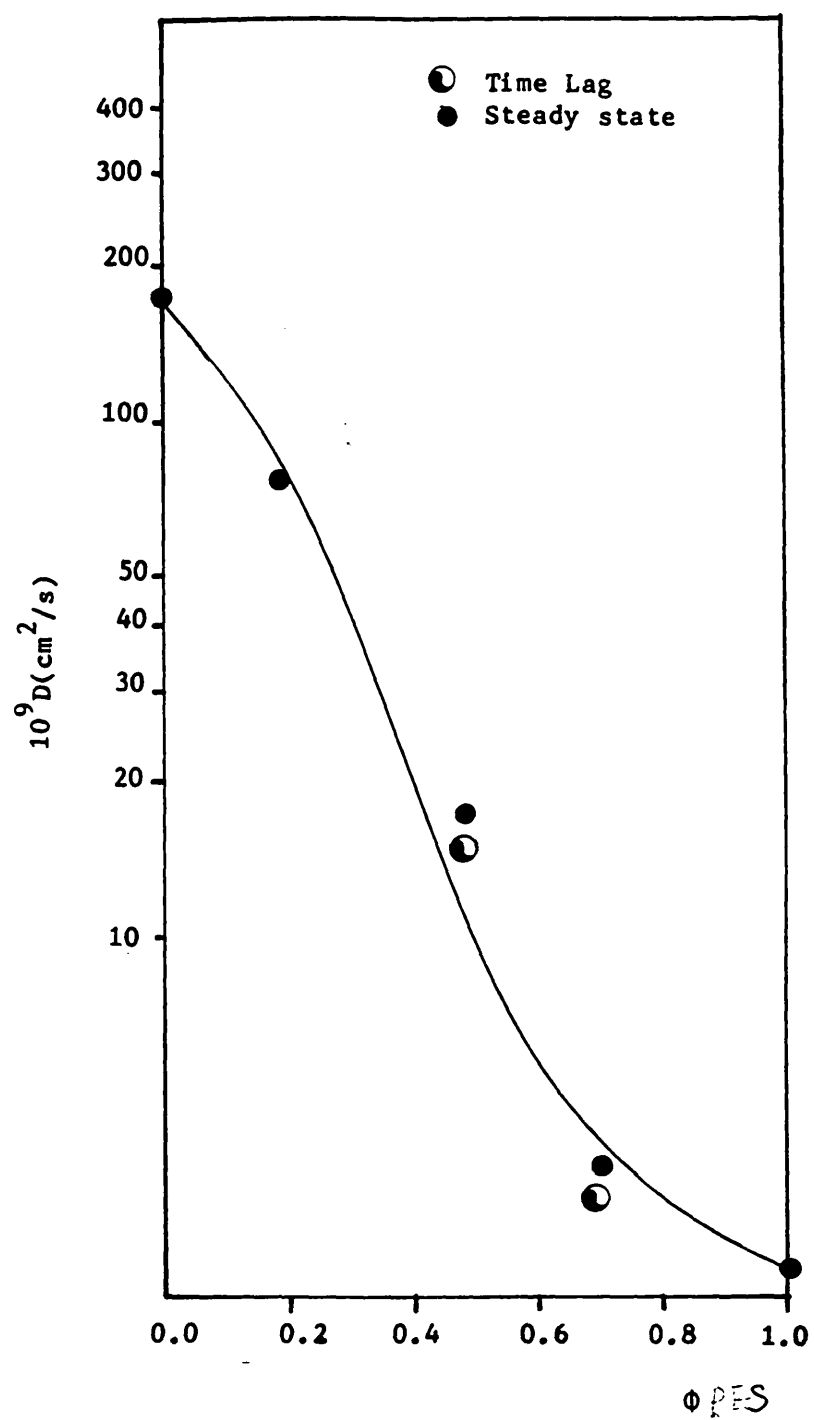


FIG. 6.11 Diffusivity of CO_2 at 30°C

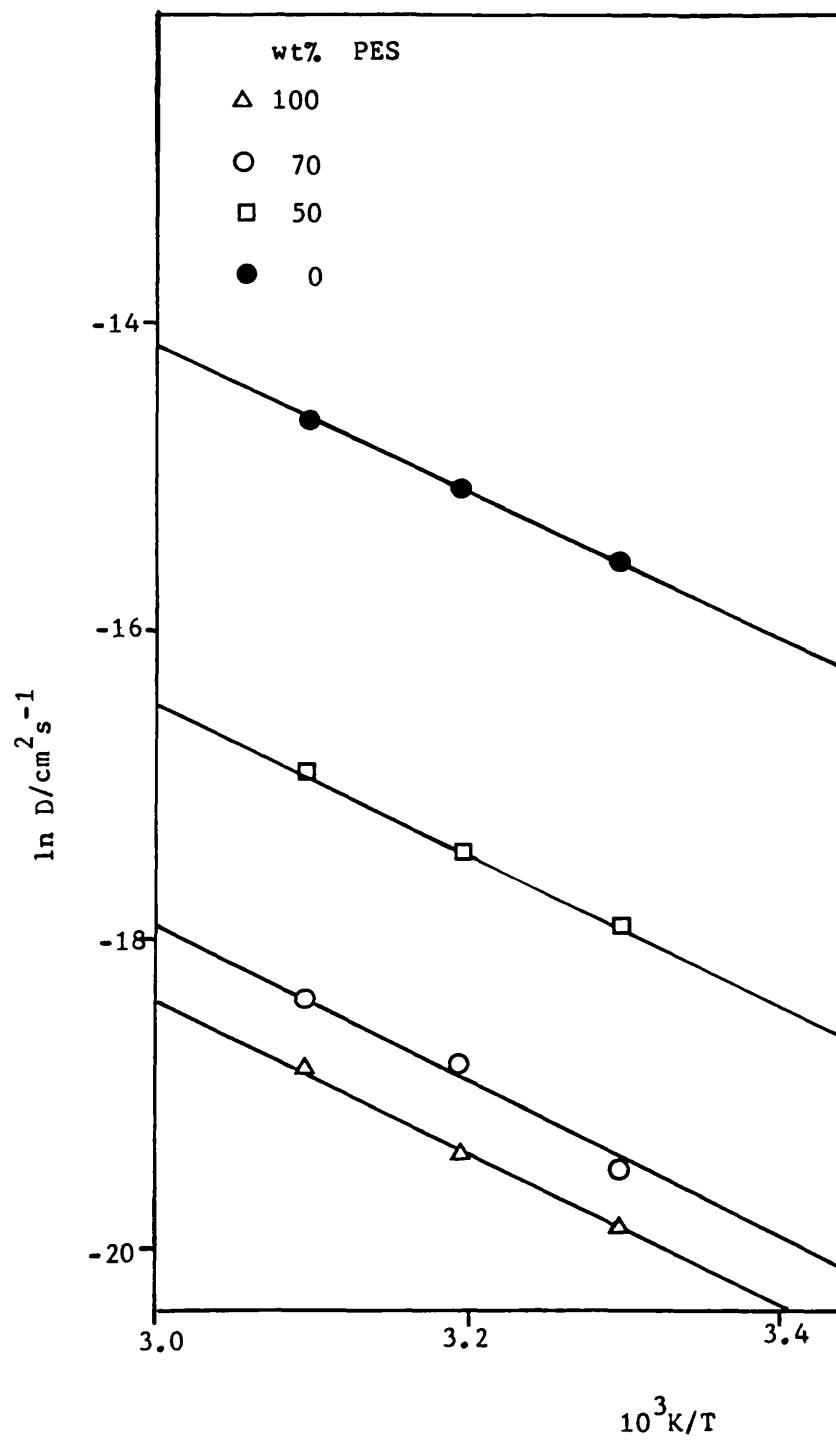


FIG. 6.12 Arrhenius plots for Diffusivity of CO_2

Table (6.7): Activation Energies Of Diffusion for CO₂

E_D : k Jmol⁻¹

Wt. % PES	E_D
0	42.5
20	-
50	40.6
80	42.9
100	47.0

6.5 Separation Factors

It was not possible to obtain the separation factors for the PES-Pu system since only CO₂ transport and sorption measurements were carried out.

6.6 Conclusion

Blends with high PES content were hazy, but those with high Pu content were clear. Glass transition temperatures indicated that the blends exhibited two phase behaviour, however such a technique do not detect mixing at micro level, which may exist in this case.

The equilibrium sorption isotherms for CO₂ at high PES content were non-linear giving the behaviour expected of glassy polymers. Those of high Pu content obeyed Henry's Law. The Henry's Law solubility coefficients showed negative departure from the simple additivity line, again indicating miscibility

between Pu-PES. Furthermore the difference between the solubility measured directly and that from $P=Dk$ was insignificant. The heat of dissolution became less exothermic as the Pu content was increased in the blend. This was the expected behaviour for rubbery blends, since energy is required to create a hole in the polymer to accommodate the gas molecule, unlike glassy polymers, where sorption occurs in pre-existing cavities.

The permeability, P , was independent of ingoing pressure for all systems. The permeability decreased with increasing PES content and a slight minimum was observed around 70% PES in the blend. The variation of P with composition lie well below the line predicted by the Maxwell model.

The corresponding E_p data are virtually independent of composition but there is slight decrease around 70% PES composition.

Finally, the diffusion coefficient for the high PES blends were a very weak function of concentration, since the isotherms, see Fig. 6.11, were non-linear. There was a reasonable agreement between the time-lag and steady state diffusion coefficients confirming the internal consistency of the measurements.

The separation factors could not be evaluated for this system since the time scale permitted the study for CO_2 only.

Further Study

Suggestions for further study in line with the present study; there are several aspects of the PES - Phenoxy and particularly PES - Polyurethane systems which merit further investigations.

Firstly, the transport and sorption of CO_2 and CH_4 in PES-Phenoxyl blends should be studied to much higher pressures (15-30 atmospheres) to see any significant changes in the transport and sorption parameters which can be associated with the glassy state of the polymers and also, since CO_2 is a strong plasticizer for PES the effect it has on the blends.

Detailed investigation of the physical characterization of the miscibility (compatibility) of the PES-Pu system and also on the transport and sorption behaviour of both CO_2 and CH_4 should be made.

This will then give an indication on the separation ability of the glassy-rubbery mixture.

APPENDIX 1

Permeation

Calculation of the permeability, P , and the time lag diffusion coefficient, D_θ , of carbon dioxide in PES is given below:

Membrane Temperature/ $^{\circ}\text{C}$	=	30.1 (± 0.1)
Membrane Area A/cm^2	=	3.301 ($\pm 1\%$)
Membrane Thickness l/cm	=	0.0065 ($\pm 1\%$)
Average Room Temperature T/K	=	296.7 (± 0.5)
Downstream volume V/cm^3	=	680.41 ($\pm 0.5\%$)
Transducer Output Tr/mV	=	14.04 ($\pm 0.1\%$)
Transducer Calibration Constant $\text{K}/\text{cmHg}\text{mV}^{-1}$	=	1.103 ($\pm 0.1\%$)
Driving pressure, $p_o = \text{Tr} \times \text{K}/\text{cmHg}$	=	15.49 ($\pm 0.15\%$)
Steady state flow rate $dp/dt/\text{cmHg}\text{s}^{-1}$	=	1.06×10^{-7} ($\pm 0.5\%$)
Time lag, θ/s	=	4200 ($\pm 2\%$)

$$\text{Steady state flux, } J = \frac{dp}{dt} \times \frac{V}{76} \times \frac{273.2}{T}$$

$$= 8.73 \times 10^{-7} \text{ cm}^3(\text{stp})\text{s}^{-1}$$

$$\text{Permeability, } P = \frac{J \times l}{A \times p_o} = 1.11 \times 10^{-10} \text{ cm}^3(\text{stp})\text{cm cm}^{-2}\text{s}^{-1}\text{cmHg}^{-1}$$

$$\text{Diffusivity, } D = \frac{l^2}{6\theta} = 1.68 \times 10^{-9} \text{ cm}^2\text{s}^{-1}$$

$$\text{Solubility } k = P/D = 0.0663 \text{ cm}^3(\text{stp})\text{cm}^{-3}(\text{poly})\text{cmHg}^{-1}$$

APPENDIX 1.1

EQUILIBRIUM SORPTION

Calculation of the equilibrium concentration of carbon dioxide dissolved in PES:-

Temperature of measurement, $T/^{\circ}\text{C}$	= 30.2 (± 0.1)
Mass of Sample, w_s/g	= 0.1071 ($\pm 0.05\%$)
Mass of Mesh, w_m/g	= 0.0553 ($\pm 0.05\%$)
Mass of counterweight, w_c/g	= 0.0963 ($\pm 0.05\%$)
Density of PES, ρ_s/gcm^{-3}	= 1.375 ($\pm 0.001\%$)
Density of Copper, $\rho_{\text{Cu}}/\text{gcm}^{-3}$	= 8.98 ($\pm 0.2\%$)
Transducer output, Tr/mV	= 16.19 ($\pm 0.1\%$)
Penetrant Pressure, $p_o = \text{Tr} \times K/\text{cmHg}$	= 20.6 ($\pm 0.15\%$)
Transducer Calibration constant, $K/\text{cmHg}\text{mV}^{-1}$	= 1.272 ($\pm 0.1\%$)
Weight Increase at equilibrium, $M_{\infty}/\mu\text{g}$	= 549 ($\pm 0.5\%$)
Molecular weight of CO_2	= 44.01

$$\text{Volume Displaced, } V, = \frac{w_s}{\rho_s} + \frac{w_m}{\rho_{\text{Cu}}} - \frac{w_c}{\rho_{\text{Cu}}} = 0.0733\text{cm}^3 (\pm 0.05\%)$$

$$\text{Buoyancy Correction, } B, = \frac{V \times 273.2}{T} \times \frac{p_o}{76} \times \frac{44.01}{22414} \pm (0.5\%)$$

$$\text{Total weight of } \text{CO}_2 \text{ sorbed} = B + M_{\infty} = 584.2\mu\text{g} \pm (1.0\%)$$

$$\begin{aligned} \text{Concentration, } c, &= (B + M_{\infty}) \times \frac{22414}{44.01} \times \frac{\sigma_s}{w_s} (\pm 1.0\%) \\ &= 3.819 \text{ cm}^3(\text{stp})\text{cm}^3(\text{poly}) \end{aligned}$$

$$\begin{aligned} \text{Equilibrium Solubility, } k &= c/p_o (\pm 1.0\%) \\ &= 0.1854 \text{ cm}^3(\text{stp})\text{cm}^3(\text{poly})\text{cmHg}^{-1} \end{aligned}$$

APPENDIX 2

Phenoxy/CO₂ Sorption Isotherm Results

Density (ρ) = 1.188 cmHg⁻¹

Weight (w) = 0.251g

T/°C	p/cmHg	C/cm ³ (stp) cm ⁻³ (poly)	k/cm ³ (stp) cm ⁻³ (poly)cmHg ⁻¹
30	4.26	0.1045	0.0245
30	9.29	0.2220	0.0239
30	11.43	0.2581	0.0226
30	13.24	0.3049	0.0230
30	20.33	0.4440	0.0218
30	24.65	0.5366	0.0218
30	28.49	0.6210	0.0215
30	38.49	0.7953	0.0207
30	47.59	0.9492	0.0199
30	49.32	0.9826	0.0199
35	6.17	0.1099	0.01781
35	13.63	0.2523	0.01851
35	19.85	0.3608	0.01814
35	30.77	0.5403	0.01756
35	44.05	0.7591	0.01723
35	51.52	0.9205	0.01787
40	6.59	0.1029	0.0156
40	10.52	0.1701	0.0162

$T/^{\circ}\text{C}$	p/cmHg	$C/\text{cm}^3(\text{stp})$ $\text{cm}^{-3}(\text{poly})$	$k/\text{cm}^3(\text{stp})$ $\text{cm}^{-3}(\text{poly})\text{cmHg}^{-1}$
40	15.15	0.2407	0.0159
40	20.14	0.3163	0.0157
40	30.48	0.4651	0.0153
40	35.16	0.5280	0.0150
40	42.12	0.6302	0.0150
40	47.75	0.7042	0.0147
45	4.09	0.0520	0.01272
45	8.05	0.1096	0.01362
45	11.83	0.1601	0.01354
45	20.39	0.2687	0.01318
45	30.17	0.3915	0.01297
45	42.03	0.5305	0.01262
45	45.51	0.5671	0.01246
45	50.08	0.6314	0.01261
50	6.04	0.0669	0.0111
50	10.53	0.1219	0.0116
50	19.92	0.2328	0.0117
50	21.09	0.2489	0.0118
50	30.56	0.3589	0.0117
50	39.93	0.4444	0.0111
50	49.98	0.5766	0.0115

Phenoxy/CH₄ Sorption Isotherm Results

T/°C	p/cmHg	C/cm ³ (stp) cm ⁻³ (poly)	k/cm ³ (stp) cm ⁻³ (poly)cmHg ⁻¹
30	12.71	0.0468	0.0037
30	15.19	0.0569	0.0037
30	20.86	0.0746	0.0036
30	23.01	0.0890	0.0039
30	31.98	0.1183	0.0037
30	42.34	0.1505	0.0036
30	49.79	0.1801	0.0037
40	11.84	0.0368	0.0031
40	20.43	0.0623	0.0031
40	22.73	0.0690	0.0030
40	27.74	0.0872	0.0031
40	30.27	0.0923	0.0030
40	33.92	0.1003	0.0030
40	41.98	0.1310	0.0031
40	50.70	0.1553	0.0031
50	5.94	0.0134	0.0023
50	11.59	0.0272	0.0023
50	16.04	0.0375	0.0023
50	21.78	0.0528	0.0024
50	31.52	0.0759	0.0024
50	40.97	0.0968	0.0024

PES/CO₂ Sorption Isotherms Results

$$\rho = 1.3754 \text{gcm}^{-3}$$

$$w = 0.1071 \text{g}$$

T/°C	p/cmHg	C/cm ³ (stp) cm ⁻³ (poly)	k/cm ³ (stp) cm ⁻³ (poly)cmHg ⁻¹
30	1.40	0.300	0.2143
30	2.00	0.490	0.2450
30	4.30	0.860	0.2000
30	6.81	1.190	0.1747
30	11.92	1.910	0.1602
30	20.65	2.910	0.1409
30	30.61	3.820	0.1247
30	41.80	4.690	0.1122
40	1.60	0.250	0.1563
40	2.80	0.450	0.1607
40	4.60	0.610	0.1326
40	8.20	0.950	0.1159
40	10.60	1.260	0.1189
40	21.10	2.130	0.1009
40	29.10	2.740	0.0942
40	32.60	2.980	0.0914
40	40.00	3.490	0.0873
40	48.60	4.000	0.0823

$T/^{\circ}\text{C}$	p/cmHg	$C/\text{cm}^3(\text{stp})$ $\text{cm}^{-3}(\text{poly})$	$k/\text{cm}^3(\text{stp})$ $\text{cm}^{-3}(\text{poly})\text{cmHg}^{-1}$
50	1.40	0.140	0.1000
50	3.80	0.410	0.1078
50	7.41	0.581	0.0784
50	10.11	0.800	0.0791
50	21.40	1.580	0.0738
50	28.01	1.960	0.0699
50	35.18	2.350	0.0668
50	42.62	2.960	0.0609

70% PES/ CO_2 Sorption Isotherm Results

$$\rho = 1.3111\text{gcm}^{-3}$$

$$w = 0.2132\text{g}$$

$T/^{\circ}\text{C}$	p/cmHg	$C/\text{cm}^3(\text{stp})$ $\text{cm}^{-3}(\text{poly})$	$k/\text{cm}^3(\text{stp})$ $\text{cm}^{-3}(\text{poly})\text{cmHg}^{-1}$
30	4.01	0.5010	0.1249
30	7.06	0.8559	0.1212
30	12.69	1.4068	0.1109
30	20.59	2.0025	0.0973
30	28.23	2.5676	0.0910
30	39.92	3.3809	0.0847
30	50.40	4.0100	0.0796
30	60.00	4.1500	0.0692

80% PES/CO₂ Sorption Isotherm Results

T/°C	p/cmHg	C/cm ³ (stp) cm ⁻³ (poly)	k/cm ³ (stp) cm ⁻³ (poly) cmHg ⁻¹
30	5.40	1.00	0.1852
30	12.83	1.58	0.1231
30	20.40	2.25	0.1103
30	31.95	3.13	0.0979
30	41.73	3.64	0.0872
30	51.11	4.21	0.0824
40	7.62	0.74	0.0971
40	11.79	1.04	0.0882
40	19.58	1.60	0.0817
40	31.38	2.30	0.0733
40	40.79	2.80	0.0686
40	52.77	3.38	0.0641
50	4.00	0.30	0.0750
50	9.86	0.64	0.0649
50	15.67	0.95	0.0606
50	19.68	1.15	0.0584
50	30.00	1.64	0.0546
50	39.10	2.05	0.0524
50	46.56	2.35	0.0505
50	50.40	2.50	0.0496
50	62.80	2.98	0.0475

PES/CH₄ Sorption Isotherm Results

T/°C	p/cmHg	C/cm ³ (stp)	k/cm ³ (stp)
		cm ⁻³ (poly)	cm ⁻³ (poly) cmHg ⁻¹
30	4.8	0.110	0.0229
	9.642	0.220	0.0228
	19.60	0.385	0.0196
	31.602	0.675	0.0214
	41.25	0.840	0.0204
	52.00	1.45	0.0279
40	7.60	0.145	0.0191
	21.20	0.325	0.0153
	32.80	0.47	0.0143
	40.40	0.60	0.0149
	50.00	0.72	0.0144
50	4.85	0.066	0.0136
	19.60	0.226	0.0115
	33.00	0.367	0.0111
	41.20	0.488	0.0118
	53.00	0.610	0.0115

Sorption Isotherm : 80% PES/CH₄

T/°C	p/cmHg	C/cm ³ (stp) cm ⁻³ (poly)	k/cm ³ (stp) cm ⁻³ (poly)cmHg ⁻¹
30	11.40	0.175	0.0154
	19.42	0.285	0.0147
	30.75	0.475	0.0154
	44.00	0.667	0.0152
	49.95	0.776	0.0155
40	7.80	0.101	0.0129
	14.60	0.169	0.0114
	25.5	0.267	0.0105
	35.41	0.414	0.0117
	50.40	0.554	0.0109
	58.11	0.650	0.0112
50	10.40	0.108	0.0104
	21.60	0.214	0.0099
	36.43	0.360	0.0098
	46.55	0.436	0.0094
	54.05	0.513	0.0095

$T/^{\circ}\text{C}$	p/cmHg	$C/\text{cm}^3(\text{stp})$ $\text{cm}^{-3}(\text{poly})$	$k/\text{cm}^3(\text{stp})$ $\text{cm}^{-3}(\text{poly})\text{cmHg}^{-1}$
40	5.79	0.5187	0.0896
40	11.22	0.9031	0.0805
40	22.91	1.6263	0.0710
40	21.33	1.9648	0.0670
40	43.41	2.6171	0.0603
40	56.40	3.1700	0.0562
50	5.42	0.3463	0.0639
50	15.42	0.8616	0.0559
50	26.36	1.3934	0.0529
50	39.43	1.8588	0.0471
50	44.27	2.0468	0.0462
50	56.40	2.74700	0.0438
50	57.20	2.4800	0.0434

50% PES/ CO_2 Sorption Isotherm Results

$$\rho = 1.274 \text{ gcm}^{-3}$$

$$w = 0.2449\text{g}$$

$T/^{\circ}\text{C}$	p/cmHg	$C/\text{cm}^3(\text{stp})$ $\text{cm}^{-3}(\text{poly})$	$k/\text{cm}^3(\text{stp})$ $\text{cm}^{-3}(\text{poly})\text{cmHg}^{-1}$
30	4.89	0.4563	0.0933
30	11.64	0.9628	0.0827

$T/^{\circ}\text{C}$	p/cmHg	$C/\text{cm}^3(\text{stp})$ $\text{cm}^{-3}(\text{poly})$	$k/\text{cm}^3(\text{stp})$ $\text{cm}^{-3}(\text{poly})\text{cmHg}^{-1}$
30	20.45	1.4770	0.0722
30	31.97	2.0726	0.0648
30	40.65	2.4470	0.0600
30	50.89	2.8553	0.0561
40	5.46	0.3505	0.0642
40	10.11	0.6153	0.0609
40	17.11	0.9637	0.563
40	20.84	1.1135	0.0534
40	30.13	1.4956	0.0496
40	40.39	1.8572	0.0460
40	40.83	1.8829	0.0461
40	51.29	2.2122	0.0431
40	52.90	2.2911	0.0433
50	3.00	0.1445	0.0482
50	4.82	0.2297	0.0477
50	7.03	0.3181	0.0452
50	10.15	0.4394	0.0433
50	21.28	0.8404	0.0395
50	32.55	1.1882	0.0365
50	42.49	1.4673	0.0345
50	51.77	1.7062	0.0330

50% PES/CH₄ Sorption Isotherm Results

T/°C	p/cmHg	C/cm ³ (stp) cm ⁻³ (poly)	k/cm ³ (stp) cm ⁻³ (poly)cmHg ⁻¹
30	7.03	0.1369	0.0195
30	12.12	0.1329	0.0110
30	14.63	0.2326	0.0159
30	19.43	0.3202	0.0165
30	33.43	0.3944	0.0118
30	52.11	0.5813	0.0112
30	60.73	0.7024	0.0116
40	6.65	0.0555	0.0084
40	12.44	0.1248	0.0100
40	17.73	0.1488	0.0084
40	20.67	0.1806	0.0087
40	22.64	0.1718	0.0076
40	31.98	0.3265	0.0102
40	32.13	0.2771	0.0086
40	38.99	0.3639	0.0093
40	39.93	0.3430	0.0086
40	52.30	0.4380	0.0084
50	2.58	0.0171	0.0066
50	10.39	0.0799	0.0077
50	22.27	0.1864	0.0084
50	25.15	0.1831	0.0073

$T/^{\circ}\text{C}$	p/cmHg	$C/\text{cm}^3(\text{stp})$ $\text{cm}^{-3}(\text{poly})$	$k/\text{cm}^3(\text{stp})$ $\text{cm}^{-3}(\text{poly})\text{cmHg}^{-1}$
50	33.15	0.2442	0.0074
50	39.97	0.2942	0.0074
50	43.66	0.3712	0.0085

30% PES/CO₂ Sorption Isotherm Results

$\rho = 1.2407$

$w = 0.1595$

$T/^{\circ}\text{C}$	p/cmHg	$C/\text{cm}^3(\text{stp})$ $\text{cm}^{-3}(\text{poly})$	$k/\text{cm}^3(\text{stp})$ $\text{cm}^{-3}(\text{poly})\text{cmHg}^{-1}$
30	3.57	0.24.0	0.0673
30	8.08	0.4312	0.0534
30	10.44	0.5145	0.0493
30	20.36	0.8983	0.0441
30	32.35	1.2954	0.0400
30	41.82	1.5651	0.0374
30	48.89	1.7710	0.0362
30	60.46	2.0497	0.0339
40	11.37	0.3837	0.0337
40	22.37	0.7095	0.0317
40	32.36	0.9695	0.0300
40	45.80	1.2817	0.0280
40	50.38	1.3895	0.0276

$T/^{\circ}\text{C}$	p/cmHg	$C/\text{cm}^3(\text{stp})$ $\text{cm}^{-3}(\text{poly})$	$k/\text{cm}^3(\text{stp})$ $\text{cm}^{-3}(\text{poly})\text{cmHg}^{-1}$
40	54.019	1.4379	0.0265
40	62.42	1.6179	0.0259
50	9.88	0.2239	0.0227
50	18.58	0.4238	0.0228
50	31.71	0.6967	0.0220
50	42.39	0.9267	0.0219
50	49.74	1.0017	0.0201
50	57.57	1.1610	0.0202

Sorption Isotherm 30% PES/CH₄

T/°C	p/cmHg	C/cm ³ (stp)	k/cm ³ (stp)
		cm ⁻³ (poly)	cm ⁻³ (poly) cmHg ⁻¹
30	10.00	0.075	0.0075
	18.11	0.114	0.0063
	36.20	0.262	0.0072
	44.06	0.304	0.0069
	50.81	0.370	0.0073
40	13.80	0.097	0.0070
	20.41	0.145	0.0071
	29.43	0.165	0.0056
	44.00	0.225	0.0051
	50.00	0.277	0.0055
50	15.33	0.052	0.0034
	26.23	0.140	0.0053
	42.40	0.166	0.0039
	48.40	0.224	0.0046

Permeation data

			Phenoxy/CO ₂		
T/°C	p/cmHg	θ/min	10 ¹¹ P/cm ³ (stp)cm cm ⁻² s ⁻¹ cmHg ⁻¹	10 ⁹ D/cm ² s ¹	k/cm ³ (stp)cm ³ (poly) cmHg ⁻¹
30	9.77	25	5.73	2.78	0.0206
30	15.86	24	5.55	2.89	0.0192
30	20.73	32	5.82	2.17	0.0268
30	21.12	30	5.43	2.31	0.0235
30	24.94	32	5.70	2.17	0.0262
30	34.70	30	5.89	2.31	0.0255
30	41.47	27	5.38	2.57	0.0209
40	11.87	17.0	7.01	4.08	0.0171
40	20.50	17.5	6.99	3.96	0.0176
40	35.15	15.0	7.31	4.39	0.0168
40	43.03	16.0	7.42	4.34	0.0171
45	10.03	9.5	8.63	7.31	0.0118
45	20.99	10.0	8.29	6.94	0.0119
45	31.20	9.0	9.24	7.71	0.0119
45	42.45	9.0	8.38	7.71	0.0108
50	10.67	7.5	10.3	9.26	0.0111
50	16.53	8.0	9.13	8.68	0.0105
50	19.91	7.5	9.31	9.26	0.0101
50	31.73	8.5	9.00	8.17	0.0110
50	42.26	8.5	8.98	8.17	0.0109
55	21.33	6.0	10.4	11.6	0.0090
55	31.24	7.0	10.3	9.92	0.0104
55	40.96	7.2	10.3	9.92	0.0104

Phenoxy/CH₄

T/°C	p/cmHg	θ/min	$10^{12} P/\text{cm}^3 (\text{stp}) \text{cm}$ $\text{cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$	$10^9 D/\text{cm}^2 \text{s}^{-1}$	$k/\text{cm}^3 (\text{stp}) \text{cm}^3$ (poly) cmHg^{-1}
30	12.62	50	1.96	0.54	0.0036
30	14.62	50	1.53	0.55	0.0028
30	22.26	60	1.56	0.46	0.0036
40	14.27	30	2.40	0.91	0.0025
40	21.05	30	2.40	0.91	0.0025
40	25.31	32	2.17	0.85	0.0025
50	14.58	17	3.60	1.61	0.0022
50	20.45	14	3.63	1.96	0.0019
50	24.06	12	3.32	2.28	0.0015
60	15.44	7	6.25	3.91	0.0016
60	20.47	9	5.44	3.04	0.0018
60	25.49	8	5.43	3.42	0.0016

PES/CO₂

T/°C	p/cmHg	θ/min	$10^{10} P / \text{cm}^3 (\text{stp}) \text{cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$	$10^9 D / \text{cm}^2 \text{s}^{-1}$	$k / \text{cm}^3 (\text{stp}) \text{cm}^3 (\text{poly}) \text{cmHg}^{-1}$
30	12.89	11.53	5.38	3.73	0.1439
30	19.93	10.39	5.47	4.14	0.1321
30	20.11	10.89	5.41	3.96	0.1366
40	10.92	6.11	5.81	7.05	0.0823
40	14.81	6.69	5.53	6.43	0.0858
40	30.06	5.99	5.95	7.19	0.0828
50	13.54	3.63	6.76	11.8	0.0569
50	21.68	3.66	6.66	11.7	0.0565
50	29.81	3.55	6.660	12.1	0.0544

PES/CH₄

T/°C	p/cmHg	θ/min	$10^{11} P / \text{cm}^3 (\text{stp}) \text{cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$	$10^9 D / \text{cm}^2 \text{s}^{-1}$	$k / \text{cm}^3 (\text{stp}) \text{cm}^3 (\text{poly}) \text{cmHg}^{-1}$
30	10.39	42.34	1.05	1.01	0.0109
30	13.89	41.14	1.02	1.04	0.0096
30	19.38	38.57	1.21	1.11	0.0108
40	12.93	11.23	1.68	3.83	0.0044
40	19.03	16.61	1.59	2.59	0.0061
40	28.66	20.48	1.61	2.10	0.0076
50	15.87	11.32	2.20	3.80	0.0058
50	22.74	11.96	2.21	3.60	0.0061
50	31.43	11.54	1.85	3.73	0.0049

PES/Phenoxy/50/50/CO₂

T/°C	p/cmHg	θ/min	$10^{10} P/\text{cm}^3 (\text{stp}) \text{cm}$ $\text{cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$	$10^9 D/\text{cm}^2 \text{s}^{-1}$	$k/\text{cm}^3 (\text{stp}) \text{cm}^3$ (poly) cmHg^{-1}
30	9.72	72	1.09	1.59	0.0689
30	15.49	70	1.11	1.68	0.0664
30	21.07	76	1.10	1.54	0.0712
30	25.25	68	1.09	1.73	0.0634
40	8.97	49	1.33	2.39	0.0559
40	17.14	47	1.32	2.79	0.0472
40	20.53	45	1.29	2.61	0.0495
40	25.42	43	1.29	2.73	0.0474
50	9.14	24.8	1.50	4.73	0.0318
50	15.41	26.4	1.52	4.46	0.0341
50	20.52	26.0	1.55	4.51	0.0344
50	25.85	24.0	1.53	4.89	0.0313
55	10.69	22.0	1.68	5.33	0.0315
55	17.48	21.5	1.68	5.46	0.0308
55	26.60	20.5	1.67	5.72	0.0292
60	9.43	15.6	1.82	7.52	0.0242
60	14.88	16.6	1.85	7.02	0.0262
60	21.13	16.5	1.82	7.11	0.0256
60	26.28	16.4	1.85	7.16	0.0259

70/30/PES/Phenoxy/CO₂

T/°C	p/cmHg	θ/min	$10^{10} P/\text{cm}^3 (\text{stp}) \text{cm}$ $\text{cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$	$10^9 D/\text{cm}^2 \text{s}^{-1}$	$k/\text{cm}^3 (\text{stp}) \text{cm}^3$ (poly) cmHg^{-1}
30	9.23	138	1.84	1.42	0.1296
30	19.67	135	1.84	1.44	0.1270
30	24.92	130	1.84	1.50	0.1227
40	8.92	86	2.19	2.27	0.0965
40	14.35	84	2.14	2.33	0.0918
40	17.99	82	2.24	2.38	0.0939
40	25.45	82	2.17	2.38	0.0918
50	10.89	50	2.53	3.91	0.0618
50	15.14	50	2.46	3.91	0.0629
50	17.95	50	2.49	3.91	0.0638
50	26.39	48	2.52	4.07	0.0618
55	9.76	43	2.79	4.55	0.0613
55	15.69	44	2.71	4.44	0.0610
55	22.55	40	2.67	4.89	0.0546

70/30/Phenoxy/PES/CO₂

T/°C	p/cmHg	θ/min	$10^{11} P / \text{cm}^3 (\text{stp}) \text{cm}$ $\text{cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$	$10^9 D / \text{cm}^2 \text{s}^{-1}$	$k / \text{cm}^3 (\text{stp}) \text{cm}^3$ (poly) cmHg^{-1}
30	13.9	126	5.75	1.13	0.0508
30	19.61	104	5.94	1.36	0.0434
30	28.27	109	6.05	1.30	0.0464
40	12.11	66.73	7.48	2.18	0.0349
40	16.32	65.7	7.46	2.17	0.0343
50	11.11	32.05	9.02	4.45	0.0202
50	18.89	34.68	9.08	4.11	0.0220
50	25.23	38.72	9.23	3.68	0.0250
50	27.09	37.84	9.12	3.77	0.0241

Diffusion Coefficients for CO₂

T/°C	Phenoxy		PES	
	c/cm ³ (stp)cm ⁻³ (poly)	10 ⁹ D/cm ² s ⁻¹	c/cm ³ (stp)cm ⁻³ (poly)	10 ⁹ D/cm ² s ⁻¹
30	0.010	2.35	0.10	2.23
	0.022	2.55	0.22	2.38
	0.044	2.83	0.33	2.55
	0.079	3.15	0.45	2.67
	0.098	3.72	0.54	2.74
			0.61	2.78
40	0.010	4.52	0.17	4.45
	0.032	4.73	0.25	4.60
	0.047	4.95	0.32	4.70
	0.063	5.40	0.45	5.01
	0.070	5.65	0.53	5.20
50	0.012	7.85	0.12	7.90
	0.023	8.05	0.23	7.85
	0.030	8.20	0.35	8.15
	0.045	8.35	0.45	8.70
	0.050	8.50	0.58	9.23

T/°C	50/50 PES-Phenoxy		80/20 PES-Phenoxy	
	c/cm ³ (stp)cm ⁻³ (poly)	10 ⁹ D/cm ² s ⁻¹	c/cm ³ (stp)cm ⁻³ (poly)	10 ⁹ D/cm ² s ⁻¹
30	0.45	1.38	1.00	1.85
	0.94	1.75	1.60	2.25
	1.48	2.12	2.24	2.76
	2.15	2.53	3.10	3.30
	2.85	2.83	4.20	4.17
40	0.35	2.20	0.70	2.95
	0.61	2.44	1.02	3.45
	1.10	3.60	1.60	3.95
	1.50	3.42	2.36	4.45
	1.89	3.90	2.80	5.00
	2.20	4.30	3.39	5.50
50	0.20	3.48	0.60	4.95
	0.44	3.88	1.14	5.75
	0.84	4.64	1.64	6.35
	1.18	5.22	2.04	7.00
	1.45	5.60	2.50	7.75
	1.70	5.90	3.00	8.75

70/30/PES/Phenoxy

$T/^{\circ}\text{C}$	$c/\text{cm}^3(\text{stp})\text{cm}^{-3}(\text{poly})$	$10^9 D/\text{cm}^2\text{s}^{-1}$
30	0.20	3.14
	0.80	3.38
	1.10	3.60
	1.60	4.05
	2.12	4.55
	2.25	4.70
40	0.20	6.20
	0.52	6.25
	0.78	6.40
	1.20	7.00
	1.68	7.50
	2.08	8.20
50	0.18	12.9
	0.35	12.6
	0.52	3.60
	0.85	13.0
	1.20	13.7
	1.50	14.3

Sorption Isotherm 50% Pu/CO₂

T/°C	p/cmHg	C/cm ³ (stp)	k/cm ³ (stp)
		cm ⁻³ (poly)	cm ⁻³ (poly)cmHg ⁻¹
30	6.10	0.1743	0.0286
	9.64	0.2705	0.0281
	14.00	0.3751	0.0268
	21.83	0.5280	0.0242
	28.60	0.6750	0.0236
	36.82	0.8534	0.0232
40	3.11	0.6520	0.0210
	9.20	0.1800	0.0196
	15.82	0.3031	0.0192
	24.10	0.4320	0.0179
	30.62	0.5402	0.0176
	41.65	0.7051	0.0169
50	2.00	0.0305	0.0153
	6.21	0.100	0.0161
	17.42	0.254	0.0146
	30.64	0.425	0.0139
	40.00	0.545	0.0136

Sorption Isotherm 20% Pu/CO₂

T/°C	p/cmHg	C/cm ³ (stp)	k/cm ³ (stp)
		cm ⁻³ (poly)	cm ⁻³ (poly)cmHg ⁻¹
30	3.08	0.3095	0.1005
	5.42	0.5824	0.1075
	9.18	0.8692	0.0947
	17.67	1.4873	0.0842
	29.41	2.1457	0.0730
40	5.25	0.0589	0.0112
	6.03	0.0654	0.0108
	9.59	0.1041	0.0109
	11.31	0.1274	0.0113
	15.79	0.1730	0.0110
	19.79	0.2239	0.0113
	23.23	0.2568	0.0111
	30.97	0.3503	0.0113
50	2.43	0.0277	0.0114
	10.20	0.1039	0.0102
	19.79	0.2026	0.0102
	30.97	0.3255	0.0105

Permeation Data

Pu/CO₂

T/°C	p/cmHg	θ/min	$10^9 P / \text{cm}^3 (\text{stp}) \text{cm}$ $\text{cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$	$10^7 D / \text{cm}^2 \text{s}^{-1}$	$k / \text{cm}^3 (\text{stp}) \text{cm}^3$ $(\text{poly}) \text{cmHg}^{-1}$
30	8.94	4.67	2.59	2.37	0.0109
30	10.41	4.50	2.55	2.46	0.0103
30	11.66	4.64	2.58	2.39	0.0107
30	15.80	4.70	2.55	2.36	0.0108
40	9.79	2.31	4.14	4.80	0.00861
40	10.19	2.41	4.01	4.61	0.00869
40	11.27	2.62	4.09	4.20	0.00973
40	14.89	2.41	4.10	4.61	0.00888
40	16.33	2.52	4.04	4.40	0.00919
50	10.55	1.35	5.77	-	-
50	16.81	1.48	5.72	-	-
50	18.20	1.36	5.75	-	-

80% Pu/CO₂

T/°C	p/cmHg	θ/min	$10^9 P/\text{cm}^3 (\text{stp}) \text{cm}$ $\text{cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$	$10^7 D/\text{cm}^2 \text{s}^{-1}$	$k/\text{cm}^3 (\text{stp}) \text{cm}^3$ $(\text{poly}) \text{cmHg}^{-1}$
30	6.92	2.84	1.45	1.65	0.0088
30	8.44	2.23	1.42	2.10	0.0068
30	13.13	2.99	1.43	1.57	0.0091
40	7.14	1.59	2.33	2.94	0.0079
40	12.87	1.83	2.29	2.56	0.0089
40	13.71	1.57	2.26	2.99	0.0075
40	18.04	1.56	2.31	2.99	0.0078
50	5.58	0.82	3.52	5.73	0.0061
50	9.90	0.84	3.43	5.59	0.0061
50	13.66	0.84	3.43	5.02	0.0068
50	14.82	0.88	3.50	5.28	0.0062

20% Pu/CO₂

T/°C	p/cmHg	θ/min	$10^9 P/\text{cm}^3 (\text{stp}) \text{cm}$ $\text{cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$	$10^7 D/\text{cm}^2 \text{s}^{-1}$	$k/\text{cm}^3 (\text{stp}) \text{cm}$ $(\text{poly}) \text{cmHg}^{-1}$
30	6.57	15	3.31	3.11	0.1063
30	8.48	14	3.32	3.33	0.0995
30	12.06	16	3.29	2.91	0.1129
30	18.89	13	3.34	3.59	0.0931
40	7.14	8	4.21	5.84	0.0721
40	14.99	8	4.21	5.84	0.0721
40	15.15	7	4.29	5.84	0.0721
40	18.63	8	4.21	5.84	0.0721
50	8.34	4.5	5.15	10.38	0.0496
50	10.94	4.5	5.15	10.38	0.0496
50	17.74	4.5	5.39	10.38	0.0519

References

1. O. Olabisi, L.M. Robeson, and M.T. Shaw, "Polymer-Polymer Miscibility", Academic Press, New York, 1979.
2. E.P. Cizek, U.S. Patent 3,383,435 Assigned to GEC, 1978.
3. G. Bommi and P. Leblanc, Mod. Plast. Encycl., 1972, 42, 53(10A).
4. D.R. Paul and S. Newman, "Polymer Blends", Academic Press, New York, 1978.
5. P.J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, New York, 1953, Chapter 8.
6. J.A. Mason, and L.H. Sperling, "Polymer Blends, Grafts and Blocks", Plenum, New York, 1974.
7. L.H. Sperling, Recent Advances in Polymer Blends, Grafts and Blocks", Plenum, New York, 1974.
8. G. Scatchard, Chem. Rev., 1931, 321, 8.
9. J.J. Van Laar, "Sechs Voltage", Zeits. f. Physick., chemie, 1910, 723, 72.
10. J.H. Hildebrand and R.L. Scott, The solubility of Non-electrolytes, 3rd ed., Reinhold, New York, 1950.
11. P.J. Flory, R.A. Orwell and A. Vrig., J. Amer. Chem. Soc., 1965, 3507, 86.
12. P.J. Flory, J. Amer. Chem. Soc., 1965, 1833, 87.
13. R.A. Orwell and P.J. Flory, J. Amer. Chem. Soc., 1967, 89, 6814.
14. A. Abe and P.J. Flory, J. Amer. Chem. Soc., 1968, 88, 2887.
15. B.E. Eichinger and P.J. Flory, Trans. Faraday Soc., 1968, 64, 2035.
16. L.D. Taylor and L.D. Cerankowski, J. of Polym. Sci. Polym.

- Chem. Ed., 1975, 2551, 13.
17. D.R. Paul and J.W. Barlow, In "Polymer Compatibility and Incompatibility : Principle and Practices"; MMI Press Symposium Series; Hardwood Academic, New York, 1982, Vol. 2, Chap. 1.
 18. I.C. Sanchez, Annu. Rev. Material Sci., 1983, 13, 387.
 19. V.B. Singh and D. Walsh, J. of Macromol. Sci. Phys., 1986, 325, 65-87.
 20. M.M. Coleman, E.J. Moskala, P.C. Painter, D.J. Walsh, and S. Rostami, Ibid., 1983, 1410, 24.
 21. E.A. Collins, J. Bares, F.W. Billmeyer, Jr., Experiments in Polymer Science, John Wiley and Sons, 1973.
 22. T.G. Fox, Bull. Amer. chem. Soc., 1956, 1, 123.
 23. F.N. Kelly and F. Bueche, J. Polym. Sci., 1961, 50, 549-556.
 24. M. Gorden and J.S. Taylor, J. Appl. Chem., 1952, 2, 493-500.
 25. S. Krause and N. Roman, J. Polym. Sci., Part A, 1965, 1631.
 26. A.E. Tonelli, Macromolecules, 1974, 7(5), 632.
 27. H. Daimon, H. Okitsu, and J. Kumanotani, Polym. J., 1975, 7(4), 460.
 28. C.H.M. Jacque, H.B. Hopfenberg and V. Stannett, Polym. Eng. Sci., 1973, 13(2), 18.
 29. C.H.M. Jacque, H.B. Hopfenberg, Polym. Eng. Sci., 1974, 14(6), 449.
 30. W.M. Prest and R.S. Porter, J. Polym. Sci. Polym. Phys. End, 1639, 10, 1972.
 31. M. Bank, J. Leffingwell and C. Thies, Macromolecules, 1971, 4(1), 43.

32. G.A. Zabrzewski, Polymer, 1973, 14, 348.
33. V.A. Kargin, J. Polym. Sci., 1963, C4, 1601.
34. G.M. Bartener and G.S. Kangarov, Rubber Chem. Technol., 1974, 47, 1188.
35. J.S. Chiou, D.R. Paul and J.W. Barlow, Polym., 1982, 23, 1545.
36. T.K. Kwei, J. Polym. Sci. Polym. Lett. Edn., 1984, 22, 307.
37. T. Nishi and T.T. Wang, Macromolecules, 1975, 8, 1975.
38. S. Akiyama, Y. Kamatsu and R. Keneko, Polym. J., 1975, 7, 172.
39. E. Janckel and H.U. Herwig, Kolloid Z., 1956, 148, 57-66.
40. L.P. McMaster, Macromolecules, 1973, 6, 760.
41. R.E. Bernstein, C.A. Cruz, D.R. Paul and J.W. Barlow, Macromolecules, 1977, 10, 681.
42. D.J. Walsh, J.S. Higgins and S. Rostami, Macromolecules, 1983, 16, 388.
43. M. Matsuo, C. Nozaki and Y. Jyo, Polym. Eng. Sci., 1969, 9, 197.
44. M.M. Coleman and Zarion, J. Polym. Sci., Polym. Phys. Ed., 1979, 17, 837.
45. D.F. Varnell and M.M. Coleman, Polymer, 1981, 22, 1324.
46. D.F. Varnell, J.P. Runt and M.M. Coleman, Polymer, 1983, 37, 24.
47. M.M. Coleman, D.F. Varnell and J.P. Runt in Contemporary Topics in Polymer Sci., Vol. 4 (W.J. Bailey and T. Tsurata Edn.), Plenum, New York, 1983.
48. D.F. Varnell, J.P. Runt and M.M. Coleman, Macromolecules, 1981, 14, 1350.

49. M.M. Coleman and E.J. Moskala, Polymer, 1983, 24, 251.
50. T. Nishi, T.T. Wang, and T.K. Kwei, Macromolecules, 1975, 8(2), 227.
51. T.K. Kwei, T. Nishi, and R.F. Roberts, Macromolecules, 1974, 7, 667.
52. E. Marhiscelli, G. Demma, E. Rossi and A.L. Segre, Polym Comm., 1983, 24, 266.
53. D.D. Deshpande, D. Patterson, H.P. Schreiber and C.S. Su, Macromolecules, 1974, 7, 530.
54. O. Olabisi, Macromolecules, 316, 8, 1975.
55. P. Masi, D.R. Paul and J.W. Barlow, J. Polym. Sci. Polym. Phys. Edn., 1982, 20, 15.
56. G. Morel and D.R. Paul, J. Membrane Sci., 1982, 10, 273.
57. R.L. Scott, J. Chem. Phys., 1949, 17, 279.
58. C.H.M. Jacques, H.B. Hopfenberg, Polym. Eng. Sci., 1974, 14(6), 441.
59. J.A. Barrie and W.D. Webb, Polymers, 1989, 30, 327.
60. W.D. Webb, Thesis, University of London, 1985.
61. T. Graham, Ph.d. Mag., 1866, 32 401.
62. J.K. Mitchell, Roy. Inst. J., 1831, 2, 101.
63. J.K. Mitchell, Roy. Inst. J., 1831, 2, 307.
64. A. Fick, Phil. Mag., 1855, 10, 30.
65. J.B. Fourier, "Theorie Analantique de la Chaleur", 1822.
66. J. Crank, and G.S. Parks, "Diffusion in Polymers", Academic Press, London 1968.
67. J. Crank, "The Mathematics of Diffusion", Clarendon Press, 2nd Edition, 1975.

68. S. Von Wroblewski, Wied. Ann. Physick, 1879, 8, 29.
69. R.M. Barrer, "Diffusion in and through solids", 2nd Edition, Cambridge University Press, New York, 1951.
70. W. Jost, "Diffusion in Solids, liquids and gases", Academic Press, New York, 1952.
71. M.H. Jacobs, "Diffusion Processes", Springer-Verlay, Berlin, 1967.
72. H.A. Daynes, Proc. Roy. Soc., 1920, 97A, 286.
73. R.M. Barrer, Trans. Faraday Soc., 1939, 35, 628.
74. R.M. Barrer, Nature, London, 1937, 140, 106.
75. R.M. Barrer, Trans. Faraday, 1943, 39, 48.
76. R.M. Barrer, ibid, 59.
77. G.J. van Amerongen, J. Polym. Sci., 1950, 5, 307.
78. G.J. van Amerongen, Rubb. Chem. Technol., 1964, 37, 1065.
79. G. Allen, M.J. Bowden, D.J. Blundell, F.G. Hutchinson, G.M. Jeffs and J. Vyvoda, Polymer, 1973, 14, 597.
80. S.A. Stern, J.T. Mulhaupt and R.J. Gareis, A. I. Ch. E. J., 1969, 15, 64.
81. G. Gee, Quart. Rev. Chem. Soc. Lond., 1947, 1, 265.
82. A.S. Michaels and H.J. Bixler, J. Polym. Sci., 1961, 50, 393.
83. P. Meares, J. Amer. Chem. Soc., 1954, 76, 3415.
84. P. Meares, Trans. Faraday Soc., 1957, 53, 101.
85. J.A. Barrie, A.S. Michaels and W.R. Vieth, J. Polym. Sci. Polym. Phys. Edn., 1975, 13, 859.
86. A.S. Michaels, W.R. Vieth, J.A. Barrie, J. Appl. Phys., 1963, 34(1), 1.
87. A.S. Michaels, W.R. Vieth, J.A. Barrie, J. Appl. Phys., 1963, 34(1), 13.

88. G.Y. Ryskin, Zhur. Tekh-Fiz, 1954, 24, 197.
89. C.A. Kumins, C.J. Rolle, and J. Roleman, J. Phys. Chem., 1957, 16, 1290.
90. R.M. Barrer, R. Mallinder and P.S.L. Wong, Polymer, 1967, 8, 321.
91. W.J. Koros and D.R. Paul, J. Polym. Sci. Polym. Phys. Edn., 1978, 16, 1947.
92. W.J. Koros and D.R. Paul, J. Polym. Sci. Polym. Phys. Edn., 1978, 16, 2171.
93. L. Zanderighi, B. Marcadelli, M.P. Faedda, I.R. Bellobono and M. Riva, Gaz. Chim. Italiana, 1979, 105, 505.
94. S.M. Allen, M. Fuji, V. Stannett, H.B. Hopfenberg and J.L. Williams, J. Membrane Sci., 1977, 2, 153.
95. W.H. Burgess, H.B. Hopfenberg and V.T. Stannett, J. Macromol Sci. Phys. Edn., 1971, B5(1) 23.
96. T. Iljima, T. Tanno and T. Nakayawa, J. Appl. Polym. Sci., 1974, 18, 1581.
97. C.A. Kumins and J. Roteman, J. Polymer Sci., 1961, 55, 683.
98. V. Stannett and J.L. Williams, J. Polymer Sci., 1965, C10, 45.
99. B.P. Tikhomirov, H.B. Hopfenberg, V.T. Stannett, J.L. Williams, Macromol. Chemie, 1968, 118, 177.
100. C.A. Kumins and T.K. Kwei, Chap. 4 in ref. 66.
101. R.M. Barrer, J. Phys. Chem., 1957, 61, 178.
102. W.W. Brandt, J. Phys. Chem. Wash., 1959, 63, 1080.
103. M.H. Cohen and D. Turnbull, 1959, 31, 1164.
104. A.T. DiBenedetto, J. Polym. Sci. A., 1963, 1, 3477.

105. R.J. Pace and A. Datyner, J. Polym. Sci. Polym. Phys. Edn., 1979, 17, 437.
106. R.J. Pace and A. Datyner, J. Polym. Sci. Polym. Phys. Edn., 1979, 17, 453.
107. R.J. Pace and A. Datyner, J. Polym. Sci. Polym. Phys. Edn., 1979, 17, 465.
108. S. Glasstone, K.J. Laidler and H. Eyring, The Theory of Rate Processes, McGraw-Hill Book Company, Inc., New York, 1941, Chapter 9.
109. G.J. van Amerongen, J. Appl. Phys., 1956, 17, 3415.
110. S. Prager and F.A. Long, J. Am. Chem. Soc., 1960, 82, 509.
111. G. Blyholder and S. Prager, J. Phys. Chem., Wash., 1960, 64, 702.
112. V. Stannett, ref. 66, Chapter 2, page 54.
113. A.S. Michaels and R.B. Parker, J. Polymer Sci., 1959, 61, 53.
114. H.A. Bent, Ibid, 1957, 24, 387.
115. C.H. Klute, Ibid, 1959, 1, 340.
116. P. Meares, Trans. Faraday Soc., 1958, 54, 40.
117. R.M. Barrer, J.A. Barrie and J. Slater, J. Polym. Sci., 1958, 27, 177.
118. W.R. Vieth, J.M. Howell and J.S. Hsieh, J. Membrane Sci., 1976, 1, 177.
119. W.J. Koros, A.H. Chan and D.R. Paul, J. Membrane Sci., 1977, 2, 165.
120. J.A. Barrie, M.J.L. Williams, and K. Munday, Polymer Eng. and Sci., 1980, 20, 20.
121. W.R. Vieth and K.J. Sladek, J. Colloid Sci., 1965, 20, 1014.
122. W.J. Koros, J. Polym. Sci. Polym. Phys. Ed., 1985, 23, 1611.

123. R.T. Chern, W.J. Koros, E. Yui, H.B. Hopfenberg and V.T. Stannett, J. Polym. Sci. Polym. Phys. Ed., 1984, 22, 1001.
124. D.R. Paul and W.J. Koros, J. Polym. Sci. Polym. Phys. Edn., 1976, 14, 675.
125. R.M. Barrer, J. Membrane Sci., 1984, 18, 25.
126. W.J. Koros, D.R. Paul and D.R. Rocha, J. Polym. Sci. Polym. Phys. Edn., 1976, 14, 687.
127. H.B. Hopfenberg and V. Stannett, Chapter 9, in The Physics of Glassy Polymers", Edited by R.N. Hayward, Wiley (1973).
128. A.S. Michaels, W.R. Vieth and H.J. Bixler, J. Polym. Soc., Polym. Letters, 1963, 1, 19.
129. D.R. Paul and J.W. Barlow, J. Macromol. Chem., Rev. Macromol. Chem., 1980, C18, 109.
130. R. Wegler and R. Schmitz-Justen in Houben-Weyl, 1963, 14/2, 462.
131. A.H. Chan and D.R. Paul, J. Appl. Polym. Sci., 1980, 25, 971.
132. H. Odani, N. Nagata, N. Kitamura, N. Nemoto and Kurata, Bull. Inst. Chem. Res., Kyoto Univ., 1982, 60, 12.
133. A.G. Wonders and D.R. Paul, J. Membrane Sci., 1979, 5, 63.
134. R.M. Felder, C.J. Patton and W.J. Koros, J. Polym. Sci. Polym. Phys. Edn., 1981, 19, 1895.
135. S.A. Stern and S.S. Kulkarni, J. Membrane Sci., 1982, 10, 235.
136. K. Toi, G. Morel and D.R. Paul, J. Appl. Polym. Sci., 1982, 27, 2997.
137. W.J. Koros, R.T. Chen V. Stannett and H.B. Hopfenberg, J. Polym. Sci. Polym. Phys. Edn., 1981, 19, 1513.

138. W.J. Koros, J. Polym. Sci. Polym. Phys. Edn., 1980, 18, 981.
139. N. Yi-Yan, R.M. Felder and W.J. Koros, J. Appl. Polym. Sci., 1980, 25, 1755.
140. C.R. Antonson, R.J. Gardner, C.F. King and D.Y. Yo, Ind. Eng. Chem. Process. Des. Dev., 1977, 16(4), 463.
141. J.M.S. Henis and M.K. Tripodi, J. Membrane Sci., 1981, 8, 233.
142. F.P. McCandless, Ind. Eng. Chem. Process. Des. Dev., 1972, 11(4), 470.
143. E.S. Sanders, W.J. Koros, H.B. Hopfenberg and V.T. Stannett, J. Membrane Sci., 1984, 18, 53.
144. N. Morosoff and V. Stannett, J. Macromol. Sci. Phys., 1980, B17(1), 157.
145. W.J. Koros, G.N. Smith and V. Stannett, J. Appl. Polym. Sci., 1981, 26, 159.
146. G.T. Paulson, A.B. Clinch and F.B. McCandless, J. Membrane Sci., 1983, 14, 129.
147. Z. Grzywna and J. Podkowka, J. Membrane Sci., 1981, 8, 23.
148. M.D. Sefcik, J. Schaefer, F.L. May, D. Raucher and S.M. Dub, J. Polym. Sci. Polym. Phys. Edn., 1983, 21, 1041.
149. M.D. Sefcik, J. Schaefer, F.L. May, D. Raucher and S.M. Dub, J. Polym. Sci. Polym. Phys. Edn., 1983, 21, 1055.
150. D. Raucher and M.D. Sefcik in "Industrial Gas Separation", ed. T.W. Whyte, C. Yon and E. Wagener, ACS Symposium Series 223, Amer. Chem. Soc., 1983.
151. T.A. Barbari, W.J. Koros, D.R. Paul, J. Polym. Sci., B Polym. Phys., 1988, 26, 729.
152. R.M. Barrer, Op. cit. 66, Chapter 6.

153. J. Crank, op cit. 67.
154. S.P. Mittof in "Advance in Material Research, Vol. 3, Ed. H. Herman, Interscience, New York, 1968.
155. J.S. Maxwell, "A Treatise on Electricity and Magnetism", vol 1, 2nd Ed. Clarendon.
156. H. Burger, Physik. Z., 1951, 20, 73.
157. W.I. Higuchi, J. Phys. Chem., 1958, 62, 649.
158. W.I. Higuchi and T. Higuchi, J. Am. Pharm. Ass., 1960, 49, 598.
159. D.A.G. Bruggeman, Ann. Physik., 1935, 24, 636.
160. C.J.F. Böttcher, "Theory of Electric Polarization", Elsevier, Amsterdam, 1952.
161. K. Lichtenecker, Physik. Z., 1926, 27, 115.
162. D.R. Paul, J. Membrane Sci., 1984, 18, 75.
163. K. Lichtenecker and K. Röther, ibid, 1931, 32, 250.
164. N.E. Weeks, F.E. Karasz and W.J. Macknight, J. Appl. Phys., 1977, 48, 4068.
165. R. McGregor in "Permeability of Plastic Films and Coatings to Gases, Vapours and Liquids, ed. H.B. Hopfenberg, Plenum Press, New York, 1974.
166. W.M. Lee, Polym. Eng. Sci., 1980, 20(1), 65.
167. J.W. Barlow and D.R. Paul, Polym. Eng. Sci., 1982, 21, 985.
168. H. Storström and B. Rånby, Advan. Chem. Series, 1971, 99, 107.
169. Y.J. Shur and B. Rånby, J. Appl. Polym. Sci., 1975, 19, 1337.
170. B. Rånby, J. Polym. Sci. Symposia, 1975, 51, 89.
171. Y.J. Shur and B. Rånby, J. Appl. Polym. Sci., 1975, 19, 2143.

172. Y.J. Shur and B. Rånby, J. Appl. Polym. Sci., 1976, 20, 3105.
173. Y.J. Shur and B. Rånby, J. Appl. Polym. Sci., 1976, 20, 3121.
174. Y.J. Shur and B. Rånby, J. Macromol. Sci., 1976, 20, 3121.
175. W.E. Preston, J.W. Barlow and D.R. Paul, J. Appl. Polym. Sci., 1984, 29, 845.
176. Y. Kang, K. Araki, K. Iwamoto and M. Seno, J. Appl. Polym. Sci., 1984, 29, 845.
177. A.E. Barnabeos W.S. Creasy and L.M. Robeson, J. Polym. Sci. Polym. Chem. Edn., 1975, 13, 1979.
178. J.A. Barrie and K. Munday, J. of Membrane Sci., 1983, 13, 175.
179. J.A. Barrie and J.B. Ismail, J. of Membrane Sci., 1983, 13, 197.
180. J.A. Barrie and M.J.L. Williams, J. of Membrane Sci., 1984, 21, 185.
181. J. Barbier, Rubber Chem. Technol., 1955, 28, 814.
182. K.D. Ziegel, J. Macromol. Sci. Phys. Edn., 11, B5(1).
183. M. Kawakoni, H. Iwanaga, H. Hara, M. Iwamoto and S. Kagawa, J of Appl. Polym. Sci., 1982, 27, 2387.
184. P. Masi and D.R. Paul, J. Membrane Sci., 1982, 12, 137.
185. H.G. Spencer and J.A. Vavorsky, J. Applied Polym. Sci., 1983, 28, 2937.
186. J.S. Chiou, J.W. Barlow and D.R. Paul, J. Appl. Polym. Sci., 1985, 30, 1173.
187. J.S. Chiou and D.R. Paul, J. Appl. Polym. Sci., 1986, 32, 2897.

188. J.S. Chiou and D.R. Paul, J. Appl. Polym. Sci., 1986, 32, 4793.
189. Y. Maeda and D.R. Paul, J. Polym. Sci.: Part B: Polym. Physics, 1987, 25, 957.
190. M.J. El-Hibri and D.R. Paul, J. Appl. Polym. Sci., 1985, 30, 3649.
191. Y. Meada and D.R. Paul, J. Polym. Sci.: Part B: Polym. Physics, 1987, 25, 981.
192. J.S. Chiou and D.R. Paul, J. Appl. Polym. Sci., 1987, 33, 2935.
193. J.S. Chiou and D.R. Paul, J. Appl. Polym. Sci., 1987, 34, 1037.
194. R.L. Stallings, H.B. Hopfenberg and V. Stannett, J. Polym. Sci., Symposium, 1973, 41, 123.
195. J. Stalling, F.E. Karaz, and W.J. MacKnight, Polymer Eng. Sci., 1970, 10(3), 133.
196. R.F. Gould, Ed. Multicomponent Polymer System Amer. Chem. Soc., Washington, D.C., 1971, Chap. 3.
197. N. Muruganandam and D.R. Paul, J. Polym. Sci.: B: Polym. Physics, 1987, 25, 2315.
198. N. Muruganandam and D.R. Paul, J. Membrane Sci., 1987, 34, 185.
199. G. Morel and D.R. Paul, J. Membrane Sci., 1982, 10, 273.
200. A.H. Chan and D.R. Paul, Polym. Eng. Sci., 1980, 20, 87.
201. J.F. Taylor and J.A. Barrie, unpublished work.
202. R.N. Johnson, A.G. Farnham and R.A. Clendinning, W.F. Hale and C.N. Merriam, J. Polym. Sci., Pt. A-I, 1967, 5, 2375.

203. H.R. Kricheldorf and G. Bier, J. Polym. Sci., Polym. Chem. Edn., 1983, 21, 2283.
204. M.E.A. Cudby, R.G. Feasey, B.E. Jennings and M.E.B. Jones & Rose, Polymer, 1965, 6, 589.
205. T.E. Attwood, D.A. Barr, T. King, A.B. Newton and J.B. Rose, Polymer, 1977, 18, 359.
206. M. Morris, M.Sc. Thesis, Sheffield City Polytechnic, 1984.
207. R.G. Pearson, Chapter 7 in Speciality Polymers, Edited by R.W. Dyson, Blakie, U.S.A. : Chapman and Hall, New York.
208. E.S. Sanders J. Membrane Sci., 1988, 37, 63.
209. P. Masi, D.F. Paul, J.W. Barlow, J. Polym. Phys. Ed., 1982, 20, 15.
210. W.J. Koros, D.R. Paul, M. Fujii, H.B. Hopfenberg, V. Stannett, J. Appl. Polym. Sci., 1977, 21, 2899.
211. G.S. Hurvard, V.T. Stannett, W.J. Koros and H.B. Hopfenberg, J. Membrane Sci., 1980, 6, 185.
212. J.H. Petropoulos, J. Polym. Sci., Polym. Phys. Ed. 1976, 14, 675.
213. W.J. Koros, J. Polym. Sci. Polym. Phys. Ed., 1985, 23, 1611.
214. R.T. Chern, W.J. Koros, E.S. Sanders, A.H. Chan, H.B. Hopfenberg, ACS Symp., 1983, 47, 223.
215. M.M. Coleman and P.C. Painter, Applied Spectroscopy Review, 1984, 20(3 and 4), 255.
216. M.M. Coleman and E.J. Moskala, Polymer, 1983, 24, 251.
217. E.J. Moskala and M.M. Coleman, Polym. Commun., 1983, 24, 206.
218. S.R. Fahrenholtz and T.K. Kwei, Macromolecules, 1981, 14(4), 1076.
219. G. Kraus and K.W. Rollman, Adv. Chem. Seri, 1971, 99, 189.

220. K.D. Ziegel, J. Macromol. Sci., 1971, 13, 11.
221. J.S. McBride, T.A. Masorro, and S.L. Cooper, J. Appl. Polym. Sci., 1979, 23, 201.
222. R.M. Barrer, J.A. Barrie, M.G. Rogers, Trans. Faraday Soc., 1962, 58, 2473.
223. S.C. Sharma, L. Mandelkern and F.C. Stehling, J. Polym. Sci., Polym. Lett., 1972, 10, 345.
224. A. Muruganandam, W.J. Koros and D.R. Paul, J. of Polymer Sci. : Part B, Polymer Physics, 1987, Vol. 25, 1999-2026.
225. Y. Meada and D.R. Paul, Polymer, 1985, 26, 2055.
226. R.M. Barrer and G. Skirrow, J. Polym. Sci., 1948, 3, 549 and 564.
227. T.K. Kwei and W.M. Arnhenium, J. Polym. Sci., 1964, 2A, 957.