

Imperial College London
Department of Chemistry

Reactivity of Biomass Relevant Esters and Alcohols in Acidic Ionic Liquids

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Statement of Originality

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Abstract

Reactivity of biomass relevant alcohols and esters in hydrogen sulfate based ionic liquids were successfully studied. A series of alcohols; methanol, 1-butanol, 2-butanol, isopropanol, and phenol were reacted with 1-butyylimidazolium hydrogen sulfate [HC₄im][HSO₄] to represent cellulose hydroxyl group reactivity in the selected acidic ionic liquids. Apart from phenol, all selected alcohols were found to undergo sulfation *via* nucleophilic substitution by [HSO₄][−] anion after 24 h. Mechanistic study of the nucleophilic substitution reactions of *p*-substituted benzyl alcohols with [HC₄im][HSO₄] and [C₄C₁im][HSO₄] were done using Hammett equation. The concave upward Hammett plots suggest there is a change in mechanism, from S_N1 for electron donating substituents (OMe and Me) to S_N2 for electron withdrawing substituents (H, Cl, CF₃ and NO₂). This chapter revealed that ILs can act as a solvent as well as a nucleophile in one reaction. Most importantly, this showed that sulfation of cellulose is probable under Ionosolv pretreatment. Hydrolysis of lignin-carbohydrate linkage model compounds, BHB and THFF were carried out in [HC₄im][HSO₄] with varying acid and water content. The rates of hydrolysis were increasing with increasing of mol% acid. The mechanistic insights of the reactions were studied using Zucker-Hammett, Bunnett-Olsen and Eyring equations. All three resulted plots are in agreement with A2 mechanism. Transesterification reactions of BHB and ethyl lactate and methanol in [HC₄im][HSO₄] were found to give low yields due to the sulfation of methanol. This again showed that the [HSO₄][−] anion are reactive and nucleophilic enough to undergo nucleophilic substitution reaction with alcohol at 80 – 120 °C in aqueous or non-aqueous condition.

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Table of Content

Statement of Originality	3
Copyright Declaration	3
Abstract	4
Acknowledgement.....	5
Table of Content.....	7
List of Figures	11
List of Tables.....	17
List of Schemes	19
Abbreviations	20
1 Introduction.....	22
1.1 Energy Challenge.....	22
1.2 Biorefinery	24
1.3 Lignocellulosic Biomass	27
1.3.1 Chemical Composition of Lignocellulosic Biomass.....	29
1.3.2 Deconstruction of Lignocellulosic Biomass	34
1.4 Introduction to Ionic Liquids	43
1.4.1 Classification of ILs	43
1.5 Synthesis of ILs.....	45
1.5.1 Acid–base Reaction	46
1.5.2 Direct Alkylation	46

1.5.3	Synthesis <i>via</i> Halides Intermediates	47
1.5.4	Purification of ILs	48
1.6	Properties of ILs and Applications	48
1.7	ILs in Biomass Processing	50
1.7.1	[HSO ₄] ⁻ ILs in Biomass Transformation Process	55
2	Reactivity of Alcohols with [HSO ₄] ⁻ ILs.....	59
2.1	Background of study	59
2.1.1	Problems with the saccharification of cellulose obtained from from Ionosolv pretreatment	59
2.1.2	Reactivity of the hydroxyl groups in cellulose	64
2.1.3	ILs as nucleophiles.....	65
2.2	Aims and Objectives	67
2.3	Results and Discussion	68
2.3.1	Reactivity of alcohols in [HC ₄ im][HSO ₄].....	68
2.3.2	Nucleophilic substitution of benzyl alcohol with [HSO ₄] ⁻ ILs	72
2.3.3	Kinetic Studies	75
2.3.4	Electronic Effects and Mechanistic Insight; Hammett equation.....	82
2.4	Conclusions.....	100
3	Ester Hydrolysis in HSO ₄ IL.....	101
3.1	Background of Study	101
3.1.1	Lignin-Carbohydrate Linkage.....	101
3.1.2	Delignification of Lignocellulosic Biomass	102
3.1.3	Ester Linkages in LCC.....	104
3.1.4	Model Compounds.....	106
3.1.5	Ester Hydrolysis Mechanisms.....	109
3.2	Aims and Objectives	111
3.3	Results and Discussion	112

3.3.1	Kinetic Studies of the Hydrolysis of the Ester Model Compounds in [HC ₄ im][HSO ₄] with Varying Water and Acid Content.....	112
3.3.2	Benzyl 4-hydroxybenzoate, BHB	113
3.3.3	Tetrahydrofurfuryl Ferulate, THFF	116
3.3.4	Hammett Acidity Function	120
3.3.5	Mechanistic Insights	124
3.3.6	Activation Parameters of the Reaction using the Eyring Equation.....	139
3.4	Conclusion	144
4	Transesterification in [HC ₄ im][HSO ₄].....	146
4.1	Background of Study	146
4.1.1	Transesterification.....	146
4.1.2	ILs in Transesterification as Solvent.....	147
4.1.3	ILs in Transesterification as Catalyst.....	149
4.1.4	Model compounds.....	152
4.2	Aims and Objectives	153
4.3	Results and Discussions.....	154
4.3.1	Transesterification of BHB with Methanol and [HC ₄ im][HSO ₄] at 80 °C	154
4.3.2	Transesterification of BHB at 120 °C.....	161
4.3.3	Transesterification of Ethyl Lactate with methanol and [HC ₄ im][HSO ₄].....	166
4.4	Conclusions.....	170
5	General Conclusions	172
6	Experimental	173
6.1	ILs Syntheses	173
6.1.1	Synthesis of [HC ₄ im][HSO ₄]	173
6.1.2	Synthesis of [C ₄ C ₁ im][MeSO ₄].....	174

6.1.3	Synthesis of [C ₄ C ₁ im][HSO ₄]	175
6.2	Nucleophilic Substitution Reaction of Alcohols with [HSO ₄] ⁻ ILs	176
6.2.1	Reaction of alcohols in [HSO ₄] ⁻ ILs	176
6.2.2	Kinetic measurements of <i>para</i> -substituted benzyl alcohols reaction in [HSO ₄] ⁻ ILs	176
6.3	Ester Hydrolysis.....	177
6.3.1	Determination of H ₀ by UV-Vis Spectroscopy.....	177
6.3.2	Synthesis of THFF	177
6.3.3	First method of kinetic measurement, <i>in situ</i> ¹ H NMR	178
6.3.4	Second method of kinetic measurements.....	178
6.4	Transesterification.....	179
6.4.1	Transesterification of BHB and tetrahydrofurfuryl ferulate with methanol and [HC ₄ im][HSO ₄]	179
	Bibliography.....	180
	Appendix	191

List of Figures

Figure 1.1	Total world consumption of marketed energy from 1990 – 2040 (in quadrillion British Therma units, Btu). The projection is divided according to Organisation for Economic Cooperation and Development (OECD) and non-OECD nations. ¹	22
Figure 1.2	Total world energy consumption by energy source, 1990-2040 (in quadrillion Btu) ¹	23
Figure 1.3	U.S. energy consumption by energy source in 2016. ²	24
Figure 1.4	Biorefinery feedstocks and conversion routes to bioenergy and renewable chemicals (adapted from Pickett <i>et al.</i>) ⁴	25
Figure 1.5	Several lignocellulosic materials for ethanol biorefinery. ⁷	26
Figure 1.6	<i>Miscanthus</i> plantation at Imperial College London, Silwood Park Campus.....	29
Figure 1.7	Cellulose, hemicellulose and lignin in plant cell wall of lignocellulosic biomass. ⁵	29
Figure 1.8	Structure of cellulose with its repeating units.....	30
Figure 1.9	Conversion of cellulose into several industry related chemicals. ³⁴	31
Figure 1.10	Chemical structure of hemicellulose.....	32
Figure 1.11	Lignin chemical structure alongside with its monomers, <i>p</i> -coumaryl, coniferyl and synapyl alcohol. ⁴³	33
Figure 1.12	(Physico)chemical deconstruction of the lignocellulose structure to make the polysaccharides become accessible. ²⁹	35
Figure 1.13	Overview of different pretreatment methods. ⁴⁸	36
Figure 1.14	Structures and abbreviations of common IL cations.	44
Figure 1.15	Structures and abbreviations of common IL anions.	44
Figure 1.16	Simplified syntheses of <i>protic</i> IL <i>via</i> acid-base reaction, and <i>aprotic</i> ILs <i>via</i> alkylation and ion metathesis.....	45
Figure 1.17	SEM micrographs of initial dissolving pulp in [C ₄ C ₁ im] Cl and after regeneration into water. ⁹⁵	50
Figure 1.18	Process configuration for IL pretreatment. ¹⁰⁶	52
Figure 1.19	Schematic illustration of lignocellulose hydrolysis in ILs with acid....	53
Figure 1.20	Deconstruction of <i>Miscanthus</i> in an [HSO ₄] [−] based IL and water mixture. ¹²⁰	56
Figure 2.1	Saccharification yield (glucose %) from pulp (carbohydrate rich material) recovered from the pretreatment of <i>Miscanthus giganteus</i> with [HC ₄ im][HSO ₄] at 120 °C for 24 h with 80% IL and 20% water mixture. ¹	60
Figure 2.2	Comparison of glucose yield of enzymatic saccharification of recovered CRMs from <i>Miscanthus</i> pretreatment with [HC ₄ im][HSO ₄] washed via Buchner and Soxhlet methods. ¹²⁰	62
Figure 2.3	Negative ion MALDI spectra of (a) Untreated-MCC; (b) Treated MCC-[HC ₄ im][HSO ₄], and; (c) Treated MCC-[C ₄ C ₁ im][HSO ₄]. (■) represents anions of sulfur-containing oligosaccharides, [((C ₆ H ₁₀ O ₅) _n OSO ₃ H)-H], (x) represents anions of deprotonated dehydrated sulfur-containing oligosaccharides, [((C ₆ H ₁₀ O ₅) _n OSO ₃ H)-H]-H ₂ O (n = degree of polymerisation). ¹²⁰	63

Figure 2.4	Overview of cellulose functionalisation pathways. ²⁶	64
Figure 2.5	Expected reaction between 4-methylbenzyl alcohol and ionic liquids with respective acids. $X^- = Cl^-$, $[HSO_4]^-$, $[H_2PO_4]^-$, and $[OAc]^-$. ⁸²	65
Figure 2.6	0 (a) and 24 h (b) 1H NMR of methanol reaction with $[HC_4im][HSO_4]$ at 80 °C.	69
Figure 2.7	0 (a) and 24 h (b) 1H NMR of 1-butanol reaction with $[HC_4im][HSO_4]$ at 80 °C.	70
Figure 2.8	0 (a) and 24 h (b) 1H NMR of 2-butanol reaction with $[HC_4im][HSO_4]$ at 80 °C.	70
Figure 2.9	0 (a) and 24 h (b) 1H NMR of isopropanol reaction with $[HC_4im][HSO_4]$ at 80 °C.	71
Figure 2.10	0 (a) and 24 h (b) 1H NMR of phenol reaction with $[HC_4im][HSO_4]$ at 80 °C.	71
Figure 2.11	1H NMR spectra of the reaction of <i>p</i> -methylbenzyl alcohol with $[HC_4im][HSO_4]$ at (a) 0 and (b) 24 h at 120 °C.	73
Figure 2.12	Plot of $\ln([A]/[A_0])$ against time of benzyl alcohol in neat $[HC_4im][HSO_4]$ at 80 °C.	79
Figure 2.13	Plot of $\ln([A]/[A_0])$ against time plots of <i>p</i> -trifluoromethylbenzyl alcohol in $[HC_4im][HSO_4]$ + 6 mol% H_2SO_4 at 80 °C.	80
Figure 2.14	Hammett plots for nucleophilic substitution reaction of <i>p</i> -X-benzylalcohol with $[HC_4im][HSO_4]$ obtained from S_N1 mechanism.	88
Figure 2.15	Hammett plots for nucleophilic substitution reaction of <i>p</i> -X-benzyl alcohol with $[HC_4im][HSO_4]$ with 1 mol% H_2SO_4 obtained from S_N1 mechanism.	88
Figure 2.16	Hammett plots for nucleophilic substitution reaction of <i>p</i> -X-benzyl alcohol with $[HC_4im][HSO_4]$ obtained from S_N2 mechanism.	90
Figure 2.17	Hammett plots for nucleophilic substitution reaction of <i>p</i> -X-benzyl alcohol with $[HC_4im][HSO_4]$ with 1 mol% H_2SO_4 obtained from S_N2 mechanism.	90
Figure 2.18	Hammett plots for nucleophilic substitution reaction of <i>p</i> -X-benzyl alcohol with $[HC_4im][HSO_4]$ assuming that the reaction with EDG (OMe and Me) of substituent proceed via S_N1 , and EWG (H, Cl, CF_3 and NO_2) of substituent proceed via S_N2 mechanism.	92
Figure 2.19	Hammett plots for nucleophilic substitution reaction of <i>p</i> -X-benzyl alcohol with $[HC_4im][HSO_4]$ and 1 mol% H_2SO_4 assuming that the reaction with EDG (OMe and Me) of substituent proceed via S_N1 , and EWG (H, Cl, CF_3 and NO_2) of substituent proceed via S_N2 mechanism.	92
Figure 2.20	Hammett plots for nucleophilic substitution reaction of <i>p</i> -X-benzyl alcohol reactions with $[C_4C_1im][HSO_4]$ obtained from the S_N1 mechanism equation.	94
Figure 2.21	Hammett plots for nucleophilic substitution reaction of <i>p</i> -X-benzyl alcohol reactions with $[C_4C_1im][HSO_4]$ with 1 mol% H_2SO_4 obtained from the S_N1 mechanism equation.	94
Figure 2.22	Hammett plots for nucleophilic substitution reaction of <i>p</i> -X-benzyl alcohol reactions with $[C_4C_1im][HSO_4]$ obtained from the S_N2 mechanism equation.	96
Figure 2.23	Hammett plots for nucleophilic substitution reaction of <i>p</i> -X-benzyl alcohol reactions with $[C_4C_1im][HSO_4]$ with 1 mol% H_2SO_4 obtained from the S_N2 mechanism equation.	96

Figure 2.24	Hammett plots for nucleophilic substitution reaction of <i>p</i> -X-benzyl alcohol with [C ₄ C ₁ im][HSO ₄] assuming that the reaction with EDG (OMe and Me) of substituent proceed via S _N 1, and EWG (H, Cl, CF ₃ and NO ₂) of substituent proceed via S _N 2 mechanism.....	98
Figure 2.25	Hammett plots for nucleophilic substitution reaction of <i>p</i> -X-benzyl alcohol with [C ₄ C ₁ im][HSO ₄] with 1 mol% H ₂ SO ₄ assuming that the reaction with EDG (OMe and Me) of substituent proceed via S _N 1, and EWG (H, Cl, CF ₃ and NO ₂) of substituent proceed via S _N 2 mechanism.	98
Figure 3.1	Lignin–carbohydrate and lignin structures: (A) phenyl glycoside, (B) γ-ester, and (C) benzyl ether LCC linkages. ¹⁷¹	102
Figure 3.2	Delignification and the lignin yield of <i>Miscanthus</i> pretreated in different 1,3-dialkylimidazolium ILs (80 wt%) water (20 wt%) mixtures at 120 °C for 22 h. The ionic liquid cation was [C ₄ C ₁ im] ⁺ , except in [C ₂ C ₁ im][MeCO ₂]. ⁸	103
Figure 3.3	Delignification and lignin recovery of <i>Miscanthus</i> , Willow and Pine with [C ₄ C ₁ im][HSO ₄] and [C ₂ C ₁ im][MeCO ₂] IL (80/20% IL/water) mixtures at 120 °C for 22 h. ⁸	104
Figure 3.4	Proposed structure for the lignin- <i>p</i> -hydroxybenzoic acid ester linkage in aspens. ¹⁷⁵	104
Figure 3.5	Proposed ferulic and <i>p</i> -coumaric acid links between lignin and hemicellulose in the grass cell wall. (a) α-Ether linkages and (b) β- ether linkages. ¹⁶⁸	105
Figure 3.6	Three types of ester bond identified in wheat straw lignin. ¹⁷⁷	106
Figure 3.7	Benzyl 4-hydroxybenzoate, BHB	107
Figure 3.8	Tetrahydrofurfuryl ferulate (tetrahydro-2-furanylmethyl 4-hydroxy-3-methoxy cinnamate).....	107
Figure 3.9	¹ H NMR of the hydrolysis of BHB in aqueous [HC ₄ im][HSO ₄] at 80 °C after 2 hr.....	108
Figure 3.10	¹ H NMR of the hydrolysis of THFF in aqueous [HC ₄ im][HSO ₄] at 80 °C after 2 hr.....	108
Figure 3.11	Plot of ln [A]/[A ₀] vs time for the hydrolysis of BHB with [HC ₄ im][HSO ₄] in 10 wt% water and 30 mol% sulfuric acid at 80 °C.	114
Figure 3.12	Relationship between the reaction rates of the hydrolysis of BHB in [HC ₄ im][HSO ₄] and the acid and water content. <i>*note: mol% acid represents mol fraction of sulfuric acid and IL and % water represents v/v of water in water and IL solution.</i>	115
Figure 3.13	Relationship between the reaction rates of the hydrolysis of BHB in [HC ₄ im][HSO ₄] and the acid and water content. <i>*note: mol% acid represents mol fraction of sulfuric acid in total solution of IL, water and sulfuric acid; % water represents v/v of water in water and IL solution.</i>	116
Figure 3.14	Plot of ln [A]/[A ₀] vs time of the hydrolysis of THFF with [HC ₄ im][HSO ₄] in 20% water and 20 mol% sulfuric acid at 80 °C.	117
Figure 3.15	Relationship between the reaction rates of the hydrolysis of THFF in [HC ₄ im][HSO ₄] with acid and water content. <i>*note: mol% acid represents mol fraction of sulfuric acid and IL and % water represents v/v of water in water and IL solution.</i>	118

Figure 3.16	Relationship between the reaction rates of the hydrolysis of THFF in [HC ₄ im][HSO ₄] with acid and water content. <i>*note: mol% acid represents mol fraction of sulfuric acid in total solution of IL, water and sulfuric acid; % water represents v/v of water in water and IL solution.</i>	119
Figure 3.17	Correlation between H ₀ and mol% sulfuric acid in 10, 20 and 30 wt% water mixture of [HC ₄ im][HSO ₄]. <i>*note: mol% acid represents mol fraction of sulfuric acid and IL and % water represents v/v of water in water and IL solution.</i>	122
Figure 3.18	H ₀ values of [C ₄ C ₁ im][HSO ₄] water and sulfuric acid mixture. ⁴⁰	123
Figure 3.19	Plot log <i>k_{obs}</i> against -H ₀ for the hydrolysis of BHB within [HC ₄ im][HSO ₄] at 80 °C.	126
Figure 3.20	Plot log <i>k_{obs}</i> against -H ₀ for the hydrolysis of THFF within [HC ₄ im][HSO ₄] at 80 °C.	128
Figure 3.21	Plot of log <i>k_{obs}</i> vs log [H ⁺] for the hydrolysis of BHB within [HC ₄ im][HSO ₄] without added sulfuric acid at 80 °C.	130
Figure 3.22	Plot of log <i>k_{obs}</i> vs log [H ⁺] for the hydrolysis of BHB within [HC ₄ im][HSO ₄] with added sulfuric acid at 80 °C.	131
Figure 3.23	Plot of log <i>k_{obs}</i> vs log [H ⁺] for the hydrolysis of THFF within [HC ₄ im][HSO ₄] without added sulfuric acid at 80 °C.	132
Figure 3.24	Plot of log <i>k_{obs}</i> vs log [H ⁺] for the hydrolysis of THFF within [HC ₄ im][HSO ₄] with added sulfuric acid at 80 °C.	132
Figure 3.25	Bunnett-Olsen plot for the hydrolysis of BHB in aqueous [HC ₄ im][HSO ₄] without added sulfuric acid at 80 °C.	136
Figure 3.26	Bunnett-Olsen plot for the hydrolysis of BHB in aqueous [HC ₄ im][HSO ₄] with added sulfuric acid at 80 °C.	136
Figure 3.27	Bunnett-Olsen plot for the hydrolysis of THFF in aqueous [HC ₄ im][HSO ₄] without added sulfuric acid at 80 °C.	137
Figure 3.28	Bunnett-Olsen plot for the hydrolysis of THFF in aqueous [HC ₄ im][HSO ₄] with added sulfuric acid at 80 °C.	138
Figure 3.29	Eyring plot for the hydrolysis of BHB in aqueous [HC ₄ im][HSO ₄].	142
Figure 3.30	Eyring plot for the hydrolysis of THFF in aqueous [HC ₄ im][HSO ₄].	143
Figure 4.1	Transesterification process to produce glycerol. ²⁰⁶	147
Figure 4.2	Lipase-catalysed methanolysis of soya bean oil with several additives. ²¹⁵	148
Figure 4.3	Benzyl 4-hydroxybenzoate, BHB	153
Figure 4.4	Ethyl lactate	153
Figure 4.5	¹ H NMR of transesterification of BHB in [HC ₄ im][HSO ₄] with methanol at 80 °C after 2 and 24 h.	155
Figure 4.6	¹ H NMR of transesterification of BHB in [HC ₄ im][HSO ₄] with methanol at 80 °C after 24 h.	156
Figure 4.7	Influence of [HC ₄ im][HSO ₄] concentration on transesterification of BHB with methanol at 80 °C.	161
Figure 4.8	Influence of reagents molar ratio and temperature on transesterification of BHB with methanol and [HC ₄ im][HSO ₄].	162
Figure 4.9	¹ H NMR of transesterification of BHB with methanol and [HC ₄ im][HSO ₄] at 120 °C.	163
Figure 4.10	Influence of reagents molar ratio and water on transesterification of BHB with methanol and [HC ₄ im][HSO ₄] at 120 °C.	165

Figure 4.11	^1H NMR of transesterification of ethyl lactate with methanol and $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 120 °C.....	168
Figure 4.12	ILs concentration effects on methanolysis of ethyl lactate at 110 °C.....	169
Figure A.2.2	Plot of $\ln (A/A_0)$ against time of <i>p</i> -methylbenzyl alcohol in neat $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80 °C.	192
Figure A.2.3	Plot of $\ln (A/A_0)$ against time of <i>p</i> -methoxybenzyl alcohol in neat $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80 °C.	193
Figure A.2.4	Plot of $\ln (A/A_0)$ against time of <i>p</i> -trifluoromethylbenzyl alcohol in neat $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80 °C.....	193
Figure A.2.5	Plot of $\ln (A/A_0)$ against time of <i>p</i> -chlorobenzyl alcohol in neat $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80 °C.	194
Figure A.2.6	Plot of $\ln (A/A_0)$ against time of <i>p</i> -nitrobenzyl alcohol in neat $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80 °C.	194
Figure A.2.7	Plot of $\ln (A/A_0)$ against time of benzyl alcohol in $[\text{HC}_4\text{im}][\text{HSO}_4]$ + 1 mol% H_2SO_4 at 80 °C.....	195
Figure A.2.8	Plot of $\ln (A/A_0)$ against time of <i>p</i> -methylbenzyl alcohol in $[\text{HC}_4\text{im}][\text{HSO}_4]$ + 1 mol% H_2SO_4 at 80 °C.....	195
Figure A.2.9	Plot of $\ln (A/A_0)$ against time of <i>p</i> -methoxybenzyl alcohol in $[\text{HC}_4\text{im}][\text{HSO}_4]$ + 1 mol% H_2SO_4 at 80 °C.....	196
Figure A.2.10	Plot of $\ln (A/A_0)$ against time of <i>p</i> -trifluoromethylbenzyl alcohol in $[\text{HC}_4\text{im}][\text{HSO}_4]$ + 1 mol% H_2SO_4 at 80 °C.....	196
Figure A.2.11	Plot of $\ln (A/A_0)$ against time of <i>p</i> -chlorobenzyl alcohol in $[\text{HC}_4\text{im}][\text{HSO}_4]$ + 1 mol% H_2SO_4 at 80 °C.....	197
Figure A.2.12	Plot of $\ln (A/A_0)$ against time of <i>p</i> -nitrobenzyl alcohol in $[\text{HC}_4\text{im}][\text{HSO}_4]$ + 1 mol% H_2SO_4 at 80 °C.....	197
Figure A.2.13	Plot of $\ln ([A]/[A_0])$ against time of benzyl alcohol in neat $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ at 80 °C.....	198
Figure A.2.14	Plot of $\ln ([A]/[A_0])$ against time of <i>p</i> -methylbenzyl alcohol in neat $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ at 80 °C.....	198
Figure A.2.15	Plot of $\ln ([A]/[A_0])$ against time of <i>p</i> -methoxybenzyl alcohol in neat $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ at 80 °C.....	198
Figure A.2.16	Plot of $\ln ([A]/[A_0])$ against time of <i>p</i> -trifluoromethylbenzyl alcohol in neat $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ at 80 °C.....	200
Figure A.2.17	Plot of $\ln ([A]/[A_0])$ against time of <i>p</i> -chlorobenzyl alcohol in neat $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ at 80 °C.....	200
Figure A.2.18	Plot of $\ln ([A]/[A_0])$ against time of <i>p</i> -nitrobenzyl alcohol in neat $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ at 80 °C.....	201
Figure A.2.19	Plot of $\ln ([A]/[A_0])$ against time of benzyl alcohol in $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ + 1 mol% H_2SO_4 at 80 °C.....	201
Figure A.2.20	Plot of $\ln ([A]/[A_0])$ against time of <i>p</i> -methylbenzyl alcohol in $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ + 1 mol% H_2SO_4 at 80 °C.....	202
Figure A.2.21	Plot of $\ln ([A]/[A_0])$ against time of <i>p</i> -methoxybenzyl alcohol in $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ + 1 mol% H_2SO_4 at 80 °C.....	202
Figure A.2.22	Plot of $\ln ([A]/[A_0])$ against time of <i>p</i> -trifluoromethylbenzyl alcohol in $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ + 1 mol% H_2SO_4 at 80 °C.....	203
Figure A.2.23	Plot of $\ln ([A]/[A_0])$ against time of <i>p</i> -chlorobenzyl alcohol in $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ + 1 mol% H_2SO_4 at 80 °C.....	203

Figure A.2.24	Plot of $\ln ([A]/[A_0])$ against time of <i>p</i> -nitrobenzyl alcohol in $[C_4C_{1im}][HSO_4] + 1 \text{ mol\% } H_2SO_4$ at 80 °C.....	204
Figure A.2.25	Nucleophilic substitution reaction of <i>p</i> -X- benzyl alcohol in $[HC_{4im}][HSO_4] + 6 \text{ mol\% } H_2SO_4$ at 80 °C.....	204
Figure A.2.26	Hydrolysis of BHB in $[HC_{4im}][HSO_4]$ with 10% water and varying acid content at 80 °C.....	205
Figure A.2.27	Hydrolysis of BHB in $[HC_{4im}][HSO_4]$ with 20% water and varying acid content at 80 °C.....	206
Figure A.2.28	Hydrolysis of BHB in $[HC_{4im}][HSO_4]$ with 30% water and varying acid content at 80 °C.....	207
Figure A.2.29	Hydrolysis of THFF in $[HC_{4im}][HSO_4]$ with 10% water and varying acid content at 80 °C.....	208
Figure A.2.30	Hydrolysis of THFF in $[HC_{4im}][HSO_4]$ with 20% water and varying acid content at 80 °C.....	209
Figure A.2.31	Hydrolysis of THFF in $[HC_{4im}][HSO_4]$ with 30% water and varying acid content at 80 °C.....	210

List of Tables

Table 1.1	Composition of cellulose, hemicellulose and lignin in several ligno-cellulosic biomass feedstock. ⁶	28
Table 1.2	Advantages and disadvantages of different pretreatment methods of lignocellulosic biomass. ^{49,61,66-68}	40
Table 2.1	Average glucose yield and pH of the media with different concentration of [HC ₄ im][HSO ₄]. ¹⁴⁸	61
Table 2.2	CHNS elemental analysis results of the Untreated-MCC and the Treated MCC-[HC ₄ im][HSO ₄].	63
Table 2.3	Nucleophilic substitution reaction of <i>p</i> -methylbenzyl alcohol with [HC ₄ im] Cl, [HC ₄ im][H ₂ PO ₄] and [C ₂ C ₁ im][OAc]. ⁸⁴	66
Table 2.4	Yields of substitution products arising from the nucleophilic substitution reaction of alcohols and [HC ₄ im][HSO ₄].	72
Table 2.5	The percentage conversion of the nucleophilic substitution reactions of <i>p</i> -methylbenzyl alcohol with [HC ₄ im][HSO ₄] and [C ₄ C ₁ im][HSO ₄].	75
Table 2.6	σ_p values of selected substituents	77
Table 2.7	k_{obs} and conversion values of the reactions of <i>p</i> -X-benzyl alcohol with [HC ₄ im][HSO ₄] and [HC ₄ im][HSO ₄] + 1 mol% H ₂ SO ₄	79
Table 2.8	k_{obs} and conversion values of the reactions of <i>p</i> -X-benzyl alcohol with [C ₄ C ₁ im][HSO ₄] and [C ₄ C ₁ im][HSO ₄] + 1 mol% H ₂ SO ₄	81
Table 2.9	Log (k_X/k_H) values for the nucleophilic substitution reaction of <i>p</i> -X-benzyl alcohol with [HC ₄ im][HSO ₄] and [HC ₄ im][HSO ₄] with 1 mol% H ₂ SO ₄ obtained from S _N 1 mechanism equation with σ	87
Table 2.10	Log (k_X/k_H) values for the nucleophilic substitution reaction of <i>p</i> -X-benzyl alcohol with [HC ₄ im][HSO ₄] and [HC ₄ im][HSO ₄] with 1 mol% H ₂ SO ₄ obtained from S _N 2 mechanism equation with σ	89
Table 2.11	Log (k_X/k_H) values for the nucleophilic substitution reaction of <i>p</i> -X-benzyl alcohol with [HC ₄ im][HSO ₄] and [HC ₄ im][HSO ₄] with 1 mol% H ₂ SO ₄ obtained from S _N 1 and S _N 2 mechanism equation with σ	91
Table 2.12	Log (k_X/k_H) values of <i>p</i> -X-benzyl alcohol reactions with [C ₄ C ₁ im][HSO ₄] and [C ₄ C ₁ im][HSO ₄] with 1 mol% H ₂ SO ₄ obtained from the S _N 1 mechanism equation with σ	93
Table 2.13	Log(k_X/k_H) values of <i>p</i> -X-benzyl alcohol reactions with [C ₄ C ₁ im][HSO ₄] and [C ₄ C ₁ im][HSO ₄] with 1 mol% H ₂ SO ₄ obtained from the S _N 2 mechanism equation with σ	95
Table 2.14	Log(k_X/k_H) values of <i>p</i> -X-benzyl alcohol reactions with [C ₄ C ₁ im][HSO ₄] and [C ₄ C ₁ im][HSO ₄] with 1 mol% H ₂ SO ₄ obtained from the S _N 1 and S _N 2 mechanism equation with σ	97
Table 3.1	k_{obs} values for the hydrolysis of BHB with [HC ₄ im][HSO ₄] at 80 °C. ..	114
Table 3.2	k_{obs} values of the hydrolysis of THFF in [HC ₄ im][HSO ₄] with varying acid and water content at 80 °C.	117
Table 3.3	H ₀ values of [HC ₄ im][HSO ₄] mixture with water and sulfuric acid.....	122
Table 3.4	Log k_{obs} and -H ₀ values for the hydrolysis of BHB with [HC ₄ im][HSO ₄] at 80 °C.	126

Table 3.5	Log k_{obs} and $-H_0$ values for hydrolysis of THFF with [HC ₄ im][HSO ₄] at 80 °C.	127
Table 3.6	Log k_{obs} and log [H ⁺] values for hydrolysis of BHB with [HC ₄ im][HSO ₄] at 80 °C.	129
Table 3.7	Log k_{obs} and log [H ⁺] values for the hydrolysis of THFF with [HC ₄ im][HSO ₄] at 80 °C.	131
Table 3.8	Bunnett-Olsen ϕ values and their related mechanism	135
Table 3.9	ϕ values and mechanism of present work and selected ester hydrolysis from literature.	138
Table 3.10	Eyring plot data for the hydrolysis of BHB in aqueous [HC ₄ im][HSO ₄].	142
Table 3.11	Eyring plot data for the hydrolysis of THFF in aqueous [HC ₄ im][HSO ₄].	142
Table 3.12	Entropy change of activation and mechanism of selected hydrolysis reactions from literatures and this study. ^{205,207,208}	144
Table 4.1	Methanolysis of PC and PLA in several ILs.	151
Table 4.2	Transesterification of β -ketoester with 1-butanol (1.5 equivalent to ester) at 80 °C after 3 h. ²³²	151
Table 4.3	Reaction of BHB with methanol in [HC ₄ im][HSO ₄] with 20 wt% water at	155
Table 4.4	Transesterification of BHB with methanol in non aqueous [HC ₄ im][HSO ₄] at 80 °C.	157
Table 4.5	Transesterification of BHB with methanol and [HC ₄ im][HSO ₄] at 120 °C	162
Table 4.6	Transesterification of ethyl lactate with methanol and [HC ₄ im][HSO ₄] at 120 °C.	167
Table A.3.1	Hammett Dyes and pKa used in this study	211
Table A.3.2	Calculation of H_0 of [HC ₄ im][HSO ₄] with 10% water and varying acid content.....	211
Table A.3.3	Calculation of H_0 of [HC ₄ im][HSO ₄] with 20% water and varying acid content.....	212
Table A.3.4	Calculation of H_0 of [HC ₄ im][HSO ₄] with 30% water and varying acid content.....	212

List of Schemes

Scheme 1.1	Conversion route of cellulose to produce ethanol.....	31
Scheme 1.2	Synthesis of [HC ₄ im][HSO ₄]	46
Scheme 1.3	Synthesis of [C ₄ C ₁ im][MeSO ₄] (i) and [C ₄ C ₁ im][HSO ₄] (ii)	47
Scheme 1.4	Conversion route of cellulose to LA	55
Scheme 2.1	Nucleophilic substitution reaction of 1,6-hexanediol with [HC ₁ im]Cl..	65
Scheme 2.2	Expected reaction of 4-methylbenzyl alcohol with [HSO ₄] ⁻ ILs.....	73
Scheme 2.3	Ionisation of benzoic acid	76
Scheme 2.4	Possible mechanism for <i>p</i> -X-benzyl alcohol nucleophilic substitution reaction with [HC ₄ im][HSO ₄] and [C ₄ C ₁ im][HSO ₄].....	83
Scheme 3.1	The acid-catalyzed carboxylic acid esterification and ester hydrolysis mechanism proposed by Watson in 1935.....	110
Scheme 3.2	A _{AC} 1 mechanism of acid catalysed ester hydrolysis.....	110
Scheme 3.3	A _{AC} 2 mechanism of acid catalysed ester hydrolysis.....	110
Scheme 3.4	Hydrolysis of BHB in [HC ₄ im][HSO ₄] with varying acid and water content at 80 °C.	113
Scheme 3.5	Hydrolysis of THFF in [HC ₄ im][HSO ₄] with varying acid and water content at 80 °C.....	117
Scheme 4.1	Methanolysis of polylactic acid in ILs	150
Scheme 4.2	Methanolysis of polycarbonate in ILs	150
Scheme 4.3	Transesterification of BHB with methanol in [HC ₄ im][HSO ₄]	154
Scheme 4.4	Mechanism of transesterification of BHB in aqueous [HC ₄ im] [HSO ₄] with methanol.....	158
Scheme 4.5	Mechanism of transesterification of BHB in nonaqueous [HC ₄ im][HSO ₄] with methanol.....	159
Scheme 4.6	Sulfation of methanol by [HSO ₄] ⁻ IL.	159
Scheme 4.7	Nucleophilic substitution reaction of [HSO ₄] ⁻ anion with BHB.....	164
Scheme 4.8	Formation of dimethyl sulfate from reaction of [HSO ₄] ⁻ anion with methanol.....	164
Scheme 4.9	Methanolysis and hydrolysis of dimethyl sulfate in methanol.....	164
Scheme 4.10	Transesterification of ethyl lactate with methanol and [HC ₄ im][HSO ₄]... ..	167

Abbreviations

[C ₂ C ₁ im]	1-Ethyl-3-methylimidazolium
[C ₄ C ₁ im]	1-Butyl-3-methylimidazolium
[C ₄ C ₁ pyrr]	1-Butyl-3-methylpyrrolidinium
[C ₄ (SO ₃ H)C ₁ im]	1-(4-Sulfobutyl)-3-methylimidazolium
[C ₄ (SO ₃ H)Pyr]	1-4-Sulfobutylpyridinium
[HC ₂ C ₂ C ₂ N]	Triethylammonium
[C ₂ C ₂ C ₂ C ₂ N]	Tetraethylammonium
[H ₂ PO ₄]	Hydrogenphosphate
[HC ₁ im]	1-Methylimidazolium
[HC ₄ im]	1-Butylimidazolium
[HC ₄ pyr]	N-butylpyrrolidinium
[HSO ₄]	Hydrogen sulfate
[NO ₃]	Nitrate
[NTf ₂]	Bis(trifluoromethanesulfonyl)imide
[OAc]	Acetate
[OTf]	Trifluoromethylsulfonate
AFEX	Ammonia fibre expansion
BHB	Benzyl 4-hydroxybenzoate
CRM	Carbohydrate-rich material
DP	Degree of polymerisation
EDG	Electron donating group

EWG	Electron withdrawing group
FAME	Fatty acid methyl esters
FFA	Free fatty acid
ILs	Ionic liquids
LCC	Lignin-carbohydrate linkage
MCC	Microcrystalline cellulose
MWL	Milled wood lignin
n.d	Non detected
NMR	Nuclear Magnetic Resonance
PLA	Polylactic acid
PC	Polycarbonate
ppm	part per million
RDS	Rate determining step
SEM	Scanning Electron Microscope
THFF	Tetrahydrofurfuryl ferulate
ToF	Time of flight

Chapter 1

1 Introduction

1.1 Energy Challenge

The modern world's intensive use, and dependence on petroleum-based products, is nearly reaching a crisis point. This is due to escalating demands and cost of fossil fuels, alarming greenhouse gas emissions, and on-going depletion of fossil reserves. According to the International Energy Outlook 2017 (IEO2017), published by U.S. Energy Information Administration (EIA), world energy consumption is projected to increase by 28% from 2015 to 2040 (Figure 1.1).²

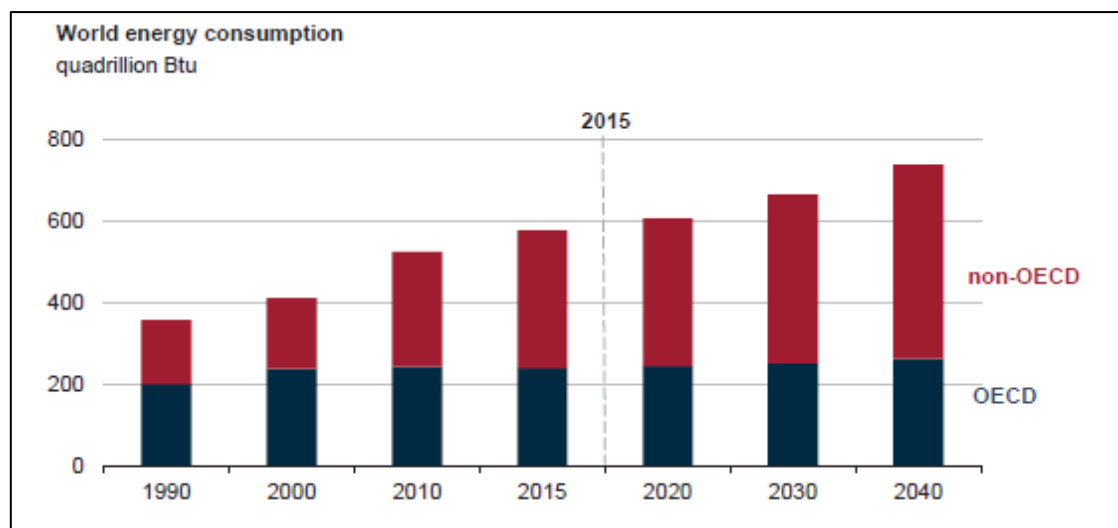


Figure 1.1 Total world consumption of marketed energy from 1990 – 2040 (in quadrillion British Thermal units, Btu). The projection is divided according to Organisation for Economic Cooperation and Development (OECD) and non-OECD nations.²

IEO2017 also projected that renewables are the world's fastest-growing energy source over the period of 2015-2040 with an associated increasing consumption of 2.8% per year (Figure 1.2). Even though liquid fuels are predicted to remain the largest source of energy consumption until 2040, the EIA predicts that the liquid fuel share of world marketed energy consumption will decline from 33% in 2015 to 30% in 2040 due to rising oil prices in the long term.²

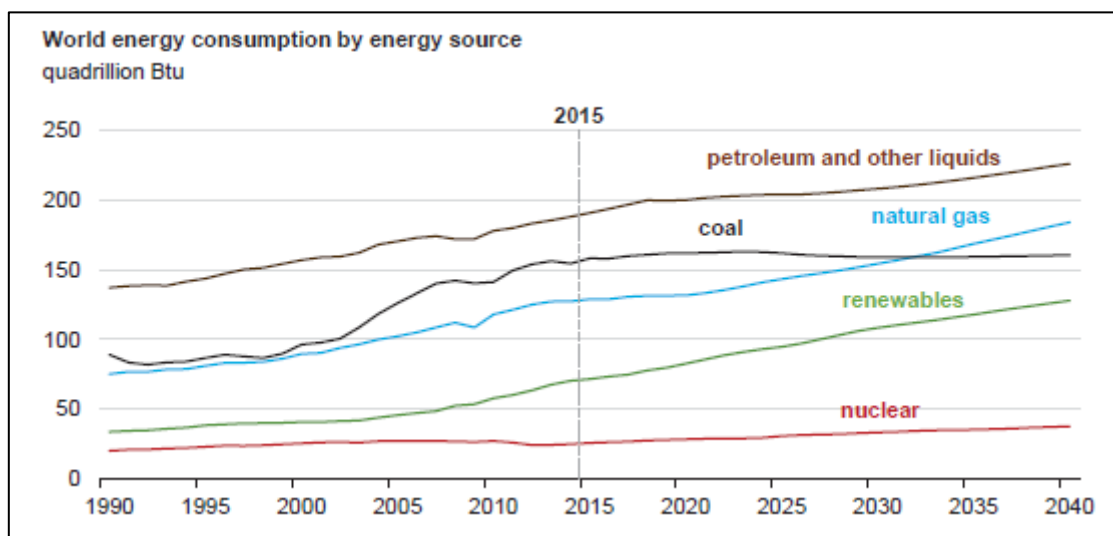


Figure 1.2 Total world energy consumption by energy source, 1990-2040 (in quadrillion Btu)²

Renewable energy sources are natural sources which naturally replenished, derived directly or indirectly from the sun, or from other natural movement and mechanism of the environment. These natural energy sources such as wind, marine, solar, hydrothermal, geothermal, and bioenergy are converted into usable forms of electricity, heat, and fuels. In 2016, 10% of total U.S. energy consumption was from renewable energy sources and the consumption of biomass was the highest, 46% among the other renewable sources, followed by hydroelectric 24%, wind 21%, solar 6%, and geothermal 2% (Figure 1.3).³

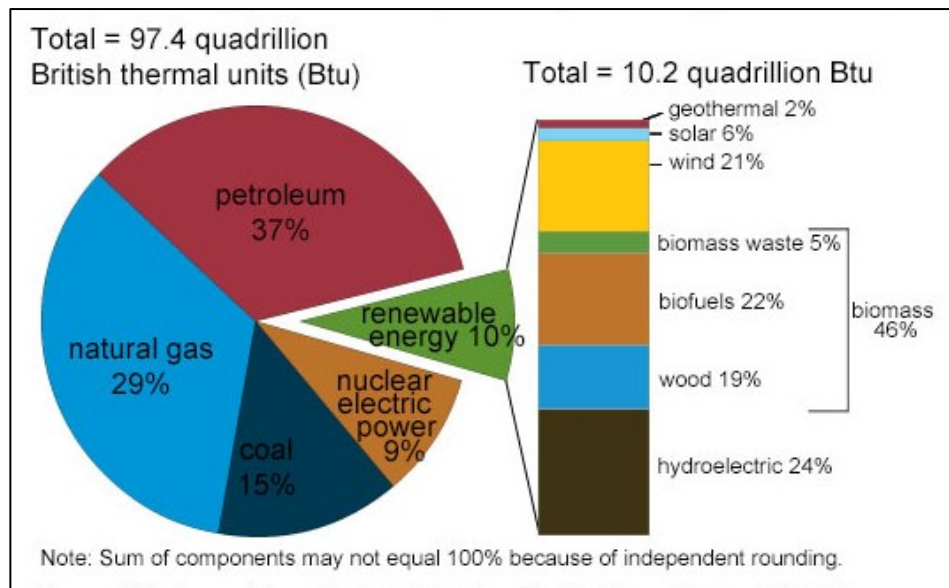


Figure 1.3 U.S. energy consumption by energy source in 2016.³

It is understood that capitalising on renewable energy can lead to massive advantages for our energy security in the future. Moreover, the utilisation of renewable energy as an alternative to petroleum based energy has the advantage of reducing greenhouse gas emissions, thus mitigating climate change.⁴

1.2 Biorefinery

In order to reduce the dependency on petroleum based energy, and mitigate climate change, scientific and political interest in the development of the bioenergy technologies is growing. One such renewable energy source is that derived from a biorefinery. A biorefinery is a facility where renewable feedstocks, such as biomass, food crops or wastes, are transformed into many value-added bio-based products such as biofuels, chemicals, biogas, etc (Figure 1.4).⁵

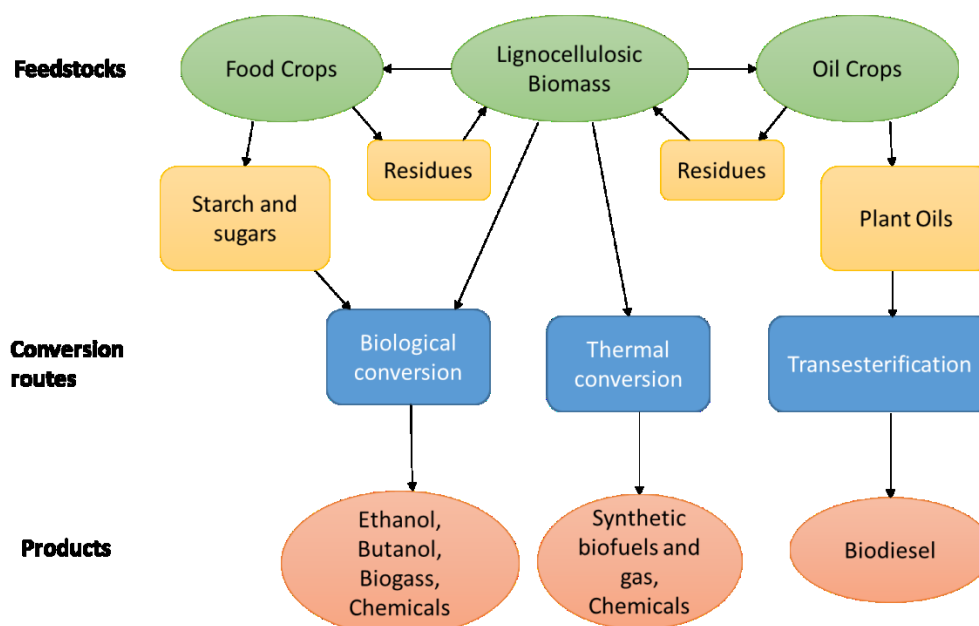


Figure 1.4 Biorefinery feedstocks and conversion routes to bioenergy and renewable chemicals (adapted from Pickett *et al.*)⁵

Biomass, which is the only carbon rich material source on the planet other than fossils fuels, is possibly the only alternative to petroleum based fuels and chemicals. Biofuels, derived from biomass are already available in the market and are identified as 1st, 2nd, 3rd and 4th generation biofuels.^{6,7} First generation biofuels are produced from food crops. Sugar and starch, isolated from food crops such as corn, sugar cane, wheat, and maize, are converted into bioethanol to replace petrol; while palm and vegetable oils are converted into biodiesel. However, these 1st generation biofuels are controversial as many critics are worried that the production of this renewable energy will be in competition with food and feed industries.⁶ Thus, 2nd generation biofuels have gained an increased global interest as its raw materials are from non-food crops biomass. For example, grasses and trees from plantations, as well as agricultural and oil crop waste products such as husks, straws, chips, and barks are categorised as lignocellulosic

biomass which can be converted into bioethanol through a series of conversion methods (Figure 1.5).⁸

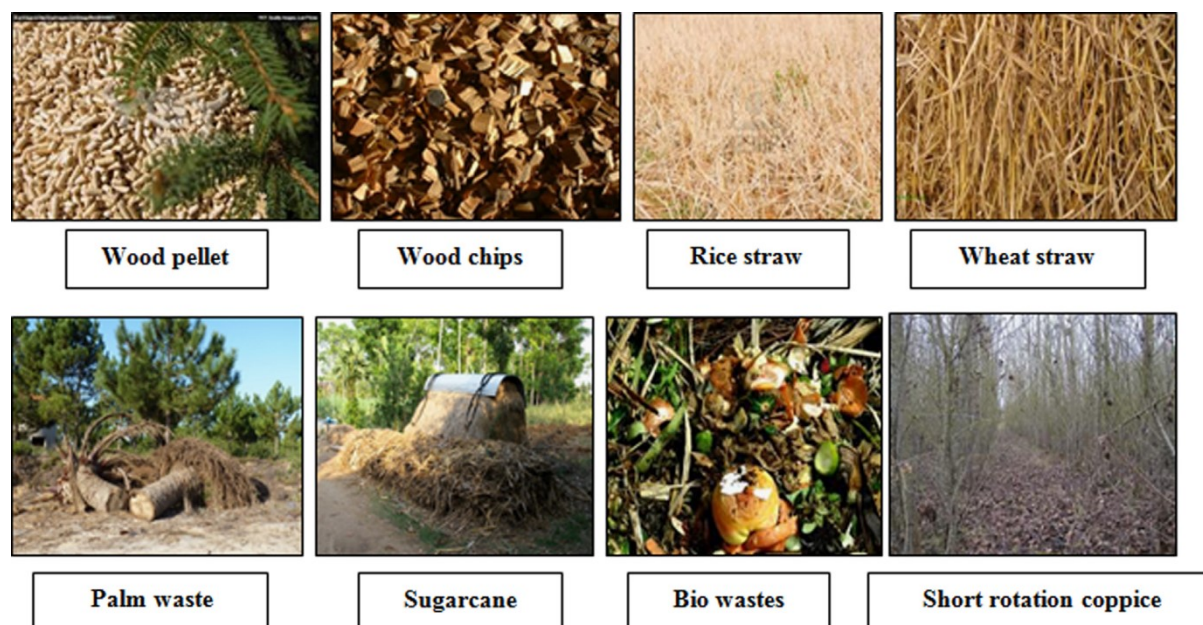


Figure 1.5 Several lignocellulosic materials for ethanol biorefinery.⁸

Technologies and production routes for this 2nd generation of biofuels and chemicals are still in the early stage but extensive scientific research and development are in progress to explore the opportunities and pathways which will allow for more effective and environmentally beneficial exploitation of plant materials for biofuels and chemicals. However, a few biorefinery plants are in operation to produce bioethanol from lignocellulosic biomass such as GranBio in Brazil, Abengoa's in the USA, Beta Renewables in Italy, and recently Finnish energy company, St1 has started planning a start-up for bioethanol plant in Kajaani, Finland.^{6,9}

The 3rd and 4th generation biofuels are from algae as the energy source.⁷ The difference between the 3rd and 4th generation are for later, specially engineered high lipid algae are being used which produces high yield, high production rate and more CO₂ capture

ability compared to the 3rd generation which are low lipid containing algae.⁷ This algae biodiesel is still at primary research stage and only few companies are currently doing target large-scale production of algae for biofuels which makes it limited for university or research institute to get access to the algae samples.¹⁰

1.3 Lignocellulosic Biomass

Lignocellulosic biomass is the most abundant renewable biomass feedstock with a worldwide production of 17-20 billion tonnes per year.¹¹ Lignocellulosic biomass is a potential feedstock candidate for ethanol production because of its high availability/supply from different low-cost raw materials. In addition, lignocellulose also has potential for high CO₂ emission saving.¹² From studies, cellulosic ethanol shows greater CO₂ saving (75 to 150 gCO₂e.km⁻¹) than wheat (15 to 110 gCO₂e.km⁻¹) or maize (40 to 60 gCO₂e.km⁻¹).¹³

The main components of lignocellulosic biomass are cellulose, hemicellulose, and lignin. Both the cellulose and hemicellulose fractions are polymers of sugars, which can be fermented and converted into ethanol and other products.^{14,15} Hemicellulose can be readily hydrolysed under mild acid or alkaline conditions, whereas cellulose is more resilient and therefore entails more rigorous treatments (high temperature and high acid concentrations). The composition of lignocellulosic biomass depends on its source. The percentages of cellulose, hemicellulose, and lignin vary significantly depending on the type of the plant; softwood, hardwood or grasses.^{6,9} Table 1.1 lists the composition of lignocellulosic biomass of several sources based on a dry weight basis.

Table 1.1 Composition of cellulose, hemicellulose and lignin in several lignocellulosic biomass feedstock.⁶

Material	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Grasses	25-40	35-50	10-30
Softwood	45-50	25-35	25-35
Hardwood	40-55	24-40	18-25
Nut shells	25-30	25-30	30-40
Newspaper	40-55	24-40	18-30

Softwoods are the main lignocellulosic feedstock in the Northern Hemisphere. Unused materials and waste products from timber and wood-pulp industries for softwood resources such as fir, pine and spruce have been used for biorefineries.¹⁷ Due to the higher lignin content compared to hardwoods and grasses, softwoods are more resistance to the delignification process and thus always requires harsher condition during the pretreatment process.¹⁸ Hardwood species such as willow, poplar, and oak are potential feedstocks for biorefineries. Hardwoods are higher in density and hardness compared to softwoods. Its lignin composition and structure also make its less recalcitrant than the softwood.¹⁹ Annual and perennial grasses also have been investigated for utilisation as lignocellulosic biomass feedstock. Perennial grasses such as switchgrass and *Miscanthus* have been found to be prominent candidates for bioethanol production as they have environmental advantages over food crops; such as they can thrive on marginal and erosive land that is unsuitable for food crops, and they often have less pesticide, herbicides or water needs.^{20,21} They also can be the solution to avoiding the ‘food vs fuel’ issue.^{22,23} Beside of having a high biomass yield and polysaccharide contents, *Miscanthus* is very appealing for second-generation

lignocellulosic biomass feedstocks as it also has a high carbon dioxide fixation rate and is commercially grown in the European Union as a combustible energy source.²⁴



Figure 1.6 *Miscanthus* plantation at Imperial College London, Silwood Park Campus.

1.3.1 Chemical Composition of Lignocellulosic Biomass

Lignocellulosic biomass has a complex internal structure. The cell walls of lignocellulosic biomass consist of crystalline cellulose fibrils surrounded by hemicellulose and lignin (Figure 1.7).⁶

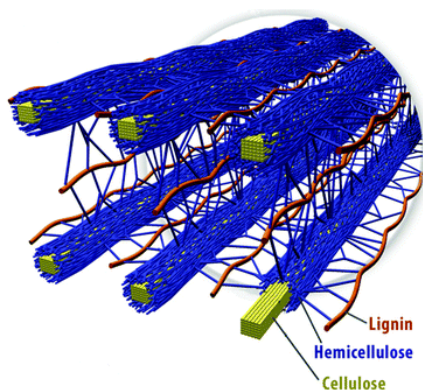


Figure 1.7 Cellulose, hemicellulose and lignin in plant cell wall of lignocellulosic biomass.⁶

1.3.1.1 Cellulose

Cellulose is the largest component of lignocellulosic biomass and is a straight-chain polymer with disaccharide cellobiose as a coupling unit (Figure 1.8). In cellulose, the β -D-glucopyranose units are linked via β -(1,4)-glycosidic linkages with degree of polymerization (DP) up to 10 000 or higher.²⁵ The presence of intra- and inter-molecular hydrogen bonding drives the cellulose chains (up to 300 units) to align to form crystalline microfibrils.²⁶ Study on the supramolecular structure of natural cellulose has shown that there are two phases interlink with each other which are crystalline and non-crystalline. The cellulose chain consists at one end of a D-glucose unit with a C4-OH group (the nonreducing end); the other end is terminated with an original C1-OH group, which is in equilibrium with the aldehyde structure (the reducing end).²⁷

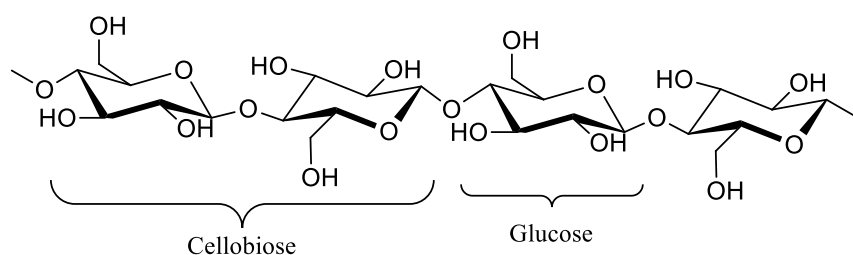
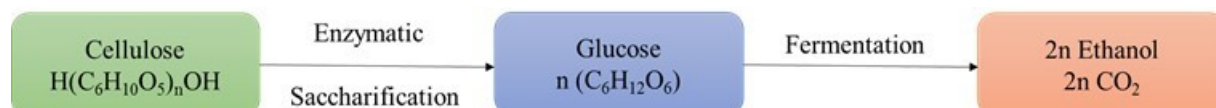


Figure 1.8 Structure of cellulose with its repeating units.

The molecular structure imparts cellulose with its characteristic properties: hydrophilicity, chirality, degradability, and broad chemical transformability initiated by the high donor reactivity of the OH groups.²⁸ Cellulose is insoluble in water, dilute acid, and dilute alkaline solution at low temperature. The solubility of the polymer is strongly related to the degree of hydrolysis achieved. Cellulose becomes soluble at higher temperature as hydrogen bonds that hold the crystalline structure are broken.²⁹

Immense attention is being focused on cellulose as its monomeric sugars can be further converted into bioethanol as a transportation fuel (Scheme 1.1),³⁰ and value-added chemicals such as alcohols, organic acids, and hydroxymethylfurfural (HMF).^{31–34}

Figure 1.9 illustrates the conversion of cellulose into several valuable chemicals.



Scheme 1.1 Conversion route of cellulose to produce ethanol.

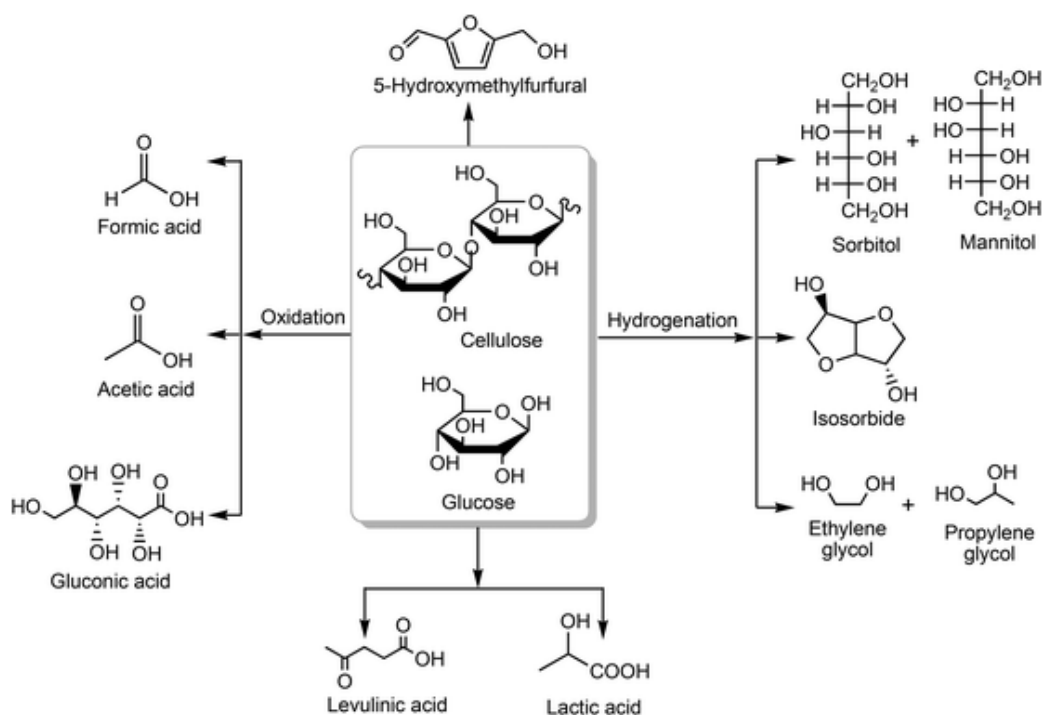


Figure 1.9 Conversion of cellulose into several industry related chemicals.³⁵

1.3.1.2 Hemicellulose

Hemicellulose is the second major component present in lignocellulosic biomass. Compared to cellulose, hemicelluloses are non-linear as they contain branched and heterogeneous polysaccharides; pentoses (xylose and arabinose), hexoses (glucose, galactose and mannose), and acetylated sugars (Figure 1.10).³⁶

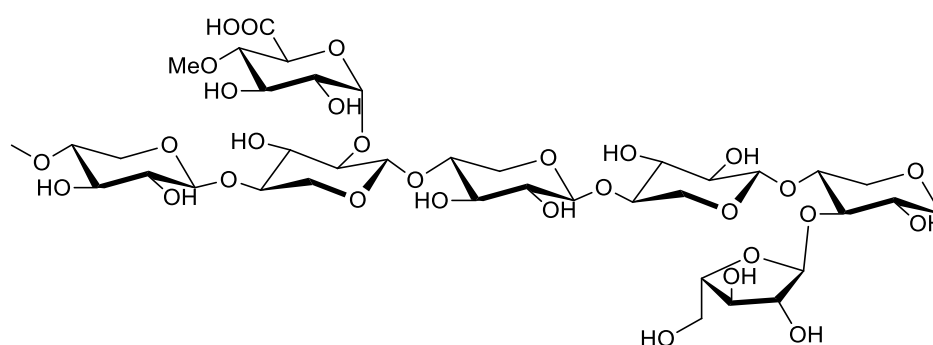


Figure 1.10 Chemical structure of hemicellulose

The structure and composition of hemicellulose differs depending on the origin of the biomass. Hemicellulose is non-covalently link to cellulose and it surrounds the cellulose microfibrils acting as a support matrix to the cellulose in the plant cell wall.³⁷ By covalently linking to lignin, hemicellulose acts as a connection between lignin and cellulose, thus imparting inflexibility to the cellulose–hemicellulose–lignin complex.³⁸ Hemicellulose can be easily hydrolysed chemically or enzymatically due to its amorphous nature and smaller size compared to cellulose.³⁹ Similar to cellulose, hemicellulose can be converted into bioethanol as well as high value platform chemical such as HMF and furfural.^{40,41}

1.3.1.3 Lignin

Lignin is a complex polymer of phenol derivatives linked by C–C and ether bonds. Lignin is a molecule with high molecular weight, which is constructed from the combination of various acids, alcohols, and phenols. Lignin polymer is built up from three monomers; *p*-coumaryl, coniferyl and sinapyl alcohol (Figure 1.11).⁴² These complex polymers constitute about 10–45% of the lignocellulosic material, this means that the bioethanol industry will generate more lignin as residual waste alongside the paper pulp industry.¹⁶ To meet the United State of America's goal of replacing 30% of fossil fuel with biofuel by 2030, about 227 hm³ of bioethanol will need to be produced which would generate around 20.4×10^7 tonnes of lignin.⁴³ Although lignin has always been considered as undervalued leftover, it is actually a very useful raw material as it can be degraded and converted into valuable chemicals such as phenols and organic acids.⁴⁴

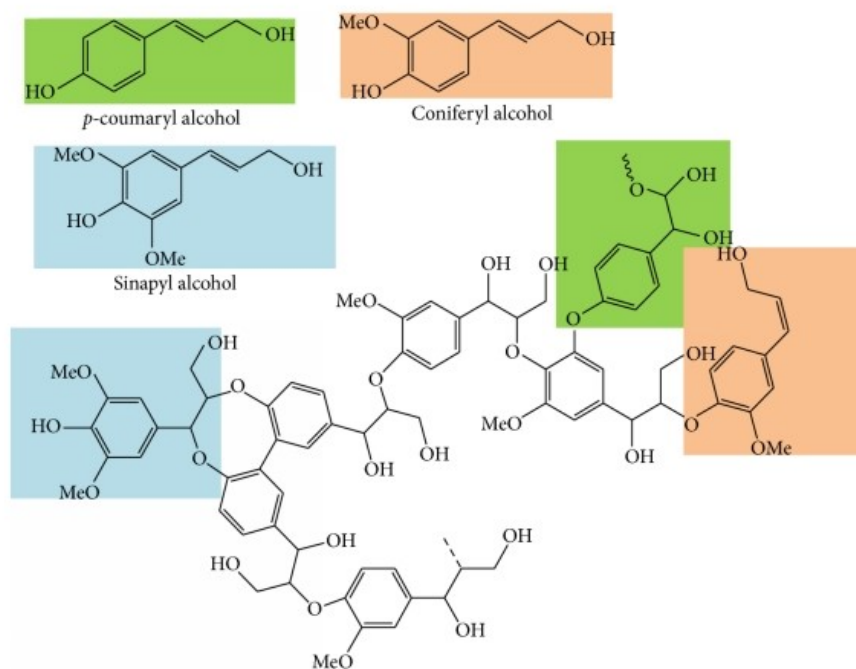


Figure 1.11 Lignin chemical structure alongside with its monomers, *p*-coumaryl, coniferyl and synapyl alcohol.⁴⁵

Lignin by nature is water-insoluble, reinforcing the plant cell wall and acting as protective barrier for the plant from microbial attack.⁴⁶ Lignin is the main cause of biomass recalcitrance during separation process. As a result, removal of lignin is crucial to enhance biomass deconstruction and increase the accessibility to hemicellulose and cellulose for the saccharification process to produce fermentable sugars.^{47,48}

1.3.2 Deconstruction of Lignocellulosic Biomass

Biomass recalcitrance is the major challenge in exploiting lignocellulosic biomass for the production of biofuels and industry relevant chemicals. To overcome the problems related with biomass recalcitrance, a number of pretreatment technologies are being developed and optimized.^{28,30,49} The main focus of deconstruction of lignocellulosic biomass is to isolate cellulose to further access the glucose for use in the fermentation process. Breaking the lignin-hemicellulose linkage allows the lignin to be separated and the cellulose exposed for further processing (Figure 1.12). The isolated cellulose is subsequently hydrolysed by enzymatic saccharification before the final fermentation step. A vast number of studies have been undertaken to effectively deconstruct the lignocellulose structure, in order to get high purity cellulose and hemicellulose, subsequently promoting efficient hydrolysis of the carbohydrates into fermentable sugars.^{6,30,50}

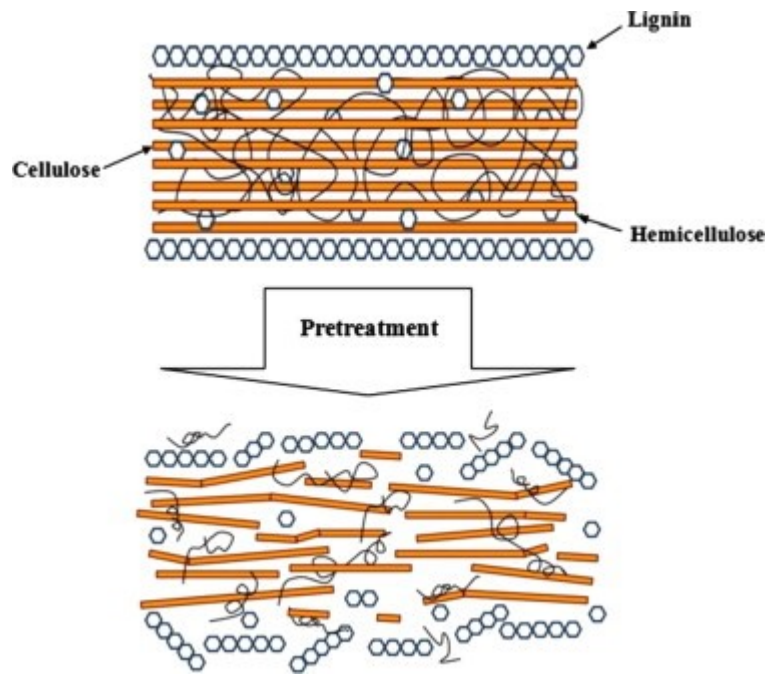


Figure 1.12 (Physico)chemical deconstruction of the lignocellulose structure to make the polysaccharides become accessible.³⁰

The pretreatment method becomes effective when these three conditions are achieved; minimal losses of the cellulose and hemicellulose, maximum delignification and easy recovery of lignin. It should also be applicable to various feedstock, be environmental friendly, and be economically feasible. Biomass pretreatment can be categorised into physical, chemical, biological and hybrid methods (Figure 1.13). Currently there are a number of effective pretreatment methods available, each with their pros and cons. Amongst the conventional and widely used strategies are acid, alkali, organic solvent, ammonia fibre expansion (AFEX) and ionic liquid pretreatments.^{48,51,52}

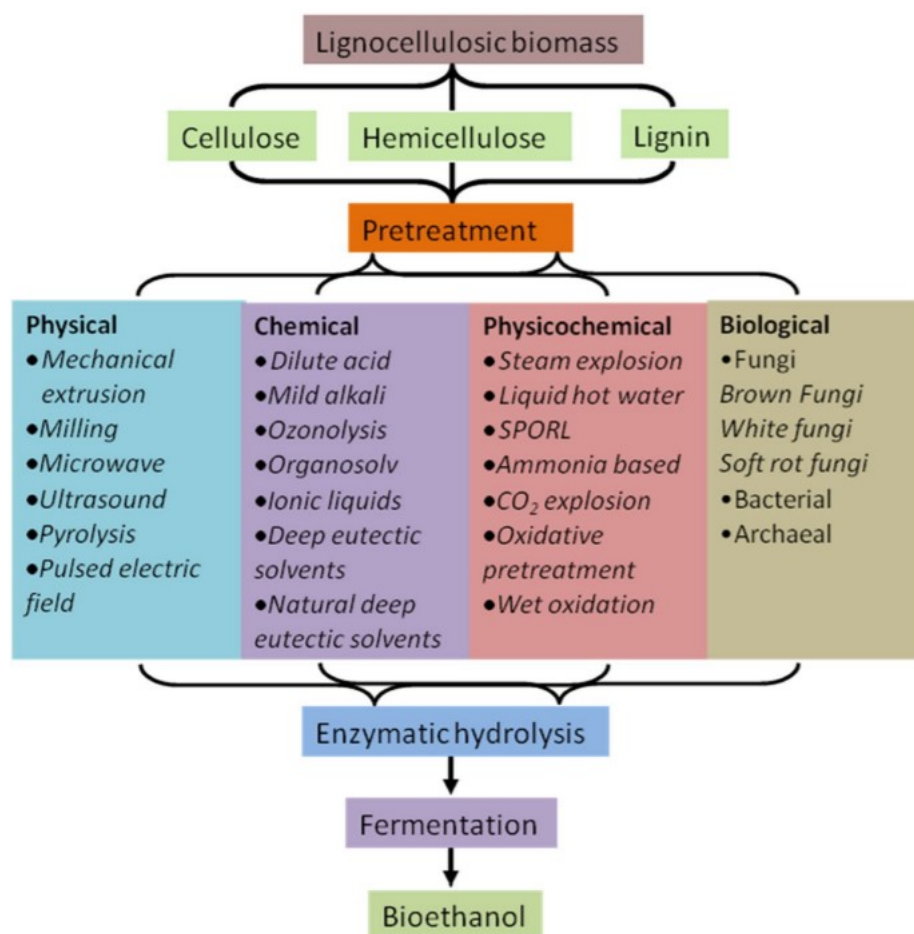


Figure 1.13 Overview of different pretreatment methods.⁵⁰

Dilute acid pretreatment is the most favourable method as it is effective in giving high hydrolysis yield and in addition, it is relatively inexpensive. There are two types of dilute acid pretreatments that have been used based on the type of end application; for short duration (1-5 min), high temperature (above 180 °C) is employed, while low temperature (<120 °C) is set for long duration (30–90 min).⁵⁰ Some studies reported that this method is not suitable for woody biomass (forest or forest-derived biomass)¹⁷ and it also produces inhibitors such as aldehyde, phenolic acids, furfurals and 5-hydroxymethylfurfural for the subsequent fermentation process.^{48,49,53} Other drawback such as corrosive and toxic nature of the acid leads to corrosion of reaction vessels.

Removal of the mentioned inhibitors and acid residues are also needed to make fermentation process feasible.⁵⁴ Besides sulfuric acid, which is widely used and common for acid pretreatment, dicarboxylic acids such as maleic and oxalic acid also have been utilised for the pretreatment purpose. These two carboxylic acids exhibited some advantages over sulfuric acid and acetic acid as they are less toxic to microorganisms, and they have two and higher pKa values than sulfuric acid.^{54,55}

Alkaline pretreatment is also an effective and economical method. The alkaline environment improves the enzymatic accessibility of the polysaccharides by cleaving the hydrolysable linkages in lignin and glycosidic bonds of polysaccharides causing a decrease in the cellulose degree of polymerization (DP) and crystallinity, swelling of the biomass and disrupting the lignin structure.⁵⁶ However, this method requires high cost and cumbersome work-up process as it uses a large quantity of water for salts removal from the biomass.⁵⁰ Similar to the acid pretreatment, alkaline pretreatment cannot be applied to biomass with high lignin content.^{48,57}

Organosolv pretreatment, involves isolation or removal of lignin from the biomass using organic solvents or solvent mixtures in aqueous solution, and is often combined together with organic or inorganic acids as catalysts under specific condition of temperature and pressure.^{58,59} The common solvents used for organosolv pretreatment include ethanol, methanol, acetone, ethylene glycol, and tetrahydrofurfural alcohol.^{16,50} The main goal of this process is to extract lignin and to expose cellulose and hemicellulose fraction for the enzymatic saccharification. Although the organosolv pretreatment is suitable for most lignocellulosic biomass feedstocks, however there are inherent drawbacks of using this method for biomass pretreatment at present. The main disadvantages of the organosolv process are it is expensive, the flammability of the organic solvents coupled

with the contamination by the solvents and catalyst residues inhibiting the subsequent enzymatic saccharification process.^{16,60}

Steam explosion is a physico-chemical treatment and one of the commonly used method for the pretreatment of lignocellulosic biomass.⁶¹ In this method, the materials undergo an explosive decompression when the biomass is treated with high-pressure and saturated hot steam (160–260 °C, 0.69–4.83 MPa) for several seconds to a few minutes before the pressure is swiftly reduced to atmospheric pressure.¹⁶ The process causes hemicellulose degradation due to high temperature, thus increasing the potential of cellulose hydrolysis. Lignin transformation also occurred during this process where it is softened, depolymerized/repolymerized and released from the cell wall and distributed evenly onto the raw material.⁶² Although steam explosion is cost-effective pretreatment process for hardwoods and agricultural residues, it is less effective for softwoods.¹⁶ Some of the limitations of this process also include destruction of a portion of the xylan fraction, incomplete disruption of the lignin–carbohydrate matrix, and generation of compounds that might be inhibitory to microorganisms used in the subsequent processes.⁶³ AFEX pretreatment is another common physico-chemical treatment which is similar to steam explosion method. In AFEX pretreatment method, ammonia is used instead of water. This method has been reported to give high sugar yields (closed to theoretical yield) at relatively low enzyme loadings.⁴⁹ Besides increasing the surface accessibility for hydrolysis, AFEX decreases cellulose crystallinity, removes acetyl groups in hemicellulose and reduces the lignin recalcitrance in the treated biomass.⁵² By disrupting the physical structure of the biomass, the surface area of the matrix expands, hence increases the wettability and water holding capacity of the treated pulp.^{61,64} But this method is found to be ineffective to high lignin content biomass such as newspaper,

hardwoods and softwoods.^{49,61,65} In addition, AFEX uses a substantial amount of ammonium which dictates high energy input for recovery and recycling.⁶⁶ The main advantage of the ammonia pretreatment is that it does not produce inhibitors for the subsequent biological processes and very effective for pretreatment of herbaceous and agricultural residues.^{49,61}

As has been discussed earlier, the success of a lignocellulose-based biorefinery depends hugely on the development and implementation of an effective pretreatment method to overcome the recalcitrance of lignocellulose. The pretreatment process should also be feasible for use with all range of feedstock and promote a smooth and efficient enzymatic saccharification process by producing a high yield of uncontaminated polysaccharides. Unfortunately, none of the current pretreatment methods fulfil all these desired criteria and have their own disadvantages for large-scale applications (Table 1.2).

Table 1.2 Advantages and disadvantages of different pretreatment methods of lignocellulosic biomass.^{49,61,66–68}

Pretreatment Method	Advantages	Disadvantages
Physical		
Milling	- Reduce crystallinity and degree of polymerization of cellulose - Expansion of specific surface area and pore size	- High power and energy requirement
Microwave	- Easy operation - Low energy requirement - Low formation of inhibitors - Short reaction time	- Need for catalyst to get higher yield
Chemical		
Concentrated acid	- High glucose yield - Ambient temperature - Increases hemicellulose solubilisation	- High cost of acid and need to be recovered - Formation of inhibitors - Corrosion of the equipment - Hazardous and toxic due to concentrated acid - Requires extensive washing to remove acid
Dilute acid	- High recovery of sugars at the end of the process - Low formation of toxic products - High hydrolysis rates	- Formation of degradation products - Formation of inhibitors - High cost compared to AFEX and steam explosion
Alkali	- Reduce crystallinity and degree of polymerization of cellulose - Lignin structure modification	- High cost - Not suitable for large-scale plant
Ozonolysis	- Effective lignin removal - Does not produce toxic inhibitors - Environmental friendly - Reaction is carried out at room temperature and	- Expensive due to high amount of ozone required - Less effective to high moisture of the sample

Organosolv	pressure - Defractionation of lignin, cellulose and hemicellulose - Suitable for high-lignin content biomass	- Solvents need to be removed and recycled - High cost of solvents and Catalyst - Hazardous due to toxicity and flammability of the solvents
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Physico-chemical

Steam explosion	- Causes lignin modification and hemicellulose degradation - Lower cost - Higher yield of glucose and hemicellulose in the two-step method - Environmental friendly - No recycling cost - Less chemical requirement - Effective for hardwoods, and agricultural residues	- Generation of fermentation inhibitor at high temperature - Incomplete disruption of lignin-carbohydrate complex
Liquid hot water	- No requirement of small particle size of biomass of the biomass - Lower temperature are used - Less inhibitors formation - No chemicals requirement	- High energy and high water consumption - Higher amount of solubilised product but lower in concentration
Ammonia Fiber Expansion (AFEX)	- Increases accessible surface area - Less inhibitors formation - No requirement of small particle size of biomass	- Not very effective for the biomass with high lignin content - High cost of high amount of ammonia
CO ₂ Explosion	- Increases accessible surface area - Low cost - No formation of inhibitors - Non-flammability - Easy recovery after extraction and environmental friendly	- Requires very high pressure - High cost of high pressure reactor
Wet oxidation	- Increases solubilisation of hemicellulose and lignin - Avoid formation of	- High cost of oxygen and hydrogen peroxide - Highly combustible due to

	degradation compounds	pure oxygen
Biological	- Low energy requirements - Higher delignification - Reduction in degree of polymerization of cellulose - Partial hydrolysis of hemicelluloses - No chemical requirements - Mild environmental conditions	- Pretreatment rate is too slow for industrial scale application - Large space and careful growth conditions requirements - Fraction of carbohydrate is consumed by the microorganism

From a simulation study which evaluated the energy requirements of each pretreatment methods, based on stoichiometric relations and yield data, steam explosion was found to be the least desirable method from the perspective of inhibition and waste minimisation while dilute acid and AFEX were predicted to be less effective from the perspective of chemical cost.⁶⁹ To overcome these drawbacks, there are many different methods that have been undertaken to find the alternatives to these conventional methods which includes pretreatment with ionic liquids. Owing to their unique properties, ionic liquids were found to be suitable to replace most of the organic solvents used by chemical industries thus they have the potential to be utilised in biomass pretreatment.^{6,70}

1.4 Introduction to Ionic Liquids

Ionic liquids (ILs) are defined as salts which melt at or below 100 °C and are composed solely of cations and anions.⁷¹ ILs studies are not new, the first study on IL, ethylammonium nitrate [H₃C₂N][NO₃] was reported in 1914 by Paul Walden.⁷² It's only upon the discovery of new air and water stable ILs ,in the 1990s, which led to the growing studies of new ILs and their potential applications.⁷³

1.4.1 Classification of ILs

ILs differ from common salts as they are often composed of bulky organic cations with low symmetry and poorly coordinating anions with delocalised charge. This combination prevents the formation of a stable crystal lattice therefore contributes to the low melting points properties.⁷⁴ Modern ILs usually consist of quaternised aromatic or aliphatic ammonium cations. While the anions are either organic or inorganic ions. A selection of common anions and cations are shown in Figure 1.14 and 1.15.

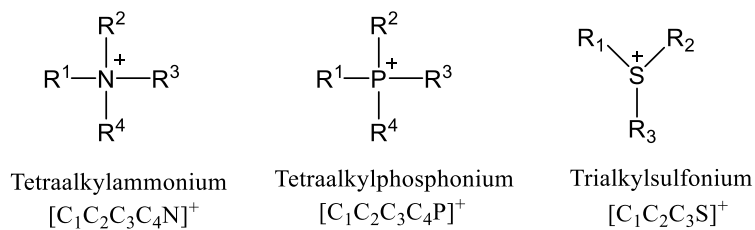
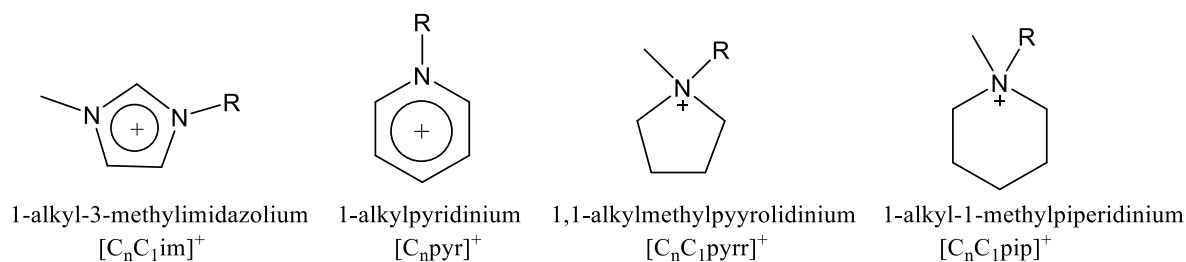


Figure 1.14 Structures and abbreviations of common IL cations.

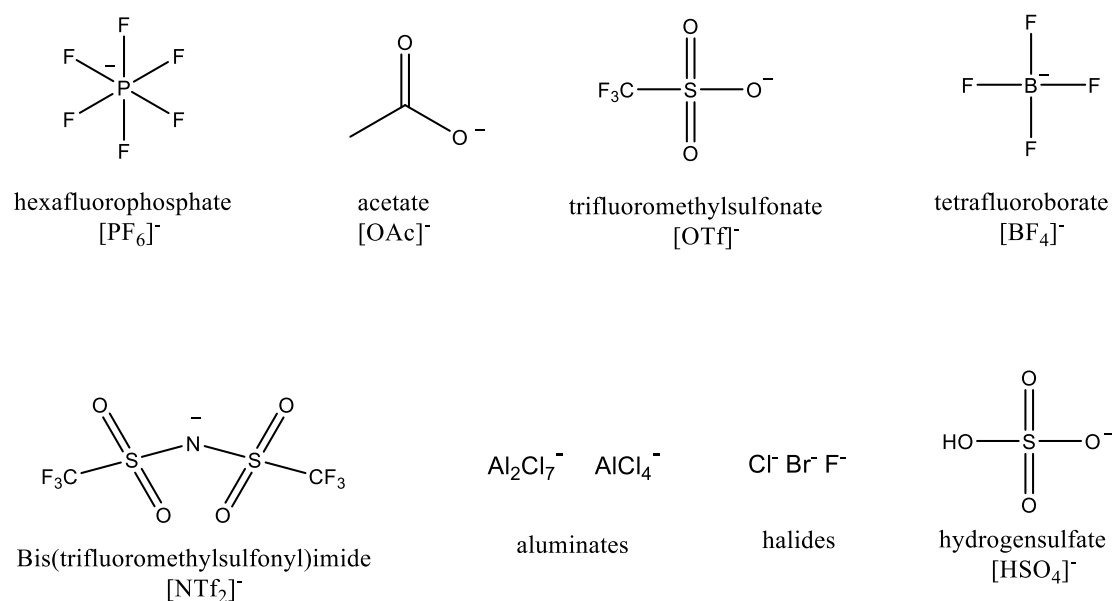


Figure 1.15 Structures and abbreviations of common IL anions.

ILs typically have long names due to their complex structures. Their cations and anions formulae are always abbreviated to their core and functional groups symbols, for example: 1-butyl-3-methylimidazolium to [C₄C₁im]⁺, and bis(trifluoromethylsulfonyl)imide to [NTf₂]⁻. Other examples can be found in Figure 1.14 and 1.15.

1.5 Synthesis of ILs

Commonly, ILs syntheses required extremely anhydrous conditions. The presence of water will result in a sluggish alkylation and low yields. This is due to deactivation of the alkylation reactions via hydrogen-bonding of the water with the nitrogen lone pair on the N-heterocycle. However, for acid-base combination method, water is often used as reaction solvent to dilute the acid and control the temperature of the exothermic reaction. But purification of the amines is still required to produce high purity and colourless ILs. Therefore, all starting materials need to be dried and purified before use. Additionally, ILs and their crystalline precursors are very hygroscopic, and need to be stored under inert gas, in sealed and dry containers to avoid contact with water from air.

The direct combination of an acid with a base in stoichiometric quantities is used to make *protic* ILs. While, *aprotic* ILs are made by an ‘irreversible’ alkylation mechanism of a nucleophile with an electrophile. Generally, ILs syntheses can be categorised into three types; alkylation, acid-base, and ion metathesis reactions (Figure 1.16).

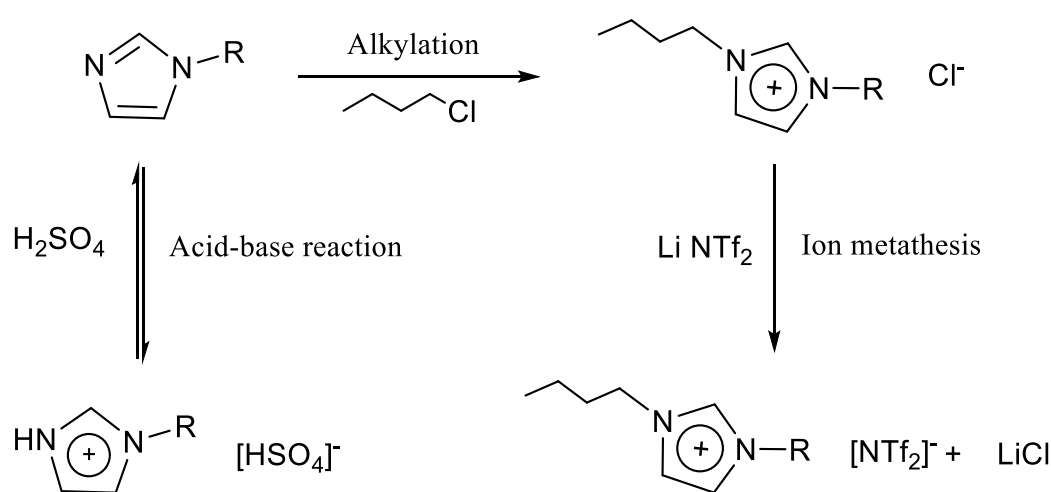
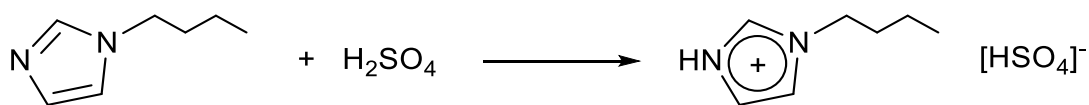


Figure 1.16 Simplified syntheses of *protic* IL via acid-base reaction, and *aprotic* ILs via alkylation and ion metathesis.

1.5.1 Acid–base Reaction

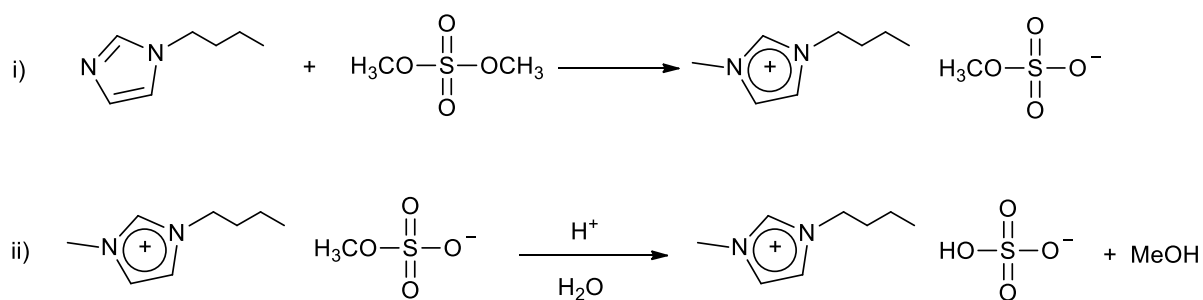
Acid–base reactions are exclusively used to prepare *protic* ILs. This method is found to be relatively clean, cheap, and fast compared to other methods. The ILs are formed when there is a successful proton transfer from the acid to the base. Strong acids are always used to drive the proton transfer.⁷⁵ Because this reaction is very fast and releases exothermic heat, the acid is often added in a drop wise manner to the amine, and water is used to dilute and cool the reaction mixture so that the reaction is easier to control.⁷⁶ In this study, 1-butylimidazolium hydrogen sulfate, [HC₄im][HSO₄] was prepared using this method by reacting sulfuric acid with 1-butylimidazolium (Scheme 1.2). The experimental details are described in Chapter 6.



Scheme 1.2 Synthesis of [HC₄im][HSO₄]

1.5.2 Direct Alkylation

Aprotic ILs are made by alkylation of cations using alkylating agents. This is the best method to prepare alkyl sulfate, alkyl carbonate and dialkyl phosphate ILs.^{77,78,79} These ILs are usually used as precursor to prepare other ILs. In this study, 1-butyl-3-methylimidazolium hydrogen sulfate, [C₄C₁im][HSO₄] was made from hydrolysis of 1-butyl-3-methylimidazolium methyl sulfate, [C₄C₁im][MeSO₄], which was first prepared by the direct alkylation reaction of 1-butylimidazolium with dimethyl sulfate (Scheme 1.3).



Scheme 1.3 Synthesis of $[\text{C}_4\text{C}_1\text{im}][\text{MeSO}_4]$ (i) and $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ (ii)

1.5.3 Synthesis *via* Halides Intermediates

Many common *aprotic* ILs, whether they are hydrophobic or moderately hydrophilic are synthesised using this method, such as $[\text{OTf}]^-$, $[\text{NTf}_2]^-$ and $[\text{BF}_4]^-$ based IL. This method consists of several steps such as quaternisation to form the halides precursor IL and then metathesis of the precursor IL to give the desired final IL.⁹ The quaternisation reaction is an alkylation reaction where nucleophilic substitution occurs between alkyl halides and amines. The products are usually alkylated amine as the cations and halide as the anions. This reaction is usually carried out under inert gas and in a solvent that dissolves the starting materials but has low solubility for the ionic product, such as ethyl acetate, 1,1,1-trichloroethane and toluene.^{9,80}

After purification of the halide IL, usually via recrystallisation, an ion metathesis reaction is carried out to form the final desired IL. The purified halide IL is reacted with a lithium or sodium salt of the desired anions to form the final ILs and the corresponding lithium/sodium halide salts.⁸¹ This method is usually performed in CH_2Cl_2 as the by-product halide salt will precipitate out. This halide precursor ILs method can be used to synthesise most ILs and achieve very high purity ILs.⁸⁰

1.5.4 Purification of ILs

Pure ILs are almost always colourless. Colouration of ILs could be due to contaminants, degradation, isothermal reaction at room temperature and prolonged heating during synthesis.^{80,82} It is important to use colourless ILs for spectroscopic measurement such as measuring Kamlet-Taft solvent polarity using UV-Vis spectroscopy.⁹ Decolourisation of ILs can be done by washing them with activated charcoal and/or passing a water-IL mixture through a pre-packed IsoluteTM C-18 Flash column to remove the chromophoric impurities.^{82,83}

ILs for catalysis need to have minimum water and halide contents. This can be achieved by washing the halide with water and subsequently drying them in *vacuo* at 65 °C over 24 h.^{81,82} Any excess of starting materials, such as alkyl halides, can be distilled off under vacuum and washed out with a suitable solvent. For the ILs that are solid at room temperature they can be further crystallised for final purification step.⁸⁴

1.6 Properties of ILs and Applications

ILs are often referred as alternative solvents to volatile organic solvents. The green properties of ILs are one of the main reason why ILs have been received widely and growing interest. ILs are generally non-volatile as they have negligible vapour pressures. These properties make ILs handling less risky due to less exposure by evaporation and non-flammability. This also makes ILs possible to be used at high temperature condition. ILs are famously cited as ‘designer solvent’. This is because, by varying the combinations of organic cations and anions or their functional groups a wide variety of ILs with preferred and targeted chemical and physical properties can be

accessed.⁸⁵ These properties include density, viscosity, conductivity, polarity, and thermal stability. For example, long and bulky cations will result in lower density and increased viscosity of the ILs.⁸⁶ The controllable hydrophobicity of ILs also makes them useful in biphasic system especially for the stabilisation of enzyme catalysts in biocatalysis reactions.⁸⁷

Acidic ILs can be prepared by introducing acidic function(s) or group(s) such as sulfonic and sulphuric acid in the cation, anion, or both.^{88,89} Furthermore, combination of different alkyl chain length and functional groups can produce ILs with targeted bioactive properties which also attributes to dual functional nature of the ILs. Long alkyl chain ILs such as 1-nonyl- and 1-decylpyrimidinium tetrafluoroborate were reported to show excellent antibacterial properties against both Gram-positive *S. aureus* (MIC = 8 and 4 $\mu\text{g mL}^{-1}$, respectively), and Gram-negative *E. coli* bacteria (MIC = 8 and 4 $\mu\text{g mL}^{-1}$, respectively).⁹⁰ 1-Ethylpyridinium docusate and tributyl(2-hydroxyethyl)phosphonium docusate have been reported as great plasticiser and antimicrobial agents.⁹¹ The effective antimicrobial behaviour of both ILs originates from both anionic and cationic surfactant properties, while the enhanced plasticising effect derived from the polarity of both cations and the presence of ester groups in the docusate anion.⁹¹

Due to their ionic composition, ILs have been found to be super-dissociating solvents toward solute salts compared to molecular solvents. In organic reactions, ILs have allowed enhanced stabilisation of charged transition states and the dissociation of ion pairs.⁹² This novel behaviour is different from observed reactions in molecular solvents. ILs are also more suitable than molecular solvents in electrochemistry applications as they have a larger electrochemical windows.⁹³ This allows electrochemical

transformations that are limited and cannot be done in molecular solvent to be performed in appropriate ILs.^{94,95}

1.7 ILs in Biomass Processing

The application of ILs in a lignocellulosic biomass transformation process was first reported in US patent in 1934 where 1-ethylpyridinium chloride $[C_2\text{pyr}]\text{Cl}$ was found to dissolve cellulose. In the patent, the chloride IL mentioned was used in the presence of organic bases but this system has a relatively high melting point and hence was considered to be of less practical value at that time.⁹⁶ In 2002, Rogers and co-workers reported that 1-butyl-3-methylimidazolium chloride, $[C_4C_1\text{im}]\text{Cl}$ can readily solubilise microcrystalline cellulose (MCC) (Figure 1.17).⁹⁷ The cellulose could then be recovered upon addition of an anti-solvent such as ethanol or water.

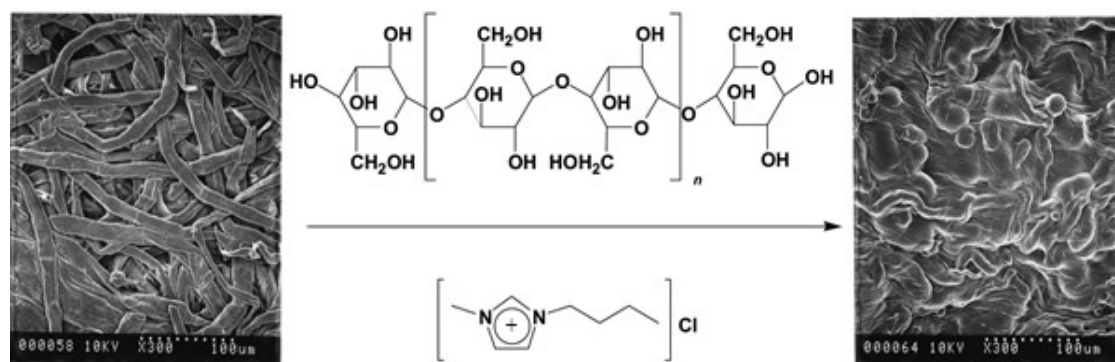


Figure 1.17 SEM micrographs of initial dissolving pulp in $[C_4C_1\text{im}]\text{Cl}$ and after regeneration into water.⁹⁷

These results led to a resurgence in the field, creating new practical methods to process cellulose and initiating extensive research in the area. The capability of ILs to dissolve

cellulose depends on the nature of the native cellulose (its degree of polymerization and its crystallinity), on the operating conditions (temperature, reaction time, initial concentration of cellulose in the IL, pressure, activation with microwaves, etc.), the presence of impurities,^{97,98} and most importantly, on the nature of the IL itself. It has been reported that the chloride anions of the IL effectively disrupted the extensive hydrogen bonding in the cellulose structure by forming hydrogen bonds with the hydroxyl groups of the polysaccharides in a 1:1 stoichiometry.⁹⁹ $[\text{OAc}]^-$ and $[\text{HCO}_2]^-$ have also been shown to be successful anions for dissolving cellulose because of their strong hydrogen bond basicity.^{100,101}

Varanasi *et al.* and Zhao *et al.* demonstrated that the IL pretreatment and regeneration process reduced the crystallinity of the regenerated cellulose, subsequently enhancing and accelerating the enzymatic hydrolysis.^{102–104} Later, 1-ethyl-3-methylimidazolium acetate, $[\text{C}_2\text{C}_1\text{im}][\text{OAc}]$ was found to be very effective as a solvent for lignocellulosic pretreatment with easy regeneration of cellulose and hemicellulose upon addition of an anti-solvent. This process also leads to complete delignification, and enhanced saccharification rates and yields.^{105–107} Figure 1.18 shows a flow diagram of IL pretreatment method.¹⁰⁸

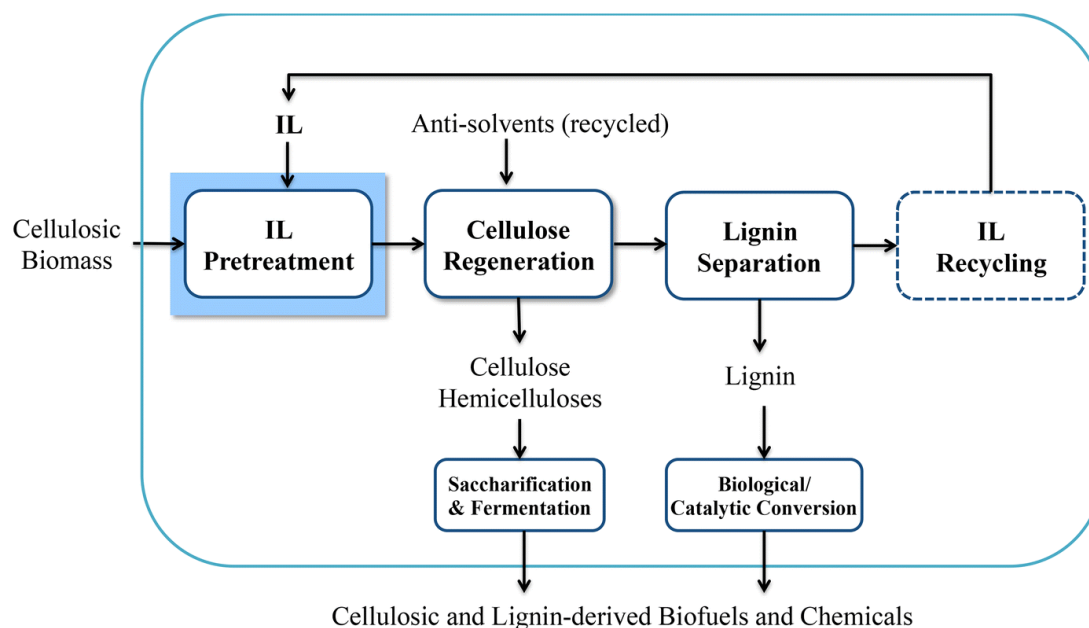


Figure 1.18 Process configuration for IL pretreatment.¹⁰⁸

To date, there are two distinct approaches to using ILs for lignocellulose biomass pretreatment. The first approach emphasises complete dissolution of lignocellulosic biomass while the second approach emphasises on the disruption of the chemical lignocellulose composite without having complete solubilisation of the biomass in the ILs.⁶ The first and most reported approach aims to solubilise the entire biomass composite and simultaneously has the carbohydrate polymers depolymerised with the lignocellulose dissolving ILs.^{109,110} As discussed earlier and as illustrated in Figure 1.16, the regeneration of the cellulose and hemicellulose is required for the subsequent saccharification step. A one step process has been attempted with this approach, where the regeneration step and enzymatic saccharification process are not required.¹¹¹ In most studies, this *in situ* chemical hydrolysis of the lignocellulose in ILs is usually paired with catalytic amounts of Bronsted acid (Figure 1.19).^{112,113} Total reducing sugars (TRS) yields of corn stalk, rice straw, pine wood and bagasse hydrolysis in [C₄C₁im] Cl in the presence of 7 wt% hydrogen chloride at 100 °C were reported up to 66%, 74%, 81%

and 68% respectively.¹¹² Sievers et al. have conducted acid-catalysed hydrolysis of pine flour in [C₄C₁im] Cl with added sulfuric acid at 100-150 °C.¹¹⁴ They found that the limited amount of water in the anhydrous system halt the hydrolysis at the oligomer stage. However, large amounts of water decreased lignocellulose solubility. Binder and Raines suggested incremental addition of water during the dissolution of corn stover with acidified [C₂C₁im] Cl can maintain a balance between solubility and hydrolysis of the cellulose.¹¹³

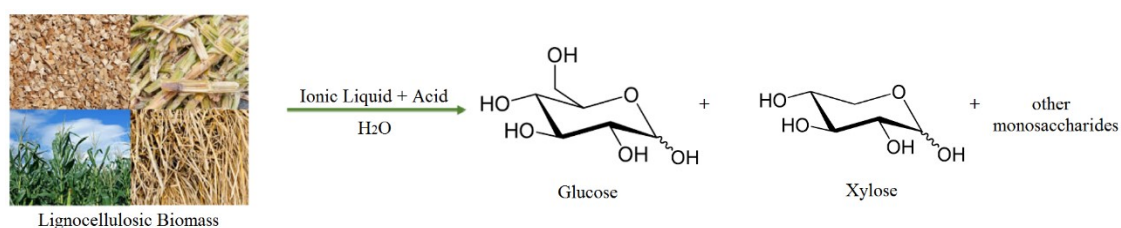


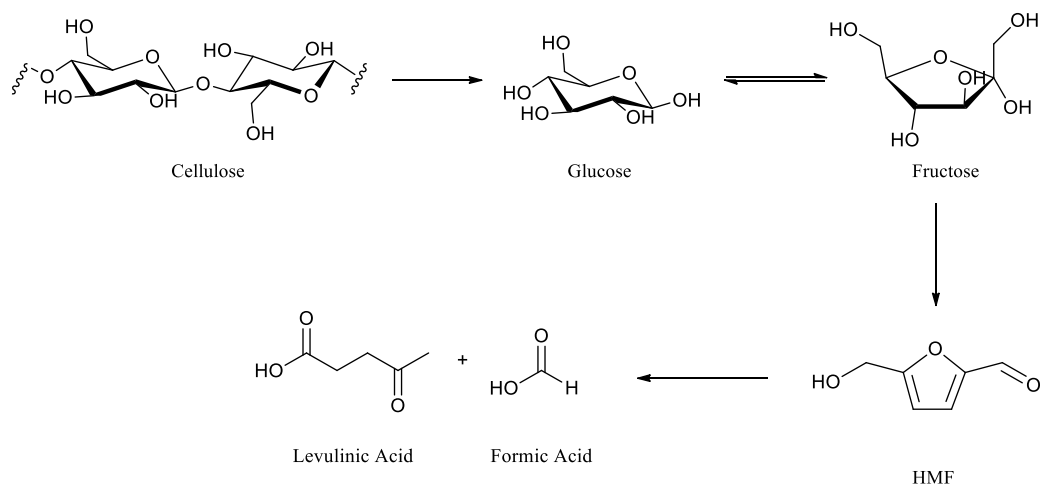
Figure 1.19 Schematic illustration of lignocellulose hydrolysis in ILs with acid.

The second approach, usually called the Dissolution Process and the Ionosolv Process,⁶ focuses on the disruption of the chemical lignocellulose composite with only partial solubilisation of the biomass components in the ILs.^{115,116} The Ionosolv process involves dissolution of lignin and hemicellulose while the cellulose fraction remains undissolved.^{6,117} The main goal of this method is to selectively delignify biomass, which is subsequently precipitated out with water. Delignification during pretreatment is considered to be important especially for high lignin content biomass. Effective delignification and hemicellulose removal is reported to lead to an increase in the glucose yield of the enzymatic hydrolysis of the pretreated pulp compared to untreated biomass.^{117,118} This process derived its name from Organosolv process, which also dissolve lignin and hemicellulose.^{60,119} Rather than using organic solvents such as

ethanol and acetic acid, *protic* ILs particularly $[\text{HSO}_4]^-$ based ILs are used in Ionosolv process.^{117,120,121}

The Dissolution process, on the other hand, involves the dissolution of the cellulose while having partial lignin and hemicellulose removal from the lignocellulose. The most reported and effective IL for this process is $[\text{C}_2\text{C}_1\text{im}][\text{MeCO}_2]$.⁶ After the pretreatment, the cellulose-enriched pulp is precipitated out from the IL-biomass mixture using an anti-solvent and subsequently washed before the enzymatic saccharification in the subsequent step. Similar to the Ionosolv process, the regenerated cellulose should be free from IL residue to avoid enzyme deactivation in any following process.^{6,122}

The employment of ILs in biomass processing is not only limited to the pretreatment process for separation of biopolymers. Recently, ILs have also been utilised in the conversion of the polysaccharides, into their sugar and furan derivatives. Acid hydrolysis of cellulose in ILs with mineral acids was found to be cost effective compared to enzymatic hydrolysis. High total reducing sugar yields were achieved in acid hydrolysis of cellulose in chloride based ILs with an addition of catalytic amount of mineral acids.^{112,123,124} The conversion of polysaccharides and reducing sugars to produce furan derivatives such as HMF and furfural were also carried out in ILs with the addition of inorganic catalysts.^{125–129} Further conversion of biopolymers to produce 4-oxopentanoic acid, better known as levulinic acid (LA) via HMF has been explored and carried out in ILs (Scheme 1.4).^{130–132}



Scheme 1.4 Conversion route of cellulose to LA

Recently, utilisation of ILs for the degradation of lignin has also received great attention. Catalytic degradation of lignin and lignin model compounds in chloride, hydrogen sulfate, and trichloroacetate based ILs were studied, and it demonstrated that the degradation of the lignin and the model compound proceeded via an alkyl-aryl, β -O-4 ether linkage cleavage.^{133–136} 1-Butylimidazolium chloride, [HC₁im]Cl and 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate, [C₄(SO₃H)C₁im][HSO₄] were also reported to act as efficient bifunctional solvents and catalysts for the depolymerisation of oak wood and bagasse lignin.^{137,138}

1.7.1 [HSO₄][−] ILs in Biomass Transformation Process

Many studies reported on the utilisation of [HSO₄][−] based ILs in biomass processing in recent years. The Welton and Hallett research groups have employed [HC₄im][HSO₄] and [C₄C₁im][HSO₄] in the pretreatment of *Miscanthus* and they were found to give high saccharification yields (up to 90%).^{118,1} Figure 1.20 shows the route of pretreatment of *Miscanthus* in [HSO₄][−] based ILs in our lab. It was also reported that pretreatment of *Miscanthus* and willow with [HSO₄][−] based ILs exhibit higher lignin and hemicellulose removal.⁶

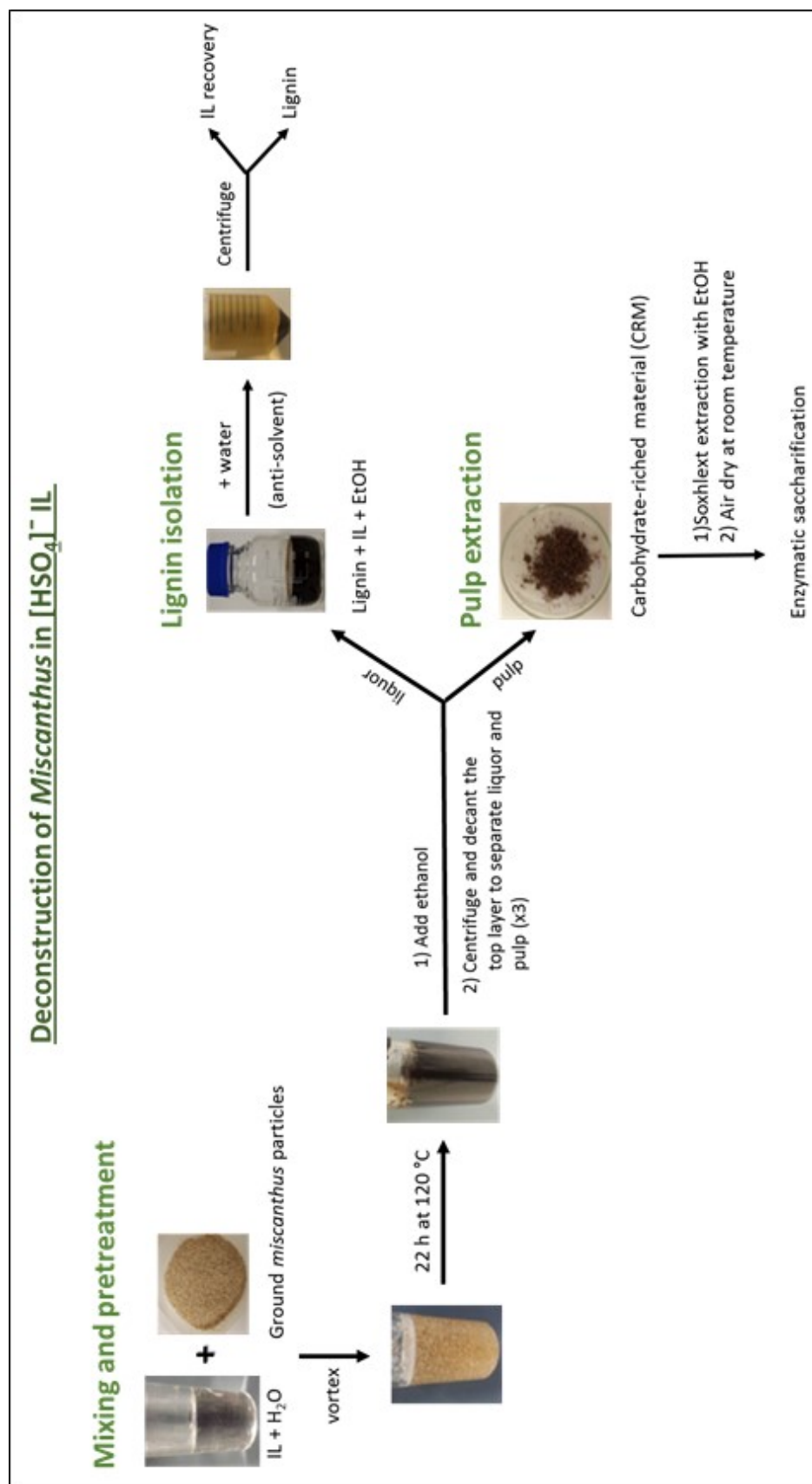


Figure 1.20 Deconstruction of *Miscanthus* in an $[\text{HSO}_4]^-$ based IL and water mixture.¹²²

Efficient delignification was achieved in these ILs due to solubilisation of the lignin. As discussed before, this method is referred as the Ionosolv process.⁶ Lignin recovery from the IL is also feasible by adding anti-solvent (water) to the mixture.^{6,9}

Although ILs are often linked to high cost, a recent study reported that series of $[\text{HSO}_4]^-$ ILs were designed to be low cost for lignocellulosic biomass pretreatment whilst demonstrating high and comparable saccharification yields to a benchmark system containing $[\text{C}_2\text{C}_1\text{im}][\text{OAc}]$, which costs around \$20-\$101 kg^{-1} .^{139,140} This techno-economic analysis demonstrated that triethylammonium hydrogen sulfate, $[\text{TEA}][\text{HSO}_4]$ and 1-butylimidazolium hydrogen sulfate, $[\text{HC}_4\text{im}][\text{HSO}_4]$ are estimated to cost \$1.24 kg^{-1} and \$2.96-5.88 kg^{-1} respectively. The price is around 3 to 5 times of the price of organic solvents, such as acetone and ethyl acetate, which cost \$1.30-\$1.40 kg^{-1} .^{76,139}

$[\text{HSO}_4]^-$ based ILs also have been used in the transformation process of biopolymers. As previously mentioned, $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ has been used as solvent in producing HMF from cellulose via hydrolysis of its reducing sugars such as sucrose and fructose.^{125,126,129} Recently, cellulose hydrolysis in 1-ethyl-3-methylimidazolium hydrogen sulfate, $[\text{C}_2\text{C}_1\text{im}][\text{HSO}_4]$ was performed with a novel enzyme-based Simultaneous-Isomerization-and-Reactive-Extraction (SIRE) process to achieve high yields of HMF by increasing the selectivity of glucose to fructose conversion.¹⁴¹ Due to the high solubility of lignin in these ILs they have been explored as solvent for the degradation and depolymerisation process of lignin.^{42,135,137} This new research scope is important as lignin has great potential to substitute petroleum feedstock for the production of industrial related chemical intermediates.

Due to their acidic nature, these ILs are suitable for hydrolysis and transesterification reactions as they can be used as solvent, catalyst or both. For conversion of oil-rich biomass to biodiesel, these two reactions are always involved in the conversion of the triglycerides to fatty acid methyl ester (FAME) and glycerol. Several studies reported on the use of $[\text{HSO}_4]^-$ based ILs as catalysts in this process.^{142–144} Recently they were used as catalysts in the conversion of rapeseed oil into FAME. 100% conversion was reached using sulfonated imidazolium ILs under optimum condition of 130 °C, 2 wt% of $[\text{C}_4(\text{SO}_3\text{H})\text{C}_1\text{im}][\text{HSO}_4]$, 12:1 methanol-to-rapeseed oil molar ratio, and over 3 h reaction time.¹⁴⁵

From these findings, $[\text{HSO}_4]^-$ based ILs have shown great potential as solvents and catalysts, or both in biomass processing. Thus, it is important to study the reactivity of biopolymers and their functional groups in $[\text{HSO}_4]^-$ based ILs to gain a better understanding and detailed insights on how biomass processing and conversion work in these ILs.

Chapter 2

2 Reactivity of Alcohols with $[\text{HSO}_4]^-$ ILs

2.1 Background of the study

2.1.1 Problems with the saccharification of cellulose obtained from from Ionosolv pretreatment

One of the main goals of biomass pretreatment is to isolate cellulose from biomass and make it available for saccharification and then for further conversion into ethanol. Previous members of the Welton and Hallett groups showed that the pretreatment of *Miscanthus* in $[\text{HC}_4\text{im}][\text{HSO}_4]$ gave very high yields of cellulose-rich pulp and lignin precipitate.¹ $[\text{HC}_4\text{im}][\text{HSO}_4]$ was found to be suitable for the fractionation of the carbohydrates and lignin as the lignin is soluble in the IL, enabling its separation from the carbohydrate components. Verdia *et. al* found that the highest levels of hemicellulose removal and delignification of *Miscanthus* in $[\text{HC}_4\text{im}][\text{HSO}_4]$ were achieved when the base:acid ratios of $[\text{C}_4\text{im}]:\text{H}_2\text{SO}_4$ were 1.00:0.99 and 1.00:1.01.¹ The saccharification yields of the recovered cellulose were found to be high, 75-89% as the base:acid ratios were varied, but never reached higher than 90% (Figure 2.1). The

enzymes inhibition by the IL residues in the pretreated polysaccharides was thought to be the reason behind this.¹

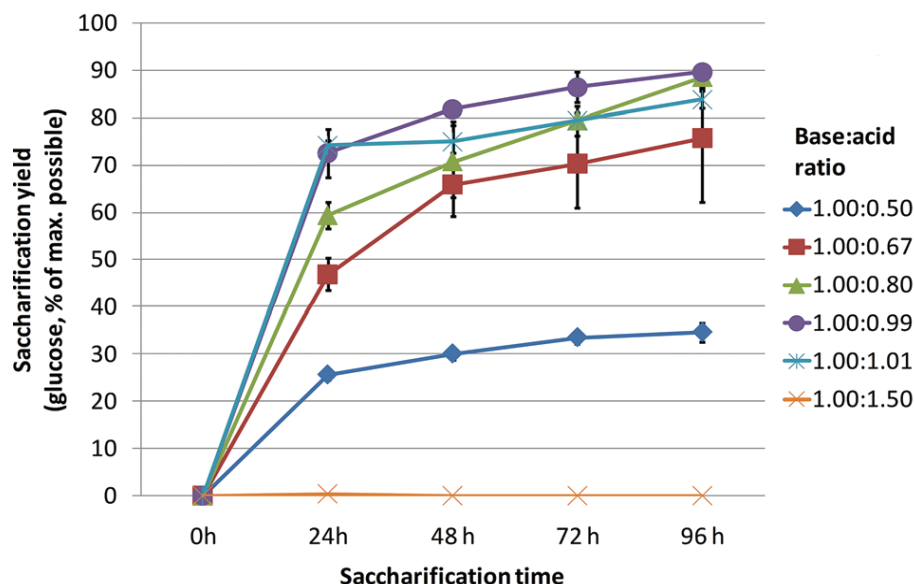


Figure 2.1 Saccharification yield (glucose %) from pulp (carbohydrate-rich-material) recovered from the pretreatment of *Miscanthus giganteus* with [HC₄im][HSO₄] at 120 °C for 24 h with 80% IL and 20% water mixture.¹

Recently, studies have reported that ILs are problematic for the saccharification process as they are incompatible with the enzymes used. Engel *et al.* reported that the viscosity of ILs and their ionic strength reduces the activity of the enzyme, thus affecting the saccharification process.¹⁴⁶ The acidity or basicity of the IL residue could also change the pH of the saccharification media thus affecting cellulase performance. Wahlstrom *et al.*, also showed that cellulase-cellulose binding and the function of the carbohydrate-binding modules are very sensitive to the presence of ILs.¹⁴⁷ Karim (2015) showed that in the saccharification of glucose, 1% (v/v) [HC₄im][HSO₄] reduces the glucose yield to 35.98% from 99.8% glucose yield in the absence of the IL (Table 2.1).¹⁴⁸

Table 2.1 Average glucose yield and pH of the media with different concentration of [HC₄im][HSO₄].¹⁴⁸

Concentration, v/v %	Glucose yield, %	pH
0	99.8	4.8
1	35.98	3.31
2	n.d	2.41
5	n.d	1.96
10	n.d	1.15

With these findings, it is clear that the presence of IL residue in the regenerated carbohydrate-rich materials (CRMs) will severely interfere with the saccharification process. To avoid this, regeneration and separation steps need to be extensively performed during the recovery process, followed by a thorough washing step. Zahari (2015) revealed that the process of washing the recovered CRMs from the IL pretreatment is indeed important to remove the IL residue physically absorbed onto the CRMs.¹²² Two methods of washing, Buchner filtration and Soxhlet extraction were compared. The results for CRM composition and saccharification yield showed that there is a significant difference between the two methods (Figure 2.2). Notably, the saccharification yield for the Soxhlet method was 69.2% compared to 48.8% for the Buchner method.

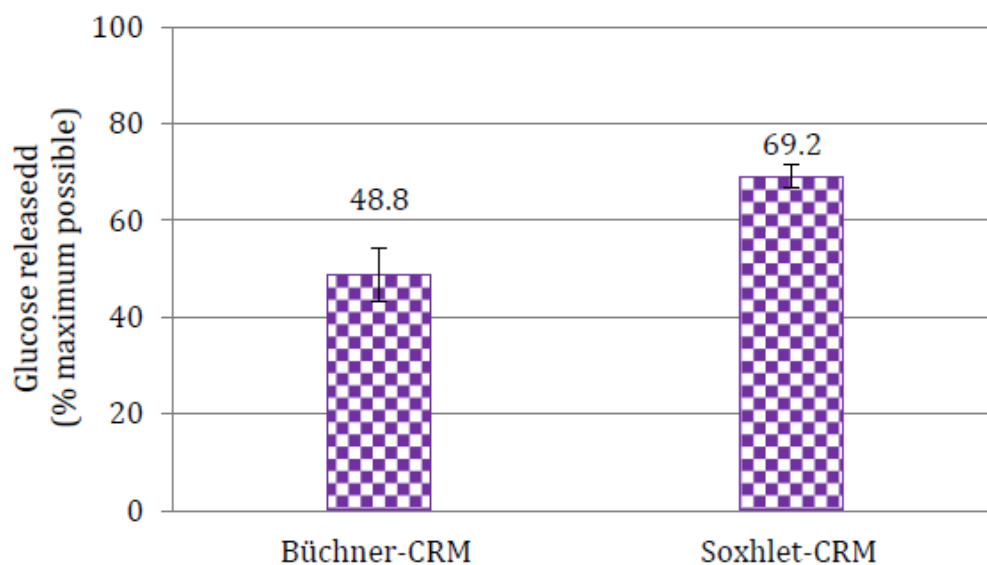


Figure 2.2 Comparison of glucose yield of enzymatic saccharification of recovered CRMs from *Miscanthus* pretreatment with $[\text{HC}_4\text{im}][\text{HSO}_4]$ washed via Buchner and Soxhlet methods.¹²²

Nonetheless, even with the extensive washing, 100% saccharification yield could not be achieved, which led Zahari to speculate that chemisorption of the anion $[\text{HSO}_4]^-$ may have occurred. They pretreated a model cellulose, Sigmacell MCC (microcrystalline cellulose obtained from cotton linters), with $[\text{HC}_4\text{im}][\text{HSO}_4]$ in water at 120 °C, reflecting the pretreatment process. The results showed that even after washing with ethanol (Soxhlet), the $[\text{HC}_4\text{im}][\text{HSO}_4]$ still remained in the pretreated MCC. From the elemental analysis (Table 2.2), small quantities of nitrogen and sulfur were identified in the samples, indicating that both the cation, $[\text{HC}_4\text{im}]^+$ and the anion $[\text{HSO}_4]^-$ may have reacted with or have been adsorbed on to the MCC. MALDI-ToF results showed that there are sulfur containing oligosaccharides indicating that the $[\text{HSO}_4]^-$ had chemically reacted with the cellulose (Figure 2.3), although the exact chemical bond that formed could not be identified.

Table 2.2 CHNS elemental analysis results of the Untreated-MCC and the Treated MCC-[HC₄im][HSO₄].

Chemical Elements	Theoretical of cellulose	Wt %	
		Untreated MCC	Treated MCC
C	44	41.5 ± 0.006	41.7 ± 0.02
H	7	6.12 ± 0.01	6.12 ± 0.007
N	-	-	0.54 ± 0.02
S	-	-	0.54 ± 0.03

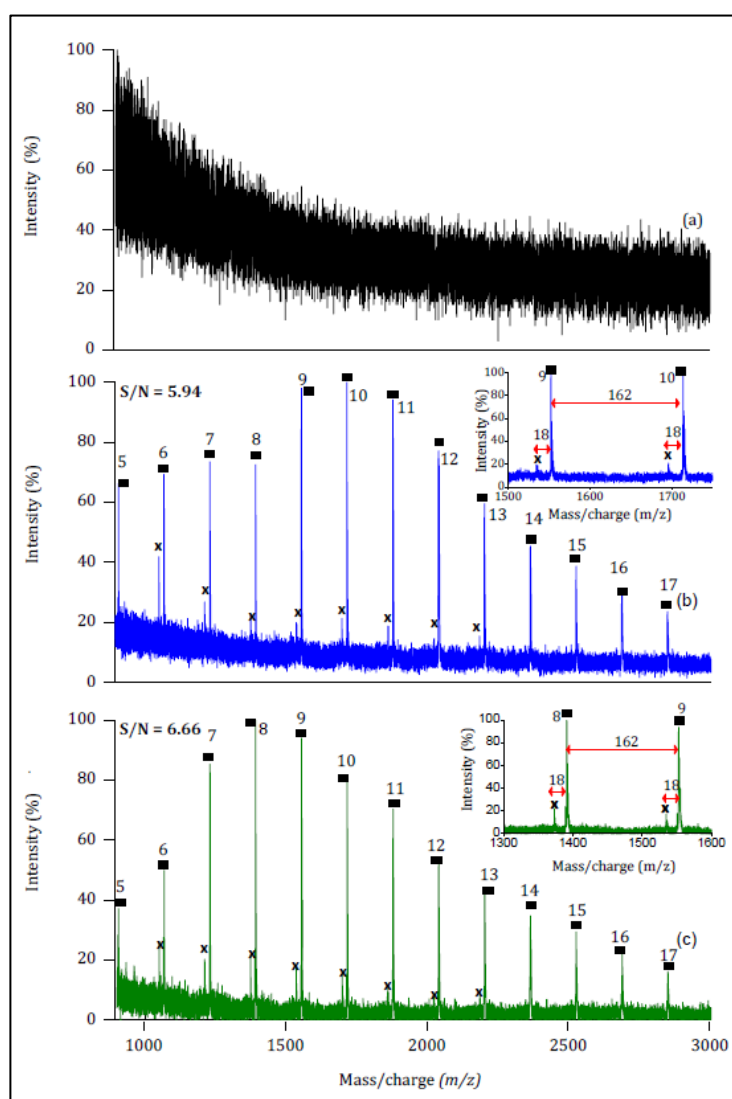


Figure 2.3 Negative ion MALDI spectra of (a) Untreated-MCC; (b) Treated MCC-[HC₄im][HSO₄], and; (c) Treated MCC-[C₄C₁im][HSO₄]. (■) represents anions of sulfur-containing oligosaccharides, [((C₆H₁₀O₅)_nOSO₃H)-H], (x) represents anions of deprotonated dehydrated sulfur-containing oligosaccharides, [((C₆H₁₀O₅)_nOSO₃H)-H]-H₂O (n = degree of polymerisation).¹²²

2.1.2 Reactivity of the hydroxyl groups in cellulose

The modification of cellulose is typically performed by replacing three free hydroxyl groups in one unit of glucose in the cellulose chain with other functional groups, such as acetyl and nitro groups, to produce new cellulose films or fabrics.¹⁴⁹ Etherification and esterification of cellulose can be done depending on the intended use and application.^{150,151} Overview of the modifications of cellulose that arise from substituting the hydroxyl groups are depicted in Figure 2.4.

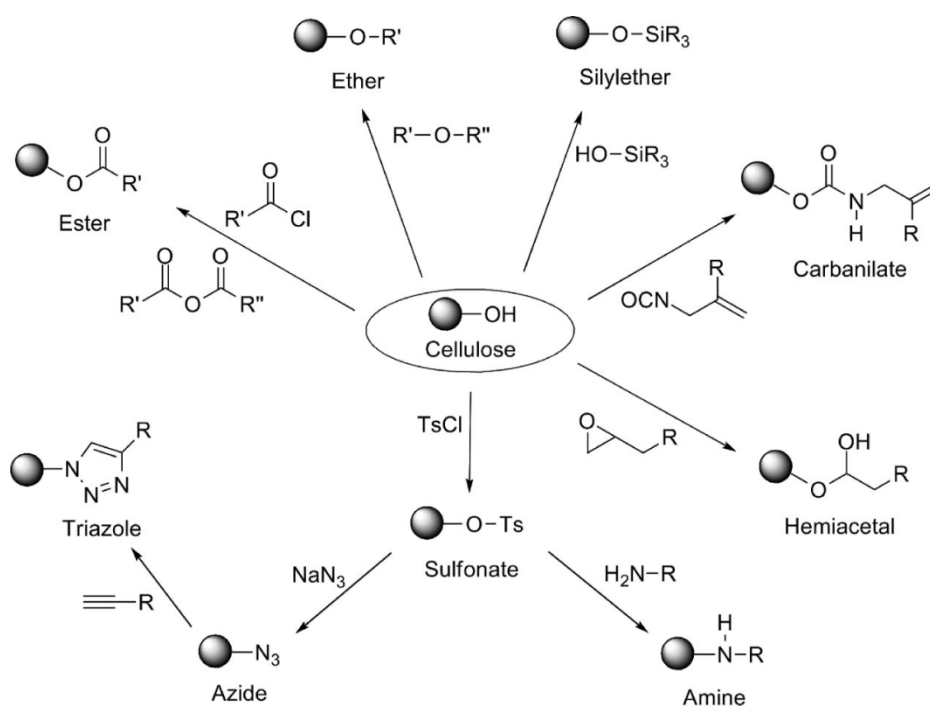
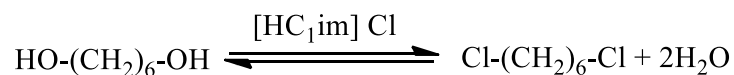


Figure 2.4 Overview of cellulose functionalisation pathways.²⁷

As the hydroxyl groups of cellulose are easily substituted, in the event of pretreatment with an IL containing the $[HSO_4]^-$ anion, the hydroxyl groups of the pretreated cellulose are expected to be substituted by the $[HSO_4]^-$ anion. Besides, sulfation of cellulose has previously been done using sulfuric acid, sulphur trioxide, chlorosulfonic acid, nitrosylsulfuric acid, sulfuryl chloride and sulfamic acid as the sulfating agents.^{152,153}

2.1.3 ILs as nucleophiles

There are studies reporting the conduct of nucleophilic substitution reactions in ILs,^{81,154,155} however an understanding of whether IL anions act as good nucleophiles and undergo nucleophilic substitution reactions has not been fully developed and the consequences of the nucleophile being part of the solvent system has not been completely explored. BASF has obtained a patent for a process where ILs act as the nucleophile, solvent and acid at the same time for a nucleophilic substitution process (Scheme 2.1).¹⁵⁶



Scheme 2.1 Nucleophilic substitution reaction of 1,6-hexanediol with [HC₁im]Cl.

To (2012) has reported in her PhD thesis the ability of the IL anions to act as a nucleophile by examining their reaction with *p*-methylbenzyl alcohol (Figure 2.5).⁸⁴ [HC₄im]Cl, [HC₄im][H₂PO₄] and [C₂C₁im][OAc] were used in her study together with added conjugated acids and the reactions performed predominantly at 120 °C for 24 h (Table 2.3). A collaborative experiment using [HC₄im][HSO₄] was performed between us, and these results will be discussed later in this chapter.

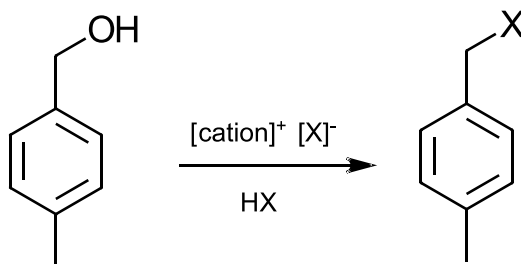


Figure 2.5 Expected reaction between 4-methylbenzyl alcohol and ionic liquids with respective acids. X⁻ = Cl⁻, [HSO₄]⁻, [H₂PO₄]⁻, and [OAc]⁻.⁸⁴

Table 2.3 Nucleophilic substitution reaction of *p*-methylbenzyl alcohol with [HC₄im]Cl, [HC₄im][H₂PO₄] and [C₂C₁im][OAc].⁸⁴

Ionic liquid + mol% acid*	Temperature (°C)	Time (h)	Conversion (%)
[HC ₄ im]Cl	120	24	No reaction
[HC ₄ im]Cl + 50 mol% HCl	120	24	100
[C ₄ C ₁ im]Cl	120	24	No reaction
[C ₄ C ₁ im] Cl + 50 mol% HCl	120	24	100
[HC ₄ im][H ₂ PO ₄]	120	24	No reaction
[HC ₄ im][H ₂ PO ₄] + 30 mol% H ₃ PO ₄	120	24	11
[HC ₄ im][H ₂ PO ₄] + 30 mol% H ₃ PO ₄	140	24	24
[C ₄ C ₂ im][OAc]	60	24	No reaction
[C ₂ C ₁ im][OAc] + 6 mol% AcOH	60	24	No reaction
[C ₂ C ₁ im][OAc]	120	24	No reaction
[C ₂ C ₁ im][OAc] + 6 mol% AcOH	120	24	No reaction

*mol% acid quoted is equivalent to the 1 to 1 molar ratio of IL to acid

Table 2.3 reveals that ILs containing the Cl[−] anion could not react with the alcohol without the addition of hydrochloric acid, but were able to achieve full conversion once hydrochloric acid was added. This is because the presence of hydrochloric acid leads to the protonation of the hydroxyl group, forming the more effective H₂O leaving group, and rendering the attack of the Cl[−] anion possible. A similar mechanism is present for the [H₂PO₄][−] ILs, which only reacted with added phosphoric acid. These ILs gave very low conversions even at a higher temperature (140 °C). This is due to the reduced acidity and concentration of phosphoric acid (pKa 2) compared to hydrochloric acid (pKa -8) limiting the protonation of the hydroxyl group. There was no reaction at all for the IL with the [OAc][−] anion, even with added acetic acid. Acetate can act as a nucleophile but

the weak acidity of acetic acid (pKa 4.7) or its low concentration resulted in no conversion of the alcohol being observed.

It appears that the acid strength is critical to reactivity hence $[\text{HSO}_4]^-$ ILs will be explored as the strength of the residual sulfuric acid will likely offset the poor nucleophilicity of $[\text{HSO}_4]^-$. Given the importance of these ILs in the Ionosolv process this will have consequences for understanding the fate of cellulose treated by this process.

2.2 Aims and Objectives

The first aim of this chapter is to study the ability of the $[\text{HSO}_4]^-$ anion to perform substitution reactions with hydroxyl groups, to develop a greater understanding of how cellulose will react under pretreatment conditions in the Ionosolv process. Preliminarily, several alcohols will be reacted with 1-butylimidazolium hydrogen sulfate ($[\text{HC}_4\text{im}][\text{HSO}_4]$) to see if reaction occurs. *p*-Methylbenzyl alcohol was then used as a model compound and its nucleophilic substitution reactions with three $[\text{HSO}_4]^-$ ILs; 1-butylimidazolium hydrogen sulfate, $[\text{HC}_4\text{im}][\text{HSO}_4]$ and 1-butyl-3-methylimidazolium hydrogen sulfate, $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, and the role of additional H_2SO_4 was explored. Kinetics of these reactions will be measured to observe the effect of acid concentration on the reaction rates and yields. Another aim of this chapter is to elucidate the mechanism of the reaction by performing a Hammett study to understand the effect of electronics on the reaction rate. This was achieved using the Hammett equation and studying the reaction rates of benzyl alcohols with different substituents with $[\text{HSO}_4]^-$ ILs and added sulfuric acid.

This chapter aims to understand the capacity of $[\text{HSO}_4]^-$ ILs to act dually as a solvent and a nucleophile in a reaction, and to reveal that they are not innocent solvents, especially in the absence of water.

2.3 Results and Discussion

2.3.1 Reactivity of alcohols in $[\text{HC4im}][\text{HSO}_4]$

To understand the reactivity of the hydroxyl groups in cellulose in the presence of $[\text{HSO}_4]^-$ ILs, a variety of alcohols have been explored as model compounds including methanol, 1-butanol, 2-butanol, isopropyl alcohol, and phenol. Using ^1H NMR, all of the alcohols were found to react after 24 h at 80 °C, with the exception of phenol. The yields of all reactions were calculated from the relative integration of CH signals adjacent to the hydroxyl group in the product and the substrate. The yields are listed in Table 2.4. All of the new CH_2 signals are matched with their predicted $\text{CH}_2\text{-OSO}_3\text{H}$ signals, where the latter is expected to appear on the left side of the spectrum to the deshielded region. Figures 2.6–2.10 show the comparison between the spectra of each reaction at 0 h and 24 h. The spectra of the reactions of methanol, 1-butanol, 2-butanol, and isopropyl alcohol at 24h show that there are new CH signals at 3.42, 3.75, 4.14, and 4.36 ppm, downfield of the substrate peaks adjacent to the hydroxyl group, suggesting that the hydroxyl group of the alcohol has been substituted by $[\text{HSO}_4]^-$. For the reaction with phenol, the spectrum at 24 h remains almost the same as the initial spectrum, although small peaks appear at 7.20–7.26 ppm. These new peaks are too small to

integrate and overlap with the reactant peaks, making any conversion difficult to determine.

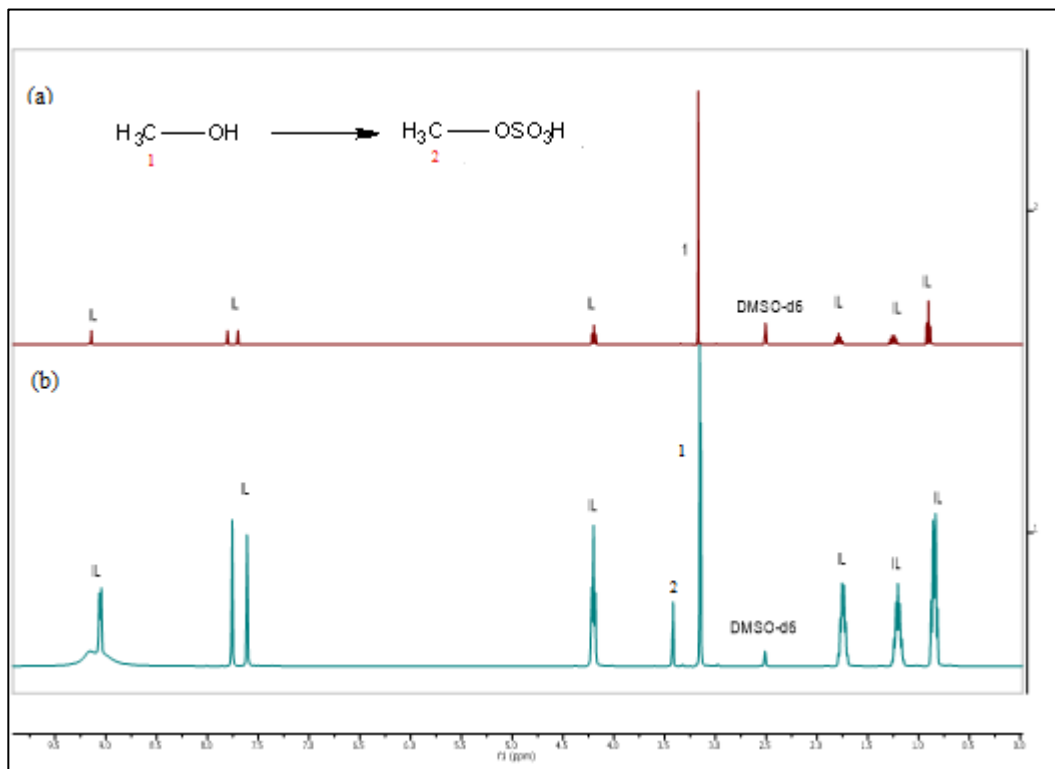


Figure 2.6 0 (a) and 24 h (b) ^1H NMR of methanol reaction with $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80°C .

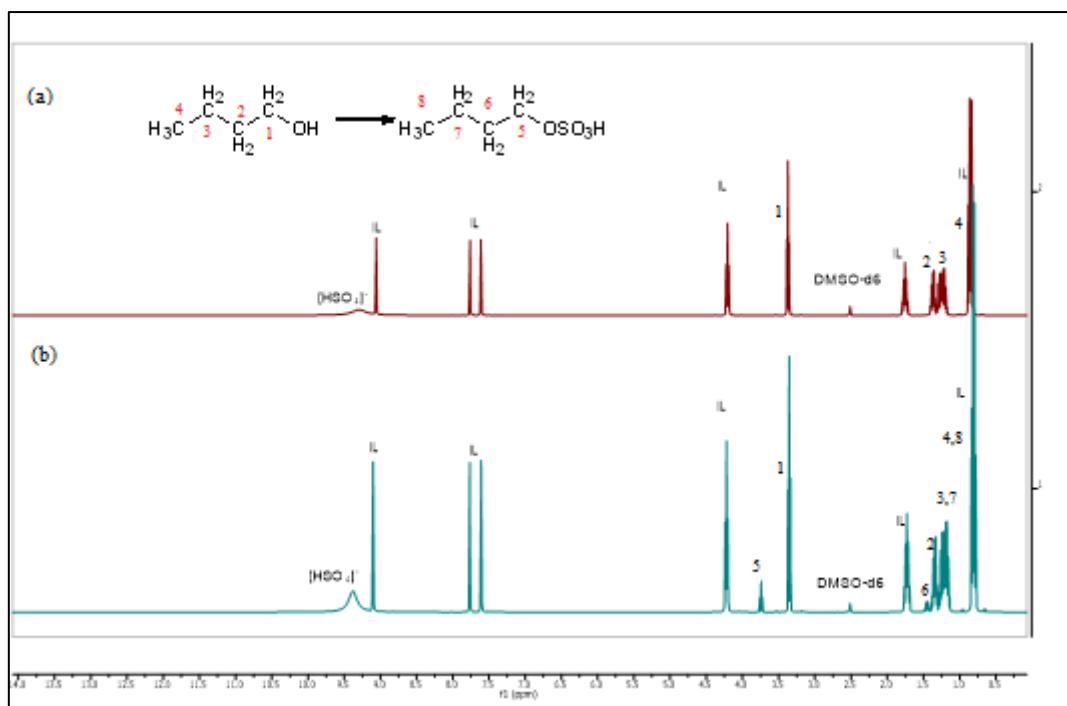


Figure 2.7 0 (a) and 24 h (b) ^1H NMR of 1-butanol reaction with $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80°C .

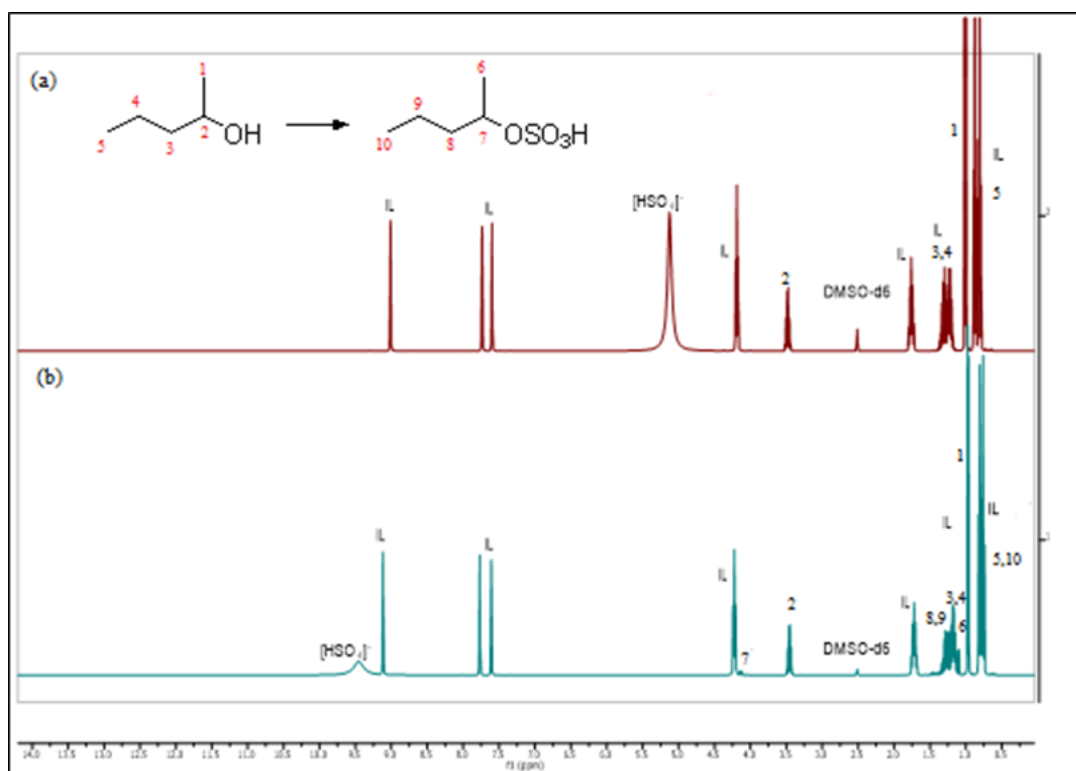


Figure 2.8 0 (a) and 24 h (b) ^1H NMR of 2-butanol reaction with $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80°C .

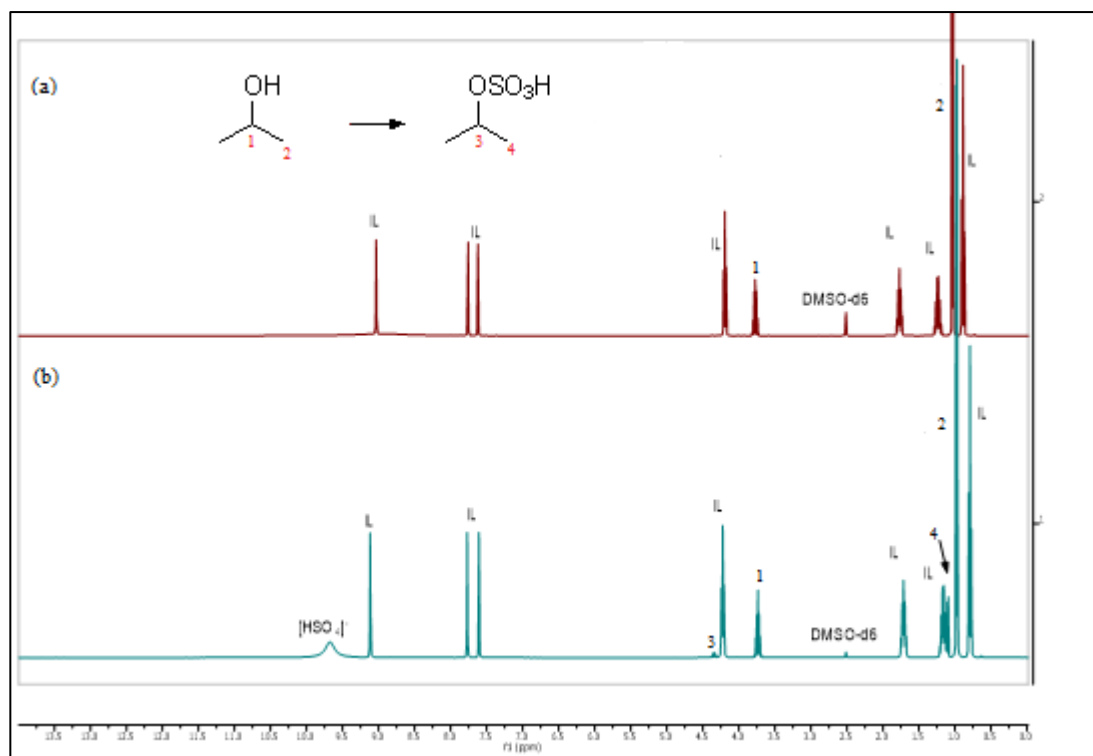


Figure 2.9 0 (a) and 24 h (b) ^1H NMR of isopropanol reaction with $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80°C .

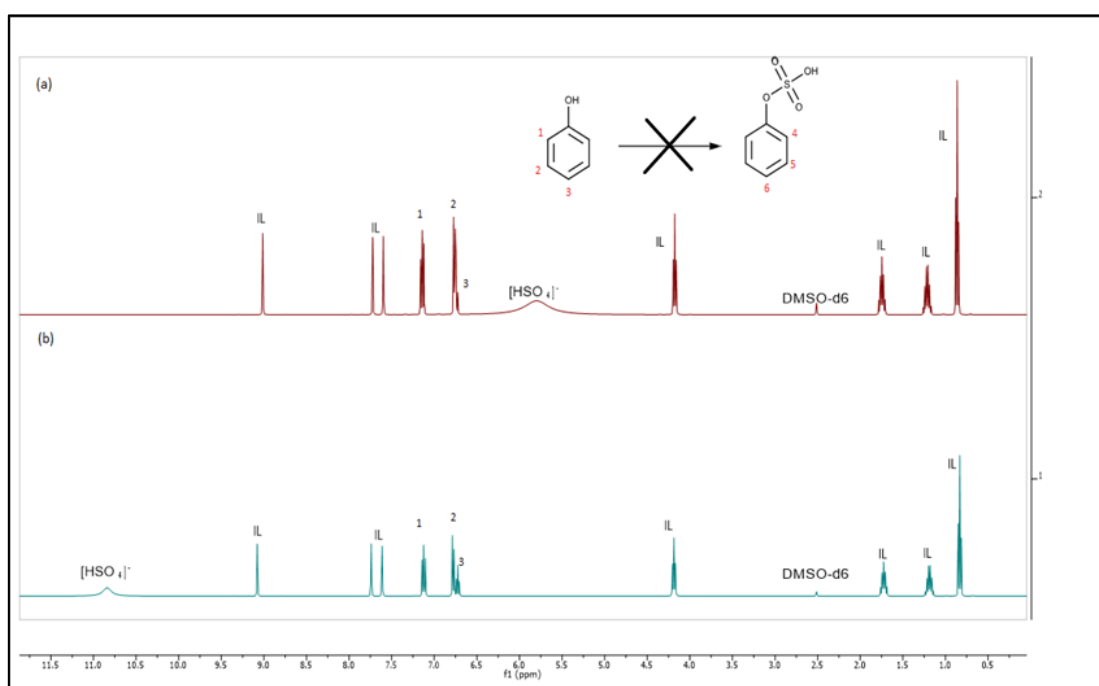


Figure 2.10 0 (a) and 24 h (b) ^1H NMR of phenol reaction with $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80°C .

Table 2.4 Yields of substitution products arising from the nucleophilic substitution reaction of alcohols and [HC₄im][HSO₄].

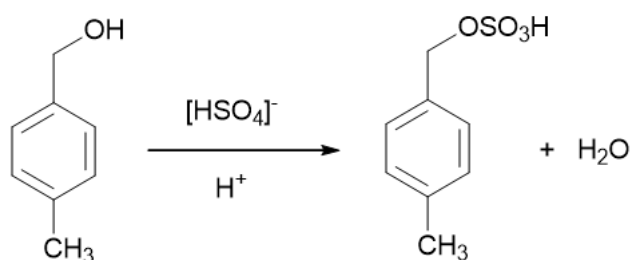
Alcohol	Type	Yield (%)
Methanol	Primary	15
1-Butanol	Primary	11
2-Butanol	Secondary	9
Isopropyl alcohol	Secondary	10
Phenol	Aromatic	n.d
Benzyl alcohol	Secondary	11

While the overall conversions of the substitution reactions are low, Table 2.4 shows that hydroxyl groups of primary and secondary alcohols can undergo nucleophilic substitution reactions with the [HSO₄][−] anion. As for phenol, the lack of hydroxyl substitution observed after 24 h is could be due to low possibility of nucleophilic aromatic substitution to occur. This substitution which occurs by addition-elimination mechanism where the initial addition step leads to a loss of the aromaticity of the benzene ring. This is highly energetically disfavoured and would only happened with a highly activated phenol.¹⁵⁷

2.3.2 Nucleophilic substitution of benzyl alcohol with [HSO₄][−] ILs

In collaboration with Trang To, the nucleophilic substitutions of 4-methylbenzyl alcohol with [HSO₄][−] ILs were performed using [HC₄im][HSO₄] and [C₄C₁im][HSO₄] as solvents, acids and nucleophiles at 120 °C (Scheme 2.2). *p*-Methylbenzyl alcohol was chosen because it is easy to monitor the CH₂ peak using ¹H NMR compared to other alcohols and it is not able to dehydrate to form alkenes (Fig. 2.11). Reaction temperature

was set at 120 °C to promote low viscosity and full conversion. Product yields were determined from ^1H NMR integrals, as described in section 2.3.1.



Scheme 2.2 Expected reaction of 4-methylbenzyl alcohol with $[\text{HSO}_4]^-$ ILs.

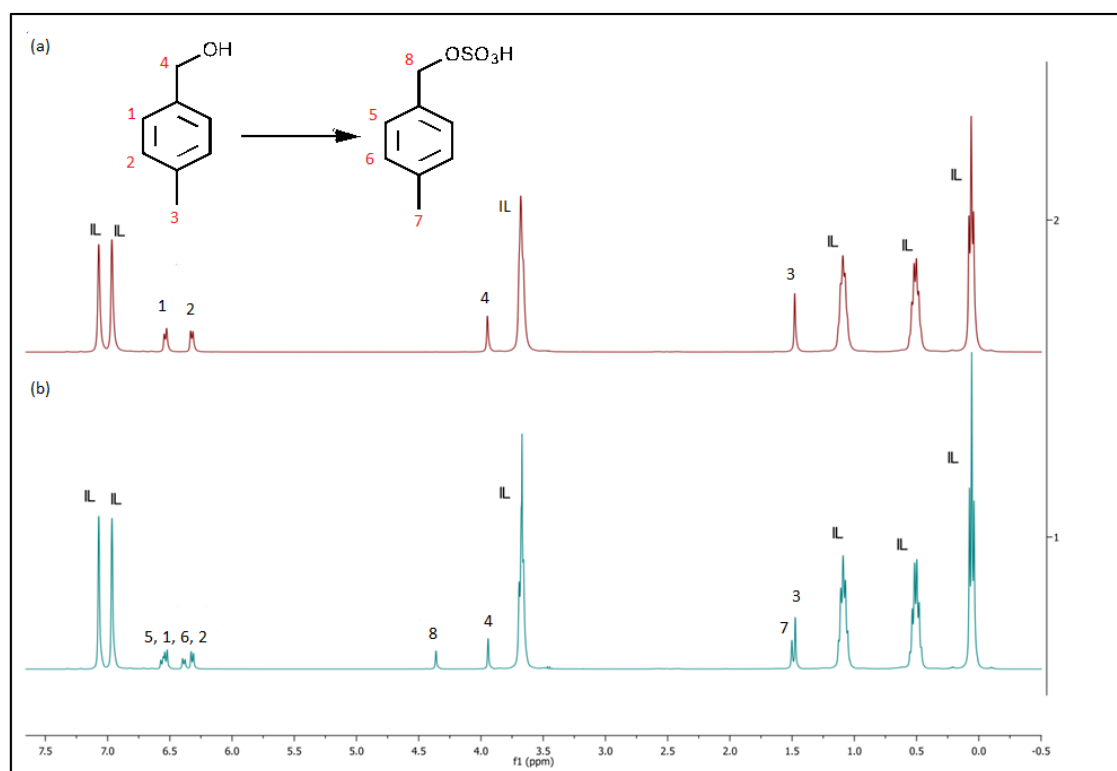


Figure 2.11 ^1H NMR spectra of the reaction of *p*-methylbenzyl alcohol with $[\text{HC}_4\text{im}][\text{HSO}_4]$ at (a) 0 and (b) 24 h at 120°C.

The appearance of a new CH_2 signal at 4.31 ppm (Figure 2.11), a downfield shift of 0.28 ppm from the CH_2 signal of *p*-methylbenzyl alcohol, with relatively small changes in

chemical shift for the other new CH signals, indicates that the substitution of the hydroxyl group has occurred within the IL. To explore the effect of changing the IL and the role of acidity, further reactions were conducted in [C₄C₁im][HSO₄] and with added sulfuric acid. Both reactions of the compound with neat [HC₄im][HSO₄] and [C₄C₁im][HSO₄] produced the same yields, 88%. The addition of 6 mol% sulfuric acid to either IL unexpectedly gave a lower yield (83% in both cases). This result may arise from the water content of sulfuric acid which led the reaction to reach equilibrium at a lower concentration of product than in the neat ILs. Both ILs and sulfuric acid are very hygroscopic, furthermore the acid used was not properly dried before it was added into the IL solution. Because it has strong affinity for water, the acid could prevent the complete removal of water molecules during the drying process of the IL and acid mixture. In the presence of water, the acidity of the [HSO₄]⁻ anion of the IL would be reduced and, more significantly, the benzyl sulfate will be hydrolysed back to alcohol. The hydrolysis of alkyl sulfates has been well-documented and is likely to lead to an equilibrium distribution of products in the presence of water.¹⁵⁸

A reaction under model biomass pretreatment conditions, i.e. with 20% water, gave a very low yield of 20%. This emphasises the hypothesis mentioned above where higher water content decreased the yield of the reaction when it promoted the reaction reached equilibrium faster than the dried reactions.

Table 2.5 The percentage conversion of the nucleophilic substitution reactions of *p*-methylbenzyl alcohol with [HC₄im][HSO₄] and [C₄C₁im][HSO₄].

Ionic Liquid	Yield (%)
[HC ₄ im][HSO ₄]	88
[HC ₄ im][HSO ₄] + 1 mol% H ₂ SO ₄ [*]	83
[HC ₄ im][HSO ₄] + 6 mol% H ₂ SO ₄ [*]	83
[HC ₄ im][HSO ₄] + 20% wt H ₂ O ^a	20
[C ₄ C ₁ im][HSO ₄]	87
[C ₄ C ₁ im][HSO ₄] + 1 mol% H ₂ SO ₄ [*]	83
[C ₄ C ₁ im][HSO ₄] + 6 mol% H ₂ SO ₄ [*]	83

^a Similar conditions to the biomass pretreatment

^{*} mol% represents the molar ratio of sulfuric acid to the IL in the mixture e.g: 50 mol% is equivalent to a 1 : 1 molar ratio of H₂SO₄ : IL

2.3.3 Kinetic Studies

Kinetic investigations of the benzyl alcohols' reactions in [HC₄im][HSO₄] or [C₄C₁im][HSO₄] were performed to study the rates of the reaction as well as the effect of the added sulfuric acid on the rate of the reaction. Finally, from this kinetic data, mechanistic insight will be attained using the Hammett equation. The kinetic experiments were conducted using ¹H NMR. A sealed DMSO-*d*₆ capillary was used to lock the samples and as an external chemical shift reference. Since the peak integration is proportional to the concentration of the reactant and product, the rates were calculated from the ratio of concentration of the remaining benzyl alcohol [A] with the sum of the concentration of product and the remaining benzyl alcohol [A₀]. As no alternative products were observed by ¹H NMR over the course of the reaction, the implicit assumption inherent to this approach of 100% selectivity to the desired product is satisfied. Based on the linearity of the ln ([A]/[A₀]) vs *time* graphs, all reactions for this study obeyed *pseudo*-first-order kinetics with regards to the benzyl alcohol, where IL

was used in excess, (10 mol equivalent to the benzyl alcohol). Observed rate constant, k_{obs} for the reactions were obtained from the gradient of the graphs.

2.3.3.1 Hammett Equation

By measuring the reaction rates of different *p*-substituted benzyl alcohols, Hammett plots can be generated and the effect of different substituents which include electronic withdrawing groups (EWG) and electron donating groups (EDG) on the rate of reactions can be studied and give insight into the mechanism of the reaction.

The Hammett equation is a way to understand the electronic changes that occur on progression to the transition state of a reaction by examining the influence of electron-donating and electron-withdrawing groups on otherwise similar reactions featuring aromatic compounds.¹⁵⁹ Initially, Hammett studied the pKa values of benzoic acids with different substituents (Scheme 2.3) before he introduced a new parameter, σ .



Scheme 2.3 Ionisation of benzoic acid and substituted benzoic acids.

This new parameter is defined as the substituent constant where its value reveals the substituent electronic influence, where EWGs have positive values while EDGs have negative values. σ is defined from Equation 2.1.1:

$$\sigma_x = \text{pKa (x)} - \text{pKa (H)} \quad (2.1.1)$$

Where x is the substituted benzoic acid and H is benzoic acid. σ for substituents at meta or para positions are called σ_m and σ_p . Only *para*-substituted benzyl alcohols were used in this study thus, Table 2.6 shows the values of σ_p for the selected substituents.

Table 2.6 σ_p values of selected substituents

Substituent	σ_p
H	0
Me	-0.17
OMe	-0.27
Cl	0.23
CF ₃	0.54
NO ₂	0.78

The Hammett equation (Equation 2.1.2) has two key variables, σ_x (substituent constant) and ρ (reaction constant), which, once enumerated, allow the sensitivity of the reaction to electronic effects to be observed.¹⁶ In this equation, k_X is the rate constant for the substituted reactant, and k_H is the rate constant for the non-substituted reactant.

$$\text{Log } \frac{k_x}{k_H} = \sigma_x \rho \quad (2.1.2)$$

ρ , the reaction constant measures the sensitivity of a reaction to the electronic effects of the substituents. ρ is generally determined by plotting $\log(k_x/k_H)$ or $\log(K_x/K_H)$ against the σ value of the respective aromatic derivative, with ρ representing the slope of this curve. Positive ρ values mean that the reaction is accelerated by EWGs, because the electrons flow towards the aromatic ring and build up a negative charge in the transition state of the rate-determining step (RDS). Alternatively, negative ρ values show that the

reaction is accelerated by EDGs because the electrons flow away from the aromatic ring and build up positive charge in the transition state of the RDS.¹⁶⁰

Hammett plots are not always linear. A nonlinear Hammett plot can indicate a change in mechanism or RDS as the electronic properties of the substituents are varied. Nucleophilic substitution reactions of benzylic compounds often give upward V-shapes which have been related to a change in mechanism from S_N1 to S_N2. Substrates bearing an EDG are found to follow an S_N1 mechanism with a negative ρ value, while those having EWGs followed an S_N2 mechanism with a positive ρ value.¹⁶¹ Meanwhile, a downward V-shaped indicates a change in RDS in the reaction.¹⁶²

2.3.3.2 Kinetic measurements of the reaction of benzyl alcohols with [HC₄im][HSO₄]

Kinetic reactions of six benzyl alcohols; benzyl alcohol, *p*-methylbenzyl alcohol, *p*-methoxybenzyl alcohol, *p*-trifluoromethylbenzyl alcohol, *p*-chlorobenzyl alcohol, and *p*-nitrobenzylalcohol with neat [HC₄im][HSO₄] and with 1 mol% of sulphuric acid added were performed. The plot of $\ln [A]/[A_0]$ of the reactions of benzyl alcohol in neat [HC₄im][HSO₄] is shown in Figure 2.12 and the rest is in Appendix (A.2.1 – A.2.12). The k_{obs} of these reactions are shown in Table 2.7.

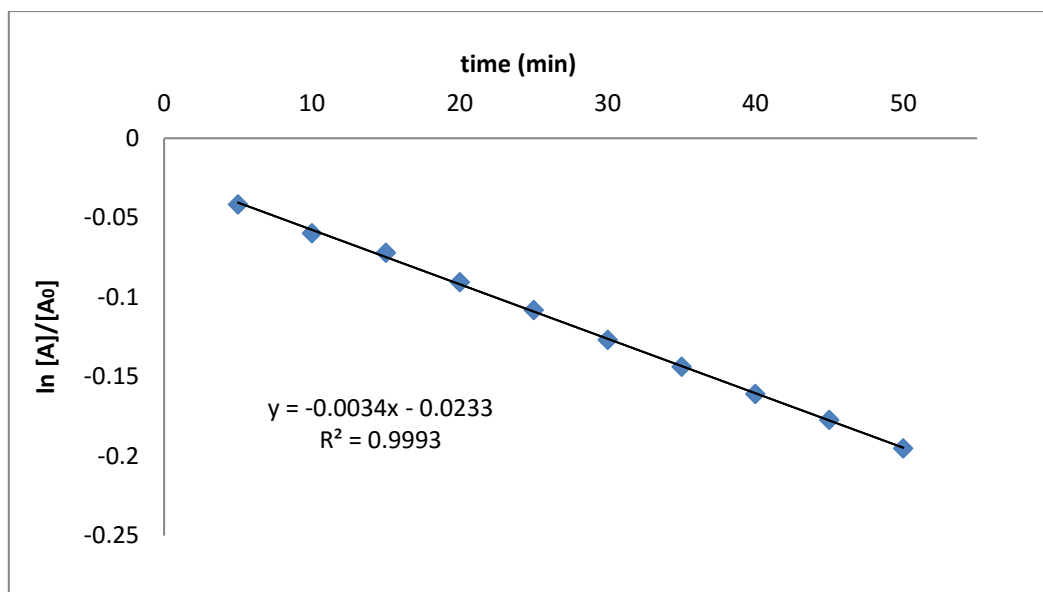


Figure 2.12 Plot of $\ln ([A]/[A_0])$ against time of benzyl alcohol in neat $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80 °C.

Table 2.7 k_{obs} and conversion values of the reactions of *p*-X-benzyl alcohol with $[\text{HC}_4\text{im}][\text{HSO}_4]$ and $[\text{HC}_4\text{im}][\text{HSO}_4] + 1 \text{ mol\% H}_2\text{SO}_4$.

<i>p</i> -X-benzyl alcohol	$[\text{HC}_4\text{im}][\text{HSO}_4]$ $k_{\text{obs}} (\text{min}^{-1})$	$[\text{HC}_4\text{im}][\text{HSO}_4] + 1 \text{ mol\% H}_2\text{SO}_4$ $k_{\text{obs}} (\text{min}^{-1})$
H	3.40×10^{-3}	1.34×10^{-1}
Me	2.10×10^{-3}	1.25×10^{-1}
OMe	1.62×10^{-4}	3.26×10^{-1}
Cl	3.10×10^{-3}	9.80×10^{-2}
CF ₃	3.40×10^{-3}	1.23×10^{-1}
NO ₂	2.80×10^{-3}	9.94×10^{-2}

From the six reactions in neat $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80°C, *p*-methoxybenzyl alcohol has the fastest rate (0.016 min^{-1}) followed by benzyl alcohol, *p*-trifluoromethylbenzyl alcohol, *p*-chlorobenzyl alcohol *p*-methylbenzyl alcohol and *p*-nitrobenzyl alcohol which have similar rates (0.0034 , 0.0034 , 0.0031 , 0.0028 and 0.0021 min^{-1} respectively). The same reactions with $[\text{HC}_4\text{im}][\text{HSO}_4]$ and 1 mol% H_2SO_4 added gave similar trends, where *p*-methoxybenzyl alcohol proceeded the fastest while others shows

similar rates. These reaction rates are 20 to 40 times faster than the rates in neat $[\text{HC}_4\text{im}][\text{HSO}_4]$ (Table 2.7). This is in agreement with the extra H_2SO_4 acting as a catalyst, accounting for the increase in the reaction rates.

Kinetic data for the same alcohols with 6 mol% of H_2SO_4 in $[\text{HC}_4\text{im}][\text{HSO}_4]$ were unable to be measured as the reactions were too fast and attained equilibrium within 2 minutes. A representative plot of $\ln ([\text{A}]/[\text{A}_0])$ against time is shown in Figure 2.13. The rest of the $\ln ([\text{A}]/[\text{A}_0])$ plots can be found in the Appendix (Figure A.2.25).

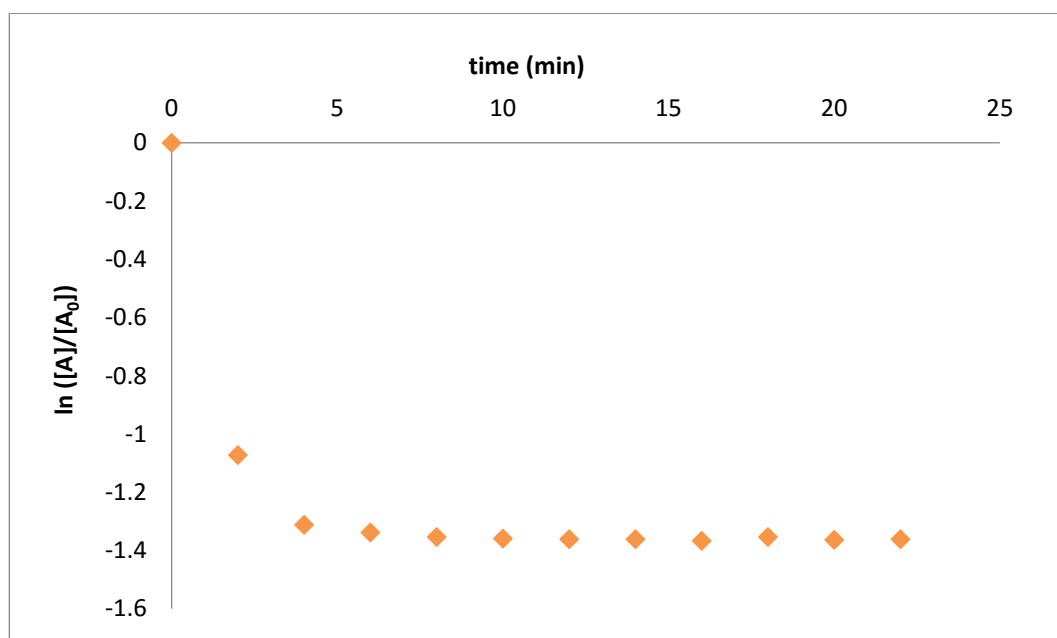


Figure 2.13 Plot of $\ln ([\text{A}]/[\text{A}_0])$ against time plots of *p*-trifluoromethylbenzyl alcohol in $[\text{HC}_4\text{im}][\text{HSO}_4] + 6 \text{ mol\% } \text{H}_2\text{SO}_4$ at 80°C

2.3.3.3 Kinetic measurements of the reaction of benzyl alcohols with [C₄C₁im][HSO₄]

The same six benzyl alcohols, (benzyl alcohol, *p*-methylbenzyl alcohol, *p*-methoxybenzyl alcohol, *p*-trifluoromethylbenzyl alcohol, *p*-chlorobenzyl alcohol, and *p*-nitrobenzylalcohol) were reacted in neat [C₄C₁im][HSO₄] and [C₄C₁im][HSO₄] with 1 mol% H₂SO₄ at 80 °C. The results are shown in Appendix (A.2.13 – A.2.24) and the k_{obs} of the reactions are summarised in Table 2.8.

Table 2.8 k_{obs} and conversion values of the reactions of *p*-X-benzyl alcohol with [C₄C₁im][HSO₄] and [C₄C₁im][HSO₄] + 1 mol% H₂SO₄.

<i>p</i> -X-benzyl alcohol	[C ₄ C ₁ im][HSO ₄]	[C ₄ C ₁ im][HSO ₄] + 1 mol% H ₂ SO ₄
	k_{obs} (min ⁻¹)	k_{obs} (min ⁻¹)
H	5.20 x 10 ⁻³	2.37 x 10 ⁻²
Me	7.11 x 10 ⁻³	3.44 x 10 ⁻²
OMe	1.21 x 10 ⁻²	5.12 x 10 ⁻²
Cl	4.80 x 10 ⁻³	1.97 x 10 ⁻²
CF ₃	4.70 x 10 ⁻³	2.99 x 10 ⁻²
NO ₂	5.70 x 10 ⁻³	2.23 x 10 ⁻²

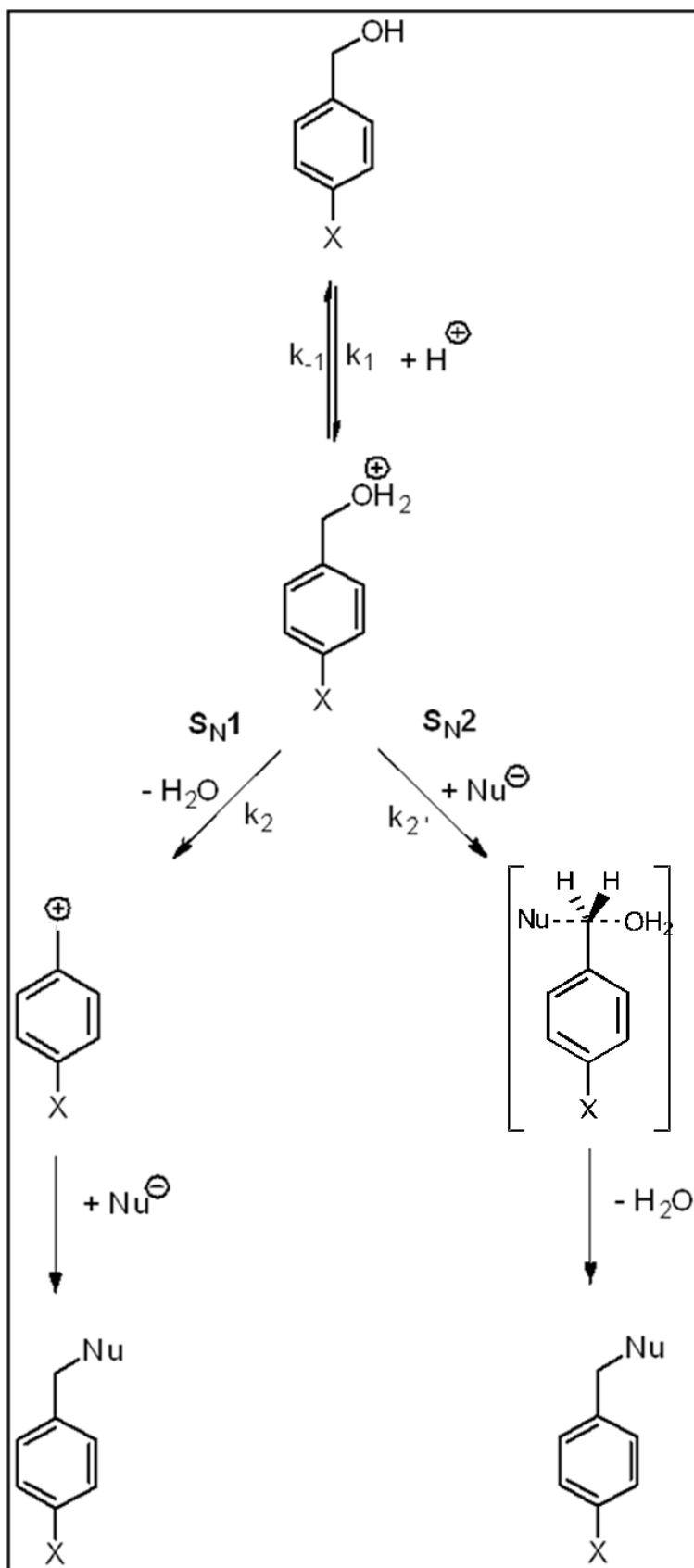
Reactions in neat [C₄C₁im][HSO₄] and with 1 mol% H₂SO₄ added show comparable trends with reactions in [HC₄im][HSO₄], where, *p*-methoxybenzyl alcohol proceed the fastest. As expected, the rates of the reactions with 1 mol% H₂SO₄ are faster than in neat [C₄C₁im][HSO₄], although unlike [HC₄im][HSO₄], in this case these rates are only 2–5 times faster, a much smaller increase. Although [HC₄im][HSO₄] is slightly more acidic (H_0 1.73) than [C₄C₁im][HSO₄] (H_0 1.96), where H_0 is the Hammett acidity of the neat liquids, the actual reason behind this is presumably due to the proton mobility is higher for the *protic* IL than the *aprotic* IL, where the proton can transfer from anion to cation,

not just from anion to another anion. The viscosity of the ILs also could be related to this as the viscosity measurement of [C₄C₁im][HSO₄] and [HC₄im][HSO₄] are 131.31 and 105.08 mPa·s respectively at 80 °C.¹⁶³

2.3.4 Electronic Effects and Mechanistic Insight; Hammett equation

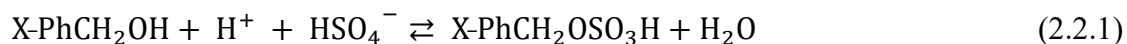
2.3.4.1 Generation of rate constants

Since the substituents of the benzyl alcohols span a wide range of both EDG (OMe, Me), H and EWG groups (Cl, CF₃, NO₂), it is possible that they could undergo either S_N1 or S_N2 reactions depending on the stabilisation of the carbocation intermediate after the protonation of the hydroxyl group.⁷⁴ Scheme 2.4 describes two possible reaction pathways for the benzyl alcohol nucleophilic substitution reactions. In the S_N1 pathway, the rate determining unimolecular step involves the departure of the leaving group and formation of the positively charged carbocation intermediate, X-PhCH₂⁺, whereas in S_N2 the rate limiting step involves both the attack of the anionic [HSO₄]⁻ and the departure of leaving group resulting in a much smaller net change in charge in the benzylic position.



Scheme 2.4 Possible mechanism for *p*-X-benzyl alcohol nucleophilic substitution reaction with $[\text{HC}_4\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$.

For the reaction in neat $[\text{HSO}_4]^-$ IL, where the anion ($[\text{HSO}_4]^-$) protonates the substrate, X-PhCH₂OH, the overall reaction is defined as below;



The protonation of the substrate is at equilibrium when the rates of the forward and reverse reaction are equal. The equilibrium constant for the reaction is written below:

$$K_{eq} = \frac{[\text{X-PhCH}_2(\text{OH}_2)^+]}{[\text{X-PhCH}_2\text{OH}] [\text{H}^+]} \quad (2.2.2)$$

The derivations of the rate constants are different depending on the respective mechanism. For S_N1, the RDS depends only on the concentration of protonated substrate while S_N2 depends on both the nucleophile and substrate concentration.

For the S_N1 route, the rate equation is:

$$r = k_2 [\text{X-PhCH}_2(\text{OH}_2)^+] \quad (2.2.3)$$

The concentration of X-PhCH₂(OH₂)⁺ depends upon the protonation equilibrium, which, assuming this equilibrium is rapidly established, gives:

$$[\text{X-PhCH}_2(\text{OH}_2)^+] = K_{eq} [\text{X-PhCH}_2\text{OH}] [\text{H}^+] \quad (2.2.4)$$

Applying equation 2.2.4 to equation 2.2.3:

$$r = k_2 K_{eq} [\text{X-PhCH}_2\text{OH}] [\text{H}^+] \quad (2.2.5)$$

While for the S_N2 mechanism, the rate equation is:

$$r = k_2, [\text{X-PhCH}_2(\text{OH}_2)^+][\text{HSO}_4^-] \quad (2.2.6)$$

Applying equation 2.2.4 to equation 2.2.6:

$$r = k_2, K_{eq} [\text{X-PhCH}_2\text{OH}][\text{H}^+][\text{HSO}_4^-] \quad (2.2.7)$$

From the Hammett equation, the ρ value of the reaction is depends on k_x which is the rate of all steps before and including the RDS. k_x of both routes are:

$$k_{X_{SN1}} = k_2 K_{eq} \quad (2.2.8)$$

$$k_{X_{SN2}} = k_2, K_{eq} \quad (2.2.9)$$

From equation 2.2.5 and 2.2.7, the final rate equations for S_N1 and S_N2 will be:

$$r = k_{X_{SN1}} [\text{X-PhCH}_2\text{OH}][\text{H}^+] \quad (2.2.10)$$

$$r = k_{X_{SN2}} [\text{X-PhCH}_2\text{OH}][\text{H}^+][\text{HSO}_4^-] \quad (2.2.11)$$

Since the reactions were performed under pseudo 1st order conditions (large excess of acid and anion), the pseudo-1st-order-rate equation for each reaction is:

$$r = k_{obs} [\text{X-PhCH}_2\text{OH}] \quad (2.2.12)$$

Thus, from this we can obtain k_x by combining equation 2.2.12 into 2.2.10 and 2.2.11.

So the k_x for S_N1 and S_N2 reactions can be calculated as in equation 2.2.13 and 2.2.14.

The concentration of H⁺ can be assumed as the same as the concentration of anion because the anion itself protonated the substrate.

$$k_{X_{SN1}} = \frac{k_{obs}}{[\text{H}^+]} = \frac{k_{obs}}{[\text{HSO}_4^-]} \quad (2.2.13)$$

$$k_{XSN2} = \frac{k_{obs}}{[H^+][HSO_4^-]} = \frac{k_{obs}}{[HSO_4^-]^2} \quad (2.2.14)$$

For the reactions with added sulfuric acid, the calculation of k_x from k_{obs} is different because the concentration of sulfuric acid should be included in the equation. In this case the $[H^+]$ is complicated to define because both sulfuric acid and $[HSO_4^-]$ are implicated in this value. Since all of the acid and IL concentrations are equal for each substrate, it is safe to assume that $[H^+]$ is constant between these reactions. This means it will not feature explicitly in the k_x/k_H term. Hence, the calculation of k_x from k_{obs} will be:

For the S_N1 route:

$$k_{XSN1} = k_{obs} \quad (2.2.15)$$

and for the S_N2 route:

$$k_{XSN2} = \frac{k_{obs}}{[HSO_4^-]} \quad (2.2.16)$$

2.3.4.2 Hammett plot of nucleophilic substitution reactions of *p*-X-benzyl alcohol with $[HC_4im][HSO_4]$ and $[HC_4im][HSO_4]$ with 1 mol% H_2SO_4

From the kinetic data, we are now able to study the effects of the substituents on the nucleophilic substitution reactions and their mechanism by using the Hammett equation. Since the exact mechanisms of the reactions are still uncertain at this stage, and since k_X

varies with mechanism thus, each reaction will be assessed assuming S_N1 and S_N2 mechanisms. Table 2.9 shows the k_X and $\log (k_X/k_H)$ values of each reaction assuming that the reactions proceed via S_N1 mechanism, where the k_X values are obtained from equation 2.2.13 for reactions in neat IL while equation 2.2.15 for reactions in IL with added sulfuric acid.

Table 2.9 Log (k_X/k_H) values for the nucleophilic substitution reaction of *p*-X-benzyl alcohol with [HC₄im][HSO₄] and [HC₄im][HSO₄] with 1 mol% H₂SO₄ obtained from S_N1 mechanism equation with σ

X	σ	Mechanism	[HC ₄ im][HSO ₄]		[HC ₄ im][HSO ₄] + 1 mol% H ₂ SO ₄	
			k_X	$\log (k_X/k_H)$	k_X	$\log (k_X/k_H)$
OMe	-0.27	S _N 1	1.92×10^{-4}	0.71	3.23×10^{-3}	0.32
Me	-0.17	S _N 1	2.41×10^{-5}	-0.20	1.36×10^{-3}	-0.05
H	0.00	S _N 1	3.79×10^{-5}	0.00	1.53×10^{-3}	0.00
Cl	0.23	S _N 1	3.47×10^{-5}	-0.04	1.22×10^{-3}	-0.09
CF ₃	0.54	S _N 1	3.80×10^{-5}	0.00	1.16×10^{-3}	-0.12
NO ₂	0.78	S _N 1	3.10×10^{-5}	-0.09	1.14×10^{-3}	-0.13

The resulting Hammett plots from Table 2.9 show non-linear correlations (Figure 2.14 and 2.15). There are two intersecting lines that look like concave upward deviation. This shows that there is a change in mechanism or transition state of the reaction, as one proceeds from EDG to EWG.¹⁶⁴

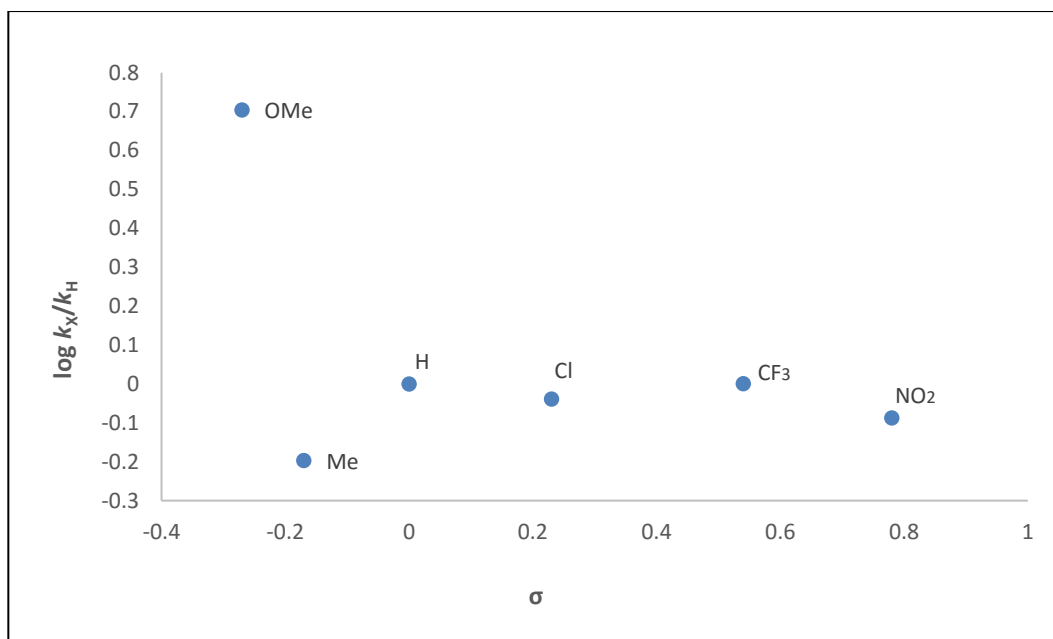


Figure 2.14 Hammett plots for nucleophilic substitution reaction of *p*-X-benzyl alcohol with [HC₄im][HSO₄] obtained from S_N1 mechanism.

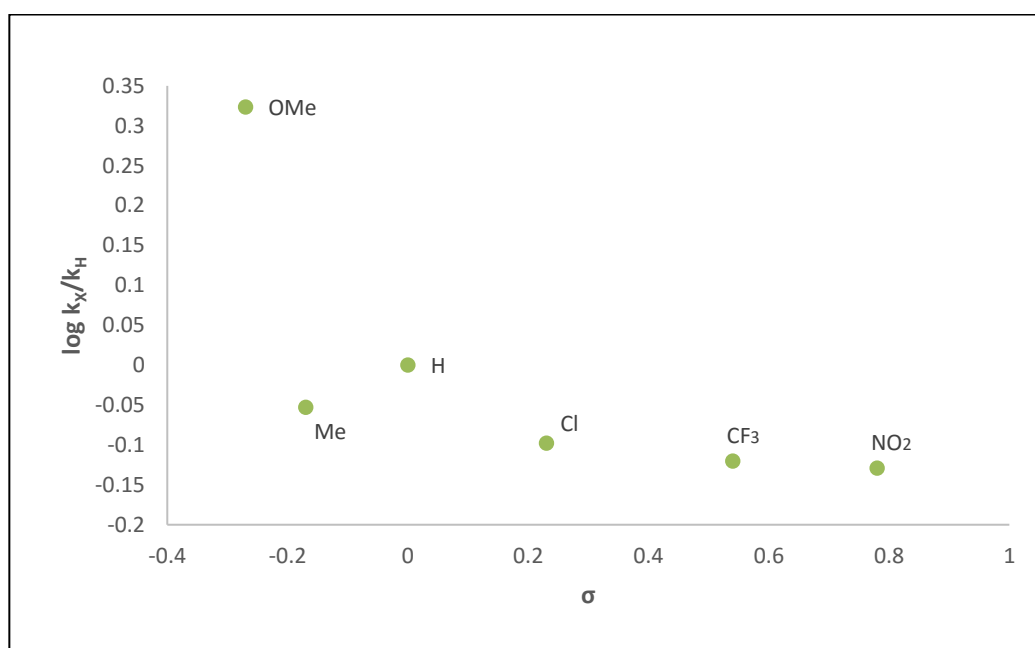


Figure 2.15 Hammett plots for nucleophilic substitution reaction of *p*-X-benzyl alcohol with [HC₄im][HSO₄] with 1 mol% H₂SO₄ obtained from S_N1 mechanism.

However, the S_N2 mechanism equation should also be tested to confirm the exact correlations. Table 2.10 shows their log (k_X/k_H) values, where the k_X values obtained from equation 2.2.14, and 2.2.16.

Table 2.10 Log (k_X/k_H) values for the nucleophilic substitution reaction of *p*-X-benzyl alcohol with [HC₄im][HSO₄] and [HC₄im][HSO₄] with 1 mol% H₂SO₄ obtained from S_N2 mechanism equation with σ

X	σ	Mechanism	[HC ₄ im][HSO ₄]		[HC ₄ im][HSO ₄] 1 mol% H ₂ SO ₄	
			k_X	log (k_X/k_H)	k_X	log (k_X/k_H)
OMe	-0.27	S _N 2	2.21 x 10 ⁻⁶	0.72	3.56 x 10 ⁻⁵	0.32
Me	-0.17	S _N 2	2.79 x 10 ⁻⁷	-0.18	1.50 x 10 ⁻⁵	-0.05
H	0.00	S _N 2	4.20 x 10 ⁻⁷	0.00	1.69 x 10 ⁻⁵	0.00
Cl	0.23	S _N 2	3.87 x 10 ⁻⁷	-0.04	1.35 x 10 ⁻⁵	-0.09
CF ₃	0.54	S _N 2	4.22 x 10 ⁻⁷	0.00	1.28 x 10 ⁻⁵	-0.12
NO ₂	0.78	S _N 2	3.44 x 10 ⁻⁷	-0.09	1.25 x 10 ⁻⁵	-0.13

Based on Table 2.10, calculations assuming a S_N2 mechanism also gave similar log (k_X/k_H) values and same pattern concave upward Hammett plots (Figure 2.16 and 2.17). This means, a change in RDS is unlikely to happen in these reactions but rather a change in mechanism.

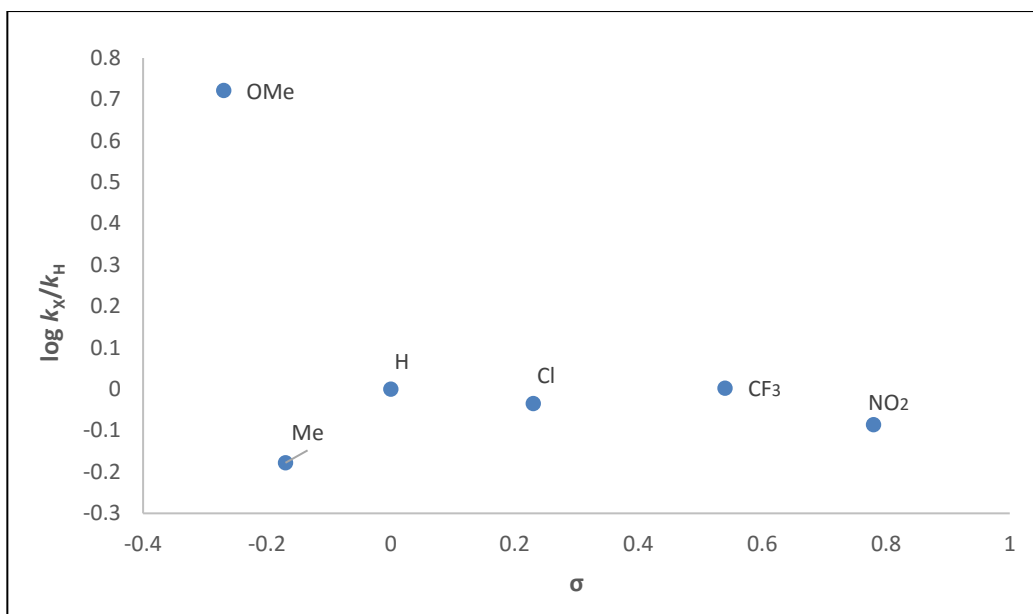


Figure 2.16 Hammett plots for nucleophilic substitution reaction of *p*-X-benzyl alcohol with [HC₄im][HSO₄] obtained from S_N2 mechanism.

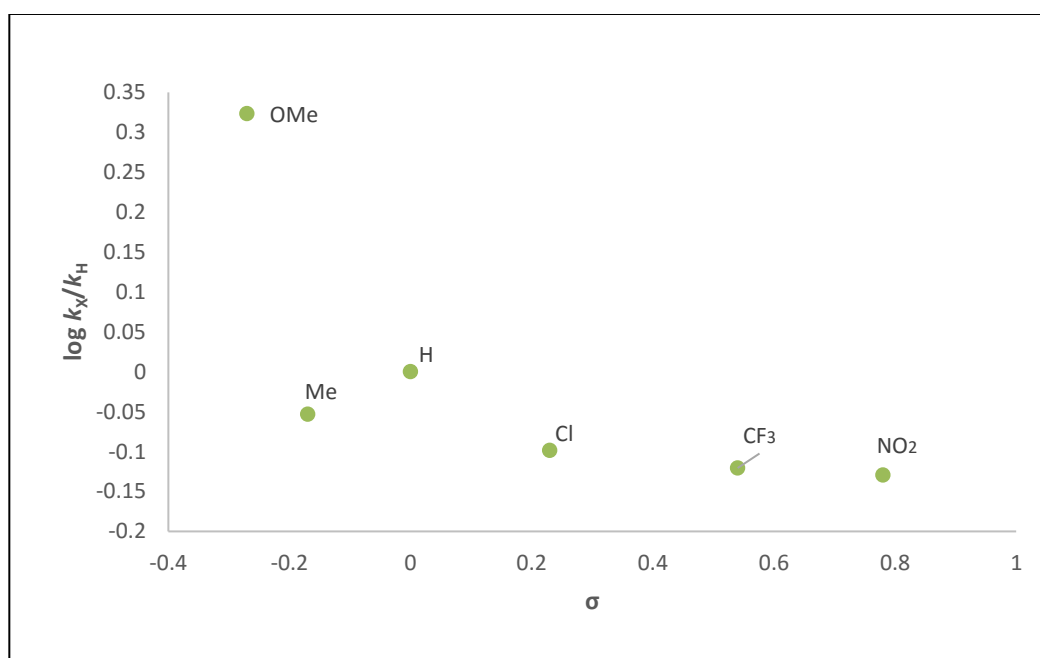


Figure 2.17 Hammett plots for nucleophilic substitution reaction of *p*-X-benzyl alcohol with [HC₄im][HSO₄] with 1 mol% H₂SO₄ obtained from S_N2 mechanism.

Based on the similar plots on Figure 2.14 – 2.17, a combination of S_N1 and S_N2 mechanism equations from Table 2.9 and 2.10 should be associated. It is sensible to

expect that the substrates with EDG substituent would preferably proceed through a S_N1 reaction due to the stabilization of the carbocation, while with EWG substituent would prefer a S_N2 mechanism due to carbocation destabilization.¹⁶⁰

Table 2.11 Log (k_X/k_H) values for the nucleophilic substitution reaction of *p*-X-benzyl alcohol with [HC₄im][HSO₄] and [HC₄im][HSO₄] with 1 mol% H₂SO₄ obtained from S_N1 and S_N2 mechanism equation with σ

X	σ	Mechanism	[HC ₄ im][HSO ₄]	[HC ₄ im][HSO ₄] + 1 mol% H ₂ SO ₄
			log (k_X/k_H)	log (k_X/k_H)
OMe	-0.27	S _N 1	0.71	0.32
Me	-0.17	S _N 1	-0.20	-0.05
H	0	S _N 2	0.00	0.00
Cl	0.23	S _N 2	-0.04	-0.09
CF ₃	0.54	S _N 2	0.00	-0.12
NO ₂	0.78	S _N 2	-0.09	-0.13

The results of these calculations gave upward V-shaped Hammett plots (Figure 2.18 and 2.19) which are in agreement with the change in mechanism interpretation, with S_N1 mechanism predominating when the substituent is EDG and S_N2 mechanism predominating when the substituents is EWG. This curvature is similar to reactions of benzyl chlorides with trimethylamine in benzene at 100 °C and benzyl bromides with pyridine in acetone at 20 °C.¹⁶⁵

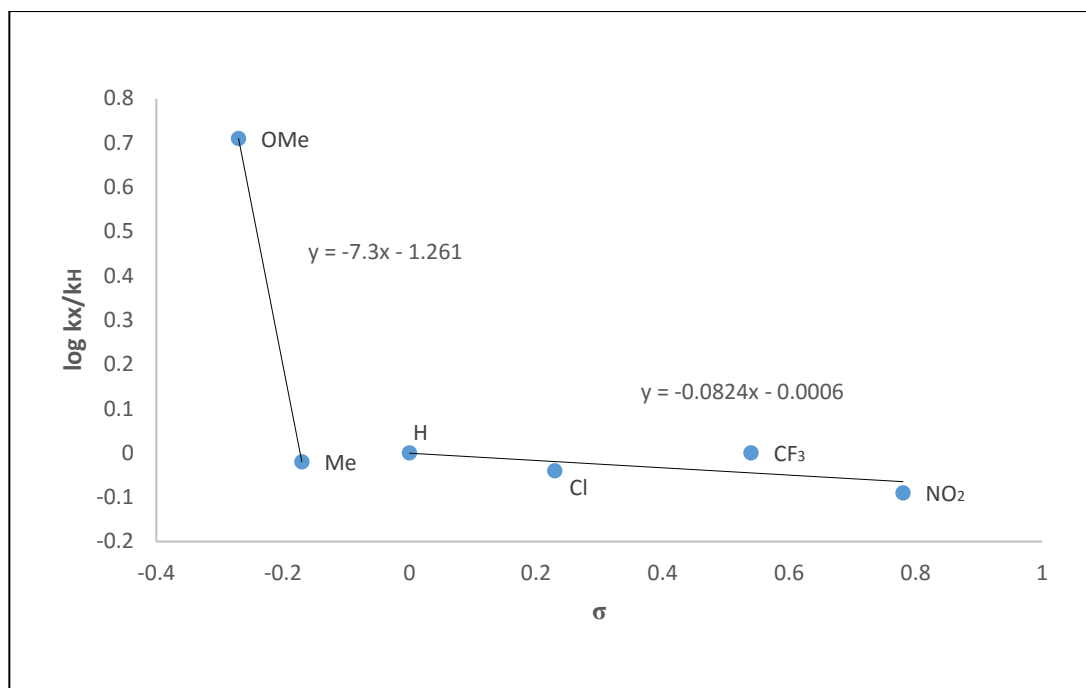


Figure 2.18 Hammett plots for nucleophilic substitution reaction of *p*-X-benzyl alcohol with [HC₄im][HSO₄] assuming that the reaction with EDG (OMe and Me) of substituent proceed via S_N1, and EWG (H, Cl, CF₃ and NO₂) of substituent proceed via S_N2 mechanism.

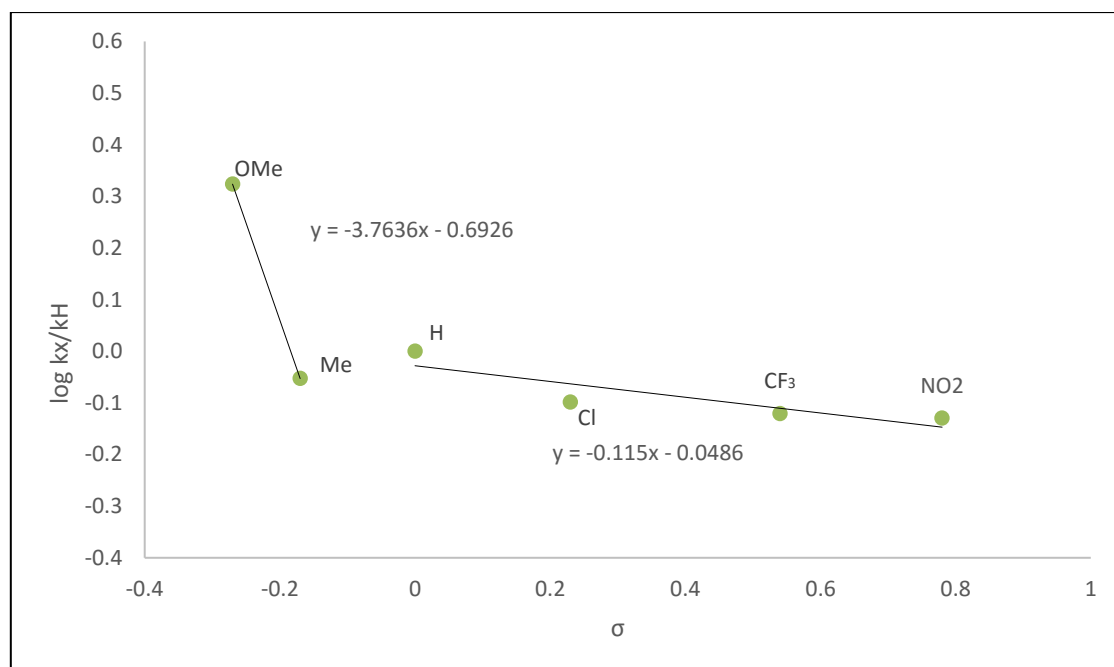


Figure 2.19 Hammett plots for nucleophilic substitution reaction of *p*-X-benzyl alcohol with [HC₄im][HSO₄] and 1 mol% H₂SO₄ assuming that the reaction with EDG (OMe and Me) of substituent proceed via S_N1, and EWG (H, Cl, CF₃ and NO₂) of substituent proceed via S_N2 mechanism.

When $\sigma < 0$, the values of the slopes are negative, $\rho = -7.30$ (neat $[\text{HC}_4\text{im}][\text{HSO}_4]$) and -3.76 ($[\text{HC}_4\text{im}][\text{HSO}_4] + 1 \text{ mol\% H}_2\text{SO}_4$) and when $\sigma > 0$, the slopes values are much less negative, $\rho = -0.08$ (neat $[\text{HC}_4\text{im}][\text{HSO}_4]$) and -0.11 ($[\text{HC}_4\text{im}][\text{HSO}_4] + 1 \text{ mol\% H}_2\text{SO}_4$). These magnitudes of ρ are consistent with the development of positive charge in the transition state, where the less negative the value of ρ , the less the positive charge builds up at the reaction centre.¹⁶⁶ It is clear to see that slopes at $\sigma < 0$ for all reactions are steeper than the slopes at $\sigma > 0$. This means the reaction with EDG substituents is significantly more affected by the transmission of electronic effects than the one with EWG substituents, consistent with these reactions proceeding via an $\text{S}_{\text{N}}1$ mechanism.⁷⁴

2.3.4.3 Hammett Plot of Nucleophilic Substitution Reactions of *p*-X-benzyl alcohol with $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ with 1 mol% H_2SO_4

To make the Hammett plots for the reactions with $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ with 1 mol% sulfuric acid, the same method was applied where the k_X values were calculated using separate assumed mechanisms. Table 2.12 shows the k_X and $\log(k_X/k_H)$ values obtained from $\text{S}_{\text{N}}1$ mechanism equation and the $\log(k_X/k_H)$ vs σ plots shown in Figure 2.20 and 2.21.

Table 2.12 Log (k_X/k_H) values of *p*-X-benzyl alcohol reactions with $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ with 1 mol% H_2SO_4 obtained from the $\text{S}_{\text{N}}1$ mechanism equation with σ .

X	σ	Mechanism	$[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$		$[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ 1 mol% H_2SO_4	
			k_X	$\log(k_X/k_H)$	k_X	$\log(k_X/k_H)$
OMe	-0.27	$\text{S}_{\text{N}}1$	1.33×10^{-4}	0.367	5.12×10^{-2}	0.335
Me	-0.17	$\text{S}_{\text{N}}1$	7.82×10^{-5}	0.135	4.40×10^{-2}	0.162
H	0	$\text{S}_{\text{N}}1$	5.73×10^{-5}	0.000	2.37×10^{-2}	0.000
Cl	0.23	$\text{S}_{\text{N}}1$	6.28×10^{-5}	-0.034	2.01×10^{-2}	-0.072
CF_3	0.54	$\text{S}_{\text{N}}1$	5.17×10^{-5}	-0.045	2.54×10^{-2}	-0.030
NO_2	0.78	$\text{S}_{\text{N}}1$	6.27×10^{-5}	-0.040	2.22×10^{-2}	-0.028

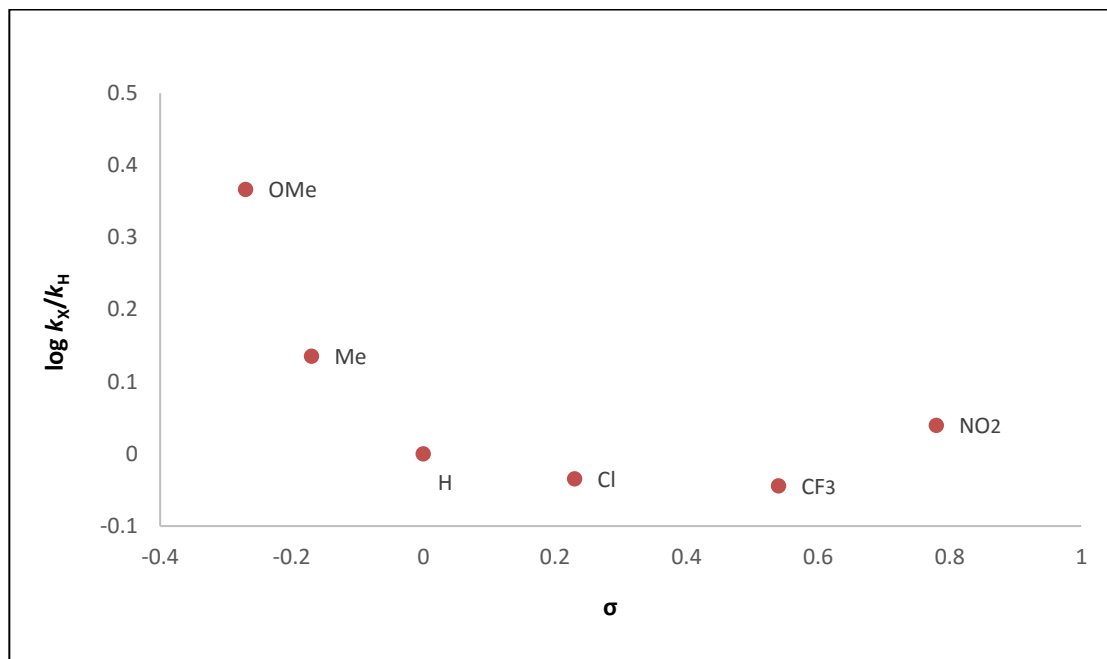


Figure 2.20 Hammett plots for nucleophilic substitution reaction of *p*-X-benzyl alcohol reactions with [C₄C₁im][HSO₄] obtained from the S_N1 mechanism equation.

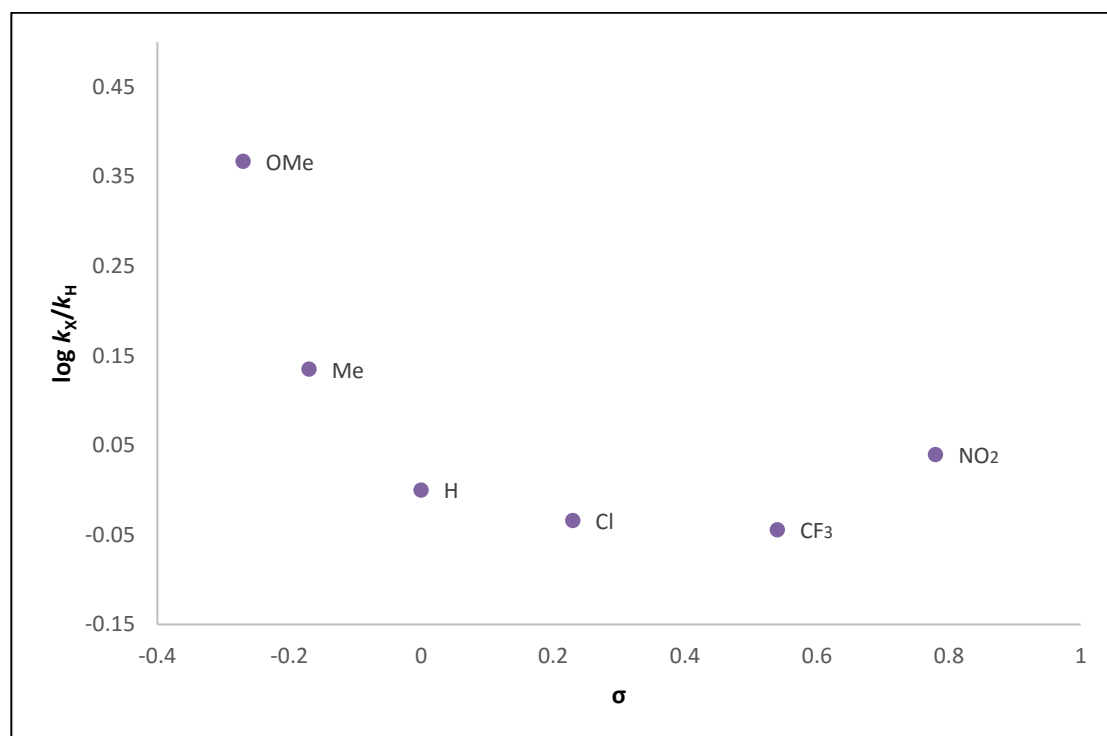


Figure 2.21 Hammett plots for nucleophilic substitution reaction of *p*-X-benzyl alcohol reactions with [C₄C₁im][HSO₄] with 1 mol% H₂SO₄ obtained from the S_N1 mechanism equation.

From these two figures (Figure 2.20 and 2.21), correlation between the $\log (k_X/k_H)$ and the σ values are similar with the Figure 2.18 and 2.19, where the concave upward plots which indicate a change in mechanism. However, to confirm the exact mechanism of the reaction, the same procedure should be tested using the calculation with the S_N2 mechanism. Table 2.13 shows the k_X and $\log (k_X/k_H)$ values obtained from the S_N2 mechanism equation and the $\log (k_X/k_H)$ vs σ plots shown in Figure 2.22 and 2.23.

Table 2.13 $\log(k_X/k_H)$ values of *p*-X-benzyl alcohol reactions with $[C_4C_{1im}][HSO_4]$ and $[C_4C_{1im}][HSO_4]$ with 1 mol% H_2SO_4 obtained from the S_N2 mechanism equation with σ .

X	σ	Mechanism	$[C_4C_{1im}][HSO_4]$		$[C_4C_{1im}][HSO_4]$ 1 mol% H_2SO_4	
			k_X	$\log (k_X/k_H)$	k_X	$\log (k_X/k_H)$
OMe	-0.27	S_N2	1.47×10^{-6}	0.367	5.00×10^{-2}	0.335
Me	-0.17	S_N2	8.60×10^{-7}	0.135	3.79×10^{-2}	0.162
H	0	S_N2	6.31×10^{-7}	0.000	4.40×10^{-2}	0.000
Cl	0.23	S_N2	6.92×10^{-7}	-0.034	1.90×10^{-2}	-0.072
CF ₃	0.54	S_N2	5.69×10^{-7}	-0.044	2.90×10^{-2}	-0.030
NO ₂	0.78	S_N2	8.00×10^{-7}	-0.040	2.10×10^{-2}	-0.028

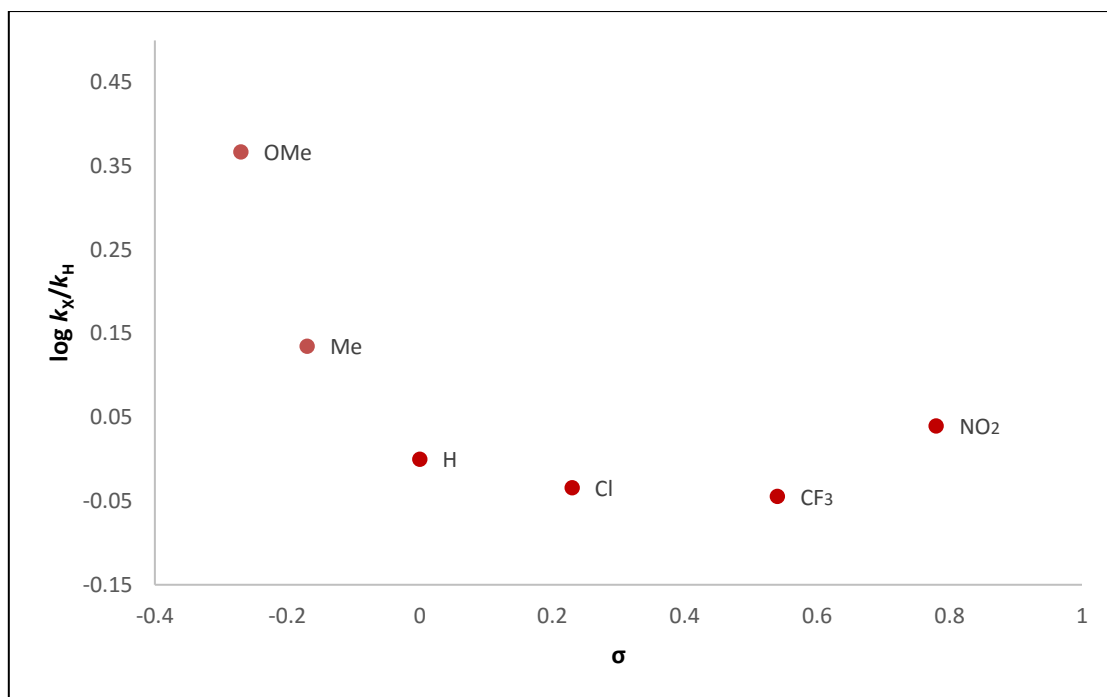


Figure 2.22 Hammett plots for nucleophilic substitution reaction of *p*-X-benzyl alcohol reactions with [C₄C₁im][HSO₄] obtained from the S_N2 mechanism equation.

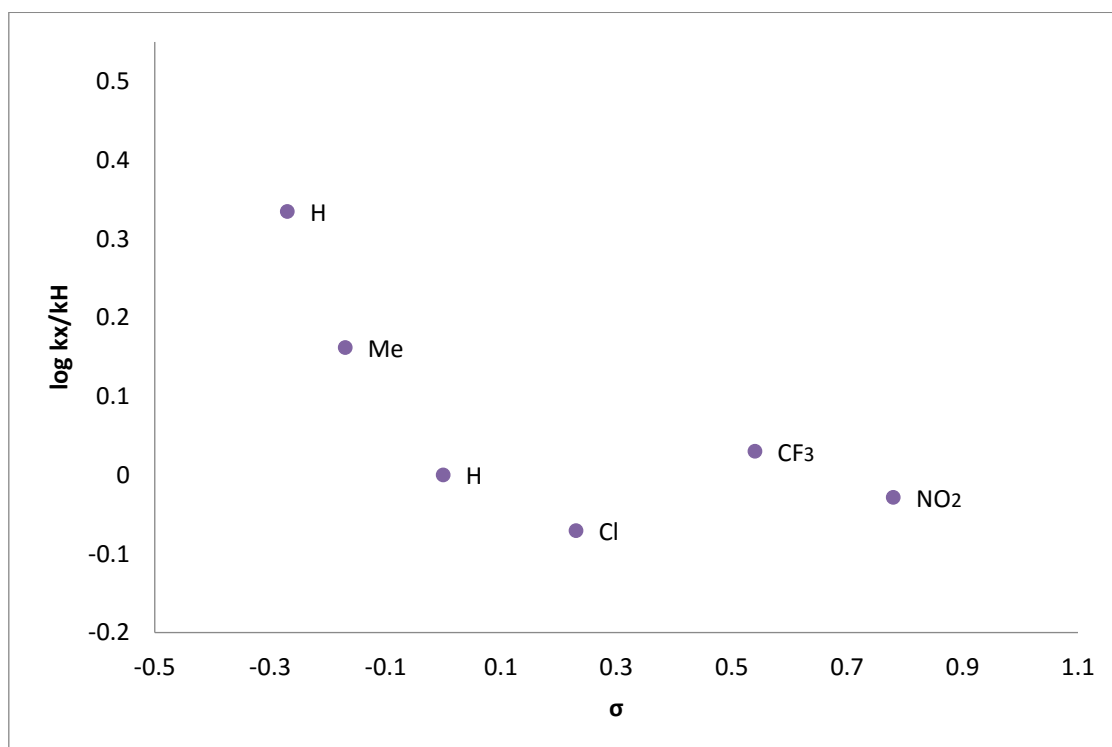


Figure 2.23 Hammett plots for nucleophilic substitution reaction of *p*-X-benzyl alcohol reactions with [C₄C₁im][HSO₄] with 1 mol% H₂SO₄ obtained from the S_N2 mechanism equation

Again, the non-linear plots show that the reactions did not all proceed via the same mechanism. Thus, it is sensible to assume they will proceed through the same mechanisms as reactions in [HC₄im][HSO₄], with the reactions featuring substrates with EDG substituents proceeding via S_N1 and those with EWG substituents proceeding via an S_N2 mechanism. The log(k_X/k_H) values for these reactions are shown in Table 2.14 and their Hammett plots are shown in Figure 2.24 and 2.25.

Table 2.14 Log(k_X/k_H) values of *p*-X-benzyl alcohol reactions with [C₄C₁im][HSO₄] and [C₄C₁im][HSO₄] with 1 mol% H₂SO₄ obtained from the S_N1 and S_N2 mechanism equation with σ .

X	σ	Mechanism	[C ₄ C ₁ im][HSO ₄]	[C ₄ C ₁ im][HSO ₄] 1 mol% H ₂ SO ₄
			log (k_X/k_H)	log (k_X/k_H)
OMe	-0.27	S _N 1	0.367	0.335
Me	-0.17	S _N 1	0.329	0.273
H	0	S _N 2	0.000	0.000
Cl	0.23	S _N 2	-0.034	-0.072
CF ₃	0.54	S _N 2	-0.044	-0.030
NO ₂	0.78	S _N 2	-0.040	-0.028

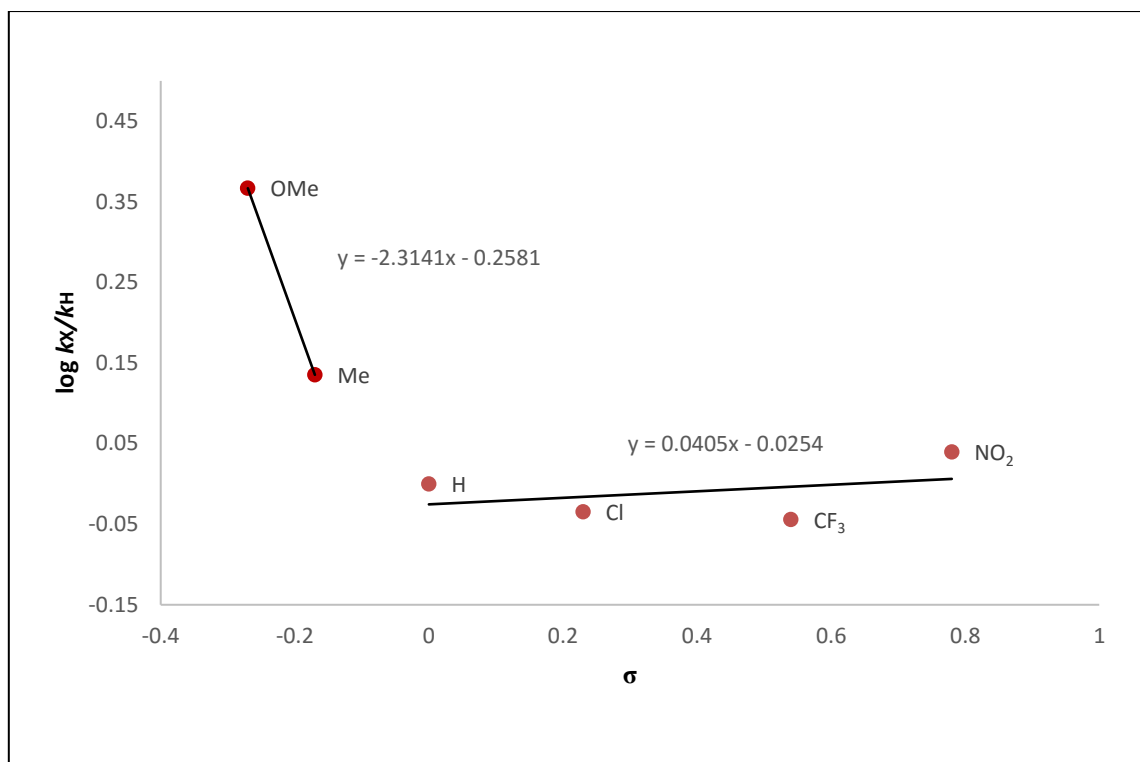


Figure 2.24 Hammett plots for nucleophilic substitution reaction of *p*-X-benzyl alcohol with $[C_4C_{1im}][HSO_4]$ assuming that the reaction with EDG (OMe and Me) of substituent proceed via S_N1 , and EWG (H, Cl, CF_3 and NO_2) of substituent proceed via S_N2 mechanism.

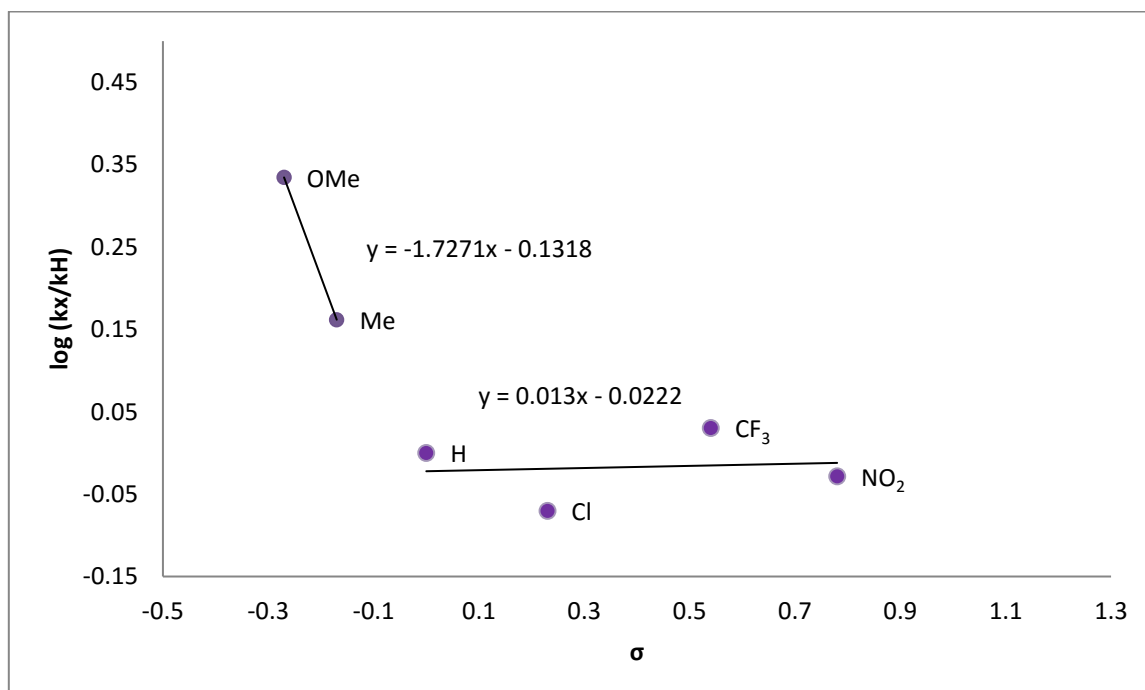


Figure 2.25 Hammett plots for nucleophilic substitution reaction of *p*-X-benzyl alcohol with $[C_4C_{1im}][HSO_4]$ with 1 mol% H_2SO_4 assuming that the reaction with EDG (OMe and Me) of substituent proceed via S_N1 , and EWG (H, Cl, CF_3 and NO_2) of substituent proceed via S_N2 mechanism.

The Hammett plots of the reactions with [C₄C₁im][HSO₄] and with 1 mol% H₂SO₄ added (Figure 2.24 and 2.25) display the same upward V-shape as was observed for the reactions with [HC₄im][HSO₄] (Figure 2.18 and 2.19). With the intersection of these two lines at $\sigma = 0$ and increasing values of ρ at higher σ , it is clear that there is a mechanistic change from S_N1 to S_N2 in these reactions. The ρ values of -2.31 and -1.72 when $\sigma < 0$, -0.04 and -0.01 when $\sigma > 0$ were observed and they are comparable to the ρ values of the reaction in [HC₄im][HSO₄]. This shows that the electronic effects are more significant in the reactions with substrates bearing EDG substituents than with those containing EWG substituents. Thus this is in agreement with our interpretation of the mechanism changing from S_N1 to S_N2 as the electron withdrawing ability of the substituents increases.

Nonetheless, both reactions plots showed large negative ρ values on the left side of the plot, signifying that the EDG substituents stabilised the intermediate carbocation and led to the departure of the leaving group H₂O, before the attack of the [HSO₄][−]. For $\sigma > 0$, small negative values of ρ specify that the EWG substituents did not greatly affect the rate constant. The positive charge at the reaction centre decreased due to the destabilisation of the carbocation, meaning that the departure of the leaving group, H₂O, occurred simultaneously with the attack of the [HSO₄][−] anion.

2.4 Conclusions

Overall the results of this chapter have allowed us to conclude that the anion, $[\text{HSO}_4]^-$ of $[\text{HSO}_4]^-$ ILs can undergo nucleophilic substitution reaction with hydroxyl groups. Based on the involvement of $[\text{HSO}_4]^-$ in the protonation of the hydroxyl group, the ILs have also acted as an acid (proton donor) as well as a solvent and a nucleophile in the reaction. The Hammett plots obtained from the reactions in neat $[\text{HC}_4\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and also with added H_2SO_4 show two intersecting lines, which specifies that the reactions in both ILs and with added acid have changed from an $\text{S}_{\text{N}}1$ to an $\text{S}_{\text{N}}2$ mechanism as the electron withdrawing strength of the substituents increases. The effect of adding 1 mol% H_2SO_4 and using different cations to the reaction produced changes in the reaction rates, with higher rate in the reactions with added H_2SO_4 . Slower rates are observed in $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ compared to in $[\text{HC}_4\text{im}][\text{HSO}_4]$. Adding water to the reaction had the effect of reducing the yield of the hydrogen sulfated product although sufficient product formed to suggest that sulfation of cellulose is probable under Ionosolv pretreatment conditions.

Chapter 3

3 Ester Hydrolysis in $[\text{HSO}_4]^-$ IL

3.1 Background of Study

3.1.1 Lignin-Carbohydrate Linkage

Lignin in lignocellulosic biomass is covalently bound to polysaccharides to form the lignin-carbohydrate complex (LCC). The lignin is mostly linked to hemicellulose and the structure varies depending on the type of plant, in particular whether it is softwood, hardwood, or grass. Ester, ether, and glycosidic bonds are the three major types of linkage that occur in LCC within native wood.^{167,168,169} Initial investigations into these linkages were biased by the pretreatment conditions used for their analysis which affected the apparent distribution of linkages present in the analysed material. For example, the ester linkage is readily hydrolysed during the alkali pretreatment, whereas the ether linkage remains largely intact and can only be cleaved by oxidation and acid degradation.¹⁷⁰ Both ester and glycosidic linkages are susceptible to acid hydrolysis. The use of 2D NMR spectroscopy to analyse milled wood lignin, MWL, was the first step towards the generation of more reliable data on the structure of the LCC, which were not biased by any chemical treatment. Since this original discovery,^{171,172} the quantity and exact structures of the LCC linkages in different types of woods have been

identified.^{173,172} Figure 3.1 shows the phenyl-glycosidic, γ -ester, benzyl ether linkages that are found in soft- and hardwoods.^{173,174}

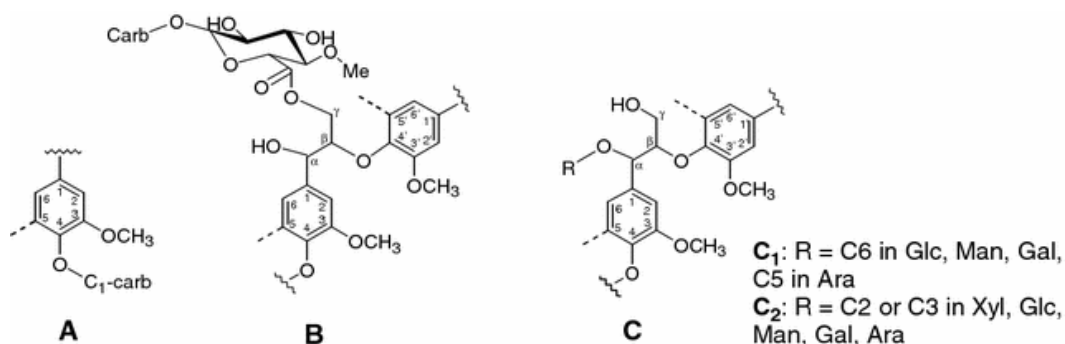


Figure 3.1 Lignin-carbohydrate and lignin structures: (A) phenyl glycoside, (B) γ -ester, and (C) benzyl ether LCC linkages.¹⁷³

3.1.2 Delignification of Lignocellulosic Biomass

Due to its complex polymeric structure, lignin is often an impediment to biomass conversion. The cross-linked molecular structure acts as a defensive barrier to the penetration of plant cells and provides resistance against hydrolytic enzymes. Studies have shown that delignification enhances the enzymatic saccharification of lignocellulosic biomass by increasing the accessible surface area for both hemicellulose and cellulose solubility and digestion.^{175,176} Thus, extensive removal of lignin is necessary before the saccharification process in order to obtain the greatest possible sugar yields. The removal of lignin has been accomplished using chemical pretreatment methods such as strong acid and alkaline pretreatment, wet oxidation, microwave radiation, ammonia fibre explosion, and imidazolium IL pretreatment.^{6,8} The influence of several imidazolium based ILs on the delignification and lignin yield of the pretreatment of *Miscanthus* (Figure 3.2) has been studied previously.⁹ $[\text{HSO}_4]^-$ ILs show the highest percentage of delignification, followed by $[\text{MeSO}_3]^-$, $[\text{MeCO}_2]^-$, Cl^- , and $[\text{OTf}]^-$.

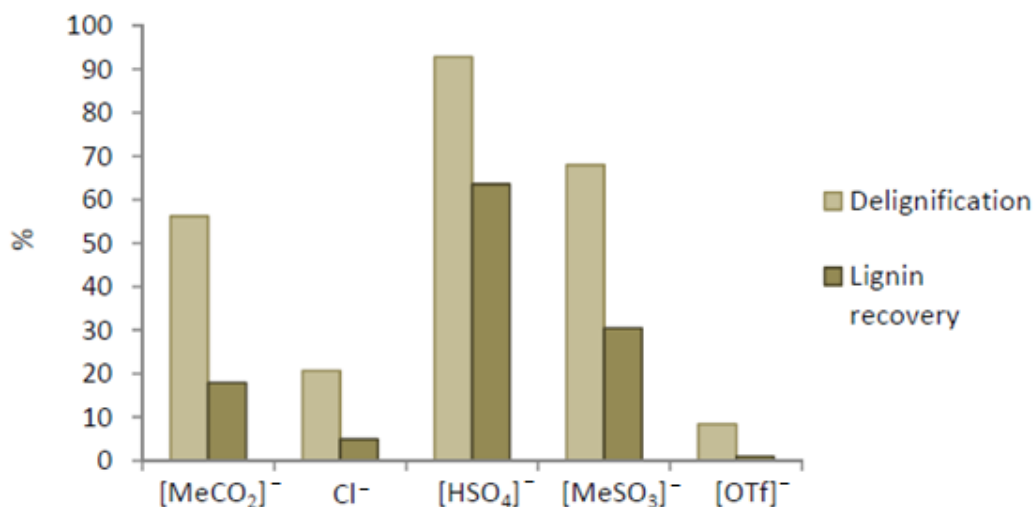


Figure 3.2 Delignification and the lignin yield of *Miscanthus* pretreated in different 1,3-dialkylimidazolium ILs (80 wt%) water (20 wt%) mixtures at 120°C for 22 h. The ionic liquid cation was [C₄C₁im]⁺, except in [C₂C₁im][MeCO₂].⁹

[C₄C₁im][HSO₄] and [C₂C₁im][MeCO₂], were further tested with two other feedstocks, Willow (debarked mix stems) and Pine (sapwood) (Figure 3.3). Again, [C₄C₁im][HSO₄] shows the better delignification and lignin recovery of all of the pretreatments compared to [C₂C₁im][MeCO₂]. Hence, this chapter will focus on [HSO₄]⁻ ILs and their effect on the reactivity of the ester linkage.

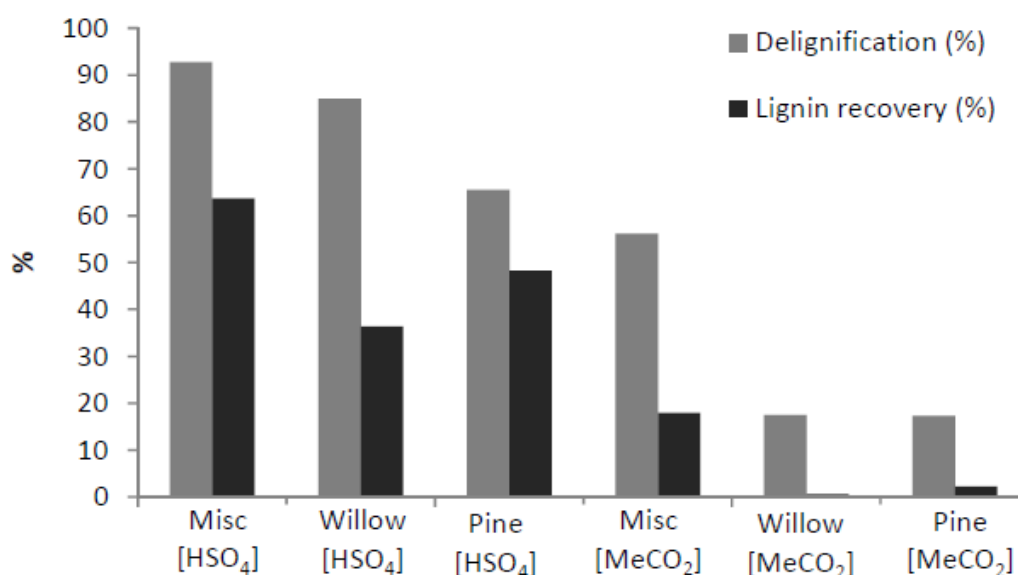


Figure 3.3 Delignification and lignin recovery of Misc (*Miscanthus*), Willow and Pine with [C₄C₁im][HSO₄] and [C₂C₁im][MeCO₂] IL (80/20% IL/water) mixtures at 120 °C for 22 h.⁹

3.1.3 Ester Linkages in LCC

During the delignification process, the ester linkages in LCC are the first to break for the separation of the lignin and the polysaccharides. The ester linkages in LCC vary depending on the type of plant. For example, *p*-hydroxybenzoic acid ester linkages are observed in aspens (Figure 3.4).¹⁷⁷

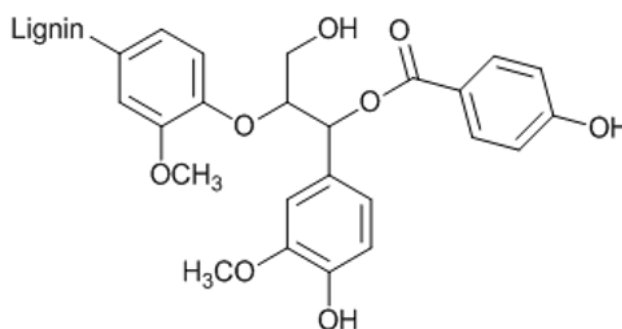


Figure 3.4 Proposed structure for the lignin-*p*-hydroxybenzoic acid ester linkage in aspens.¹⁷⁷

The frequent occurrence of hydroxycinnamic acids, particularly ferulic acid (FA, 4-hydroxy-3-methoxycinnamic acid) and *p*-coumaric acid (PCA, 4-hydroxycinnamic acid), in *Graminaceous* plants suggested that there are FA and PCA ester and ether bonds in the plant cell wall.¹⁷⁰ Ferulic acid ester linkages that are found in switchgrass, corn, wheat, and barley are mostly linked via its carboxylic acid group to the C(O)5 position of the arabinofuranose (Figure 3.5) unit of hemicellulose but in bamboo the carboxylic acid group is linked to the C(O)4 position of the xylose side chain (Figure 3.6).¹⁷⁸

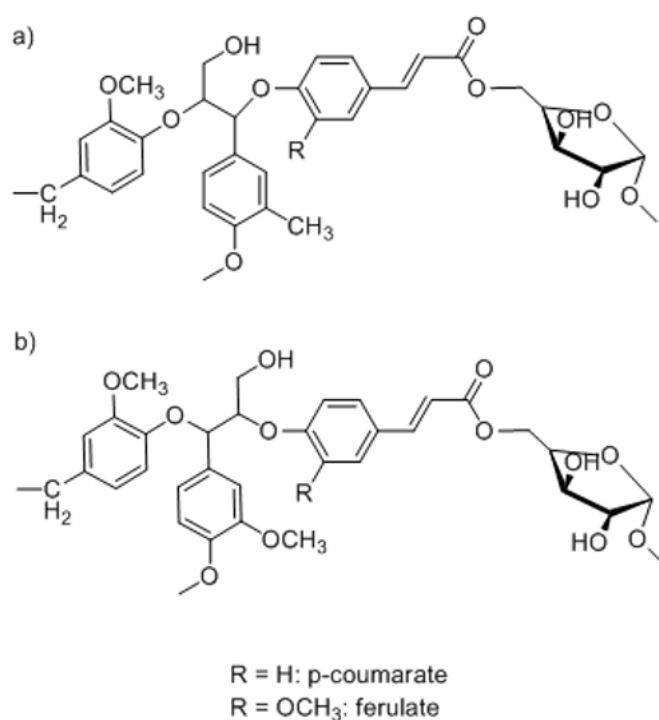


Figure 3.5 Proposed ferulic and *p*-coumaric acid links between lignin and hemicellulose in the grass cell wall. (a) α -Ether linkages and (b) β - ether linkages.¹⁷⁰

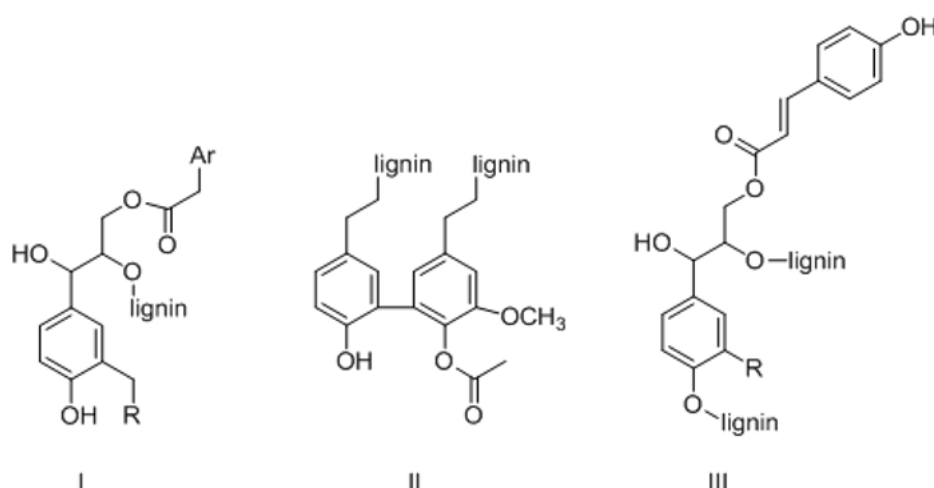


Figure 3.6 Three types of ester bond identified in wheat straw lignin.¹⁷⁹

p-Coumarate is also esterified to the lignin side chain in grasses such as *Miscanthus*, wheat straw and maize.^{180,181} Figure 3.6 illustrates the structure of some wheat lignin side chains where *p*-coumarate was present in the terminal units of the lignin.¹⁷⁹ Other types of hydroxycinnamic esters were also identified in *Miscanthus giganteus* lignin.¹⁸² It is well-established that these ester linkages intensify the cross-linking in LCC which contributes to the recalcitrance of the biomass.¹⁸³ Therefore, studying the mechanisms of hydrolysis of these cross-links in $[\text{HSO}_4]^-$ ILs will provide a deeper understanding on how to improve biomass transformations within acidic ILs.

3.1.4 Model Compounds

Due to the diversity of the structure of the real LCC ester linkages, model compounds representative of the plant cell wall were selected for study. A kinetic study of the hydrolysis of these model compounds within acidic ILs was undertaken to provide insight into the biomass deconstruction process in acidic ILs. In this study, two compounds were chosen to represent the hydroxybenzoic and cinnamic acid linkages in

the plant cell wall. The first compound, benzyl 4-hydroxybenzoate, BHB is similar to the LCC structure in hardwood or aspen (Figure 3.7)¹⁷⁷ while the second compound, tetrahydrofurfuryl ferulate, THFF is similar to the LCC structure of grasses (Figure 3.8).^{170,183}

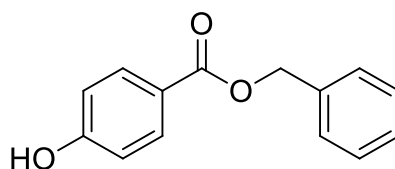


Figure 3.7 Benzyl 4-hydroxybenzoate, BHB

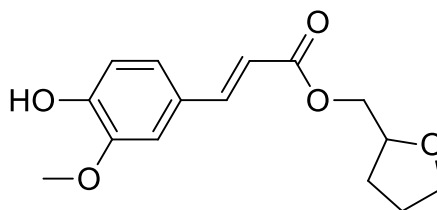


Figure 3.8 Tetrahydrofurfuryl ferulate (tetrahydro-2-furanylmethyl 4-hydroxy-3-methoxycinnamate), THFF

BHB was purchased from Sigma Aldrich while THFF was synthesised by the esterification of *trans*-ferulic acid and tetrahydrofurfuryl alcohol catalysed by *p*-toluenesulfonic acid. The detailed experimental method and characterisation data of the product are described in the experimental section. Several other compounds such as methyl-, ethyl- and benzyl *p*-nitrobenzoate were initially considered for this study, including some for which their kinetic reaction progress could be monitored by UV-Vis spectroscopy, but these esters were insoluble in [HC₄im][HSO₄] and hence were not used. The two compounds selected were suitable for ¹H NMR spectroscopic monitoring as the resonances of the product and reactants are distinguishable. Figures 3.9 and 3.10 depict the ¹H NMR spectra of these reactions and the resonances which were monitored for each of the substrates.

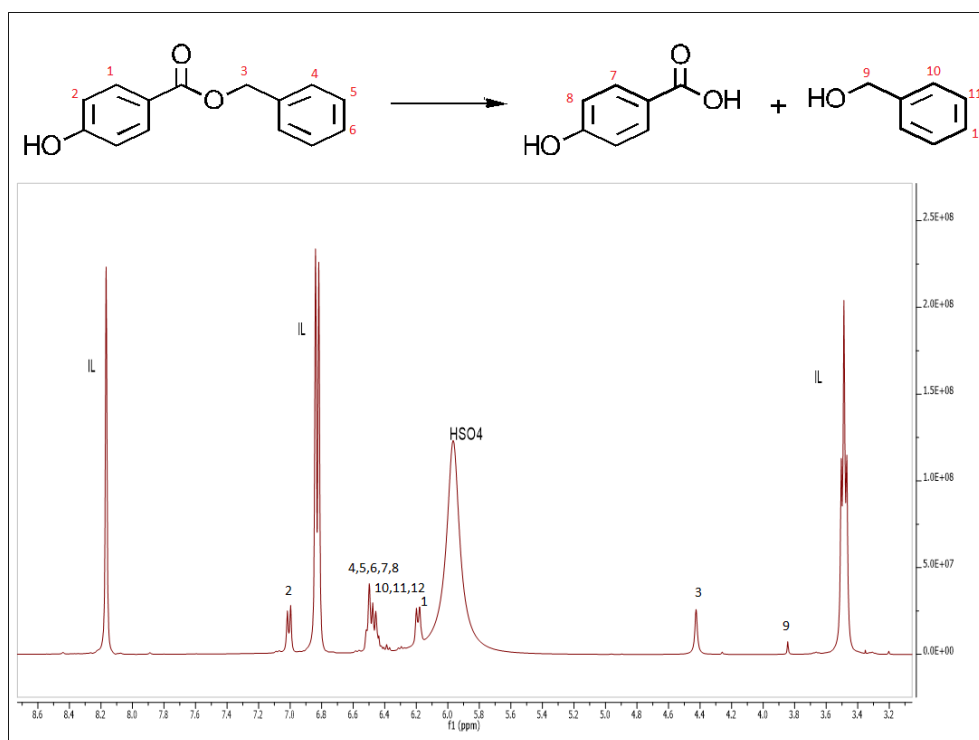


Figure 3.9 ^1H NMR of the hydrolysis of BHB in aqueous $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80°C after 2 hr.

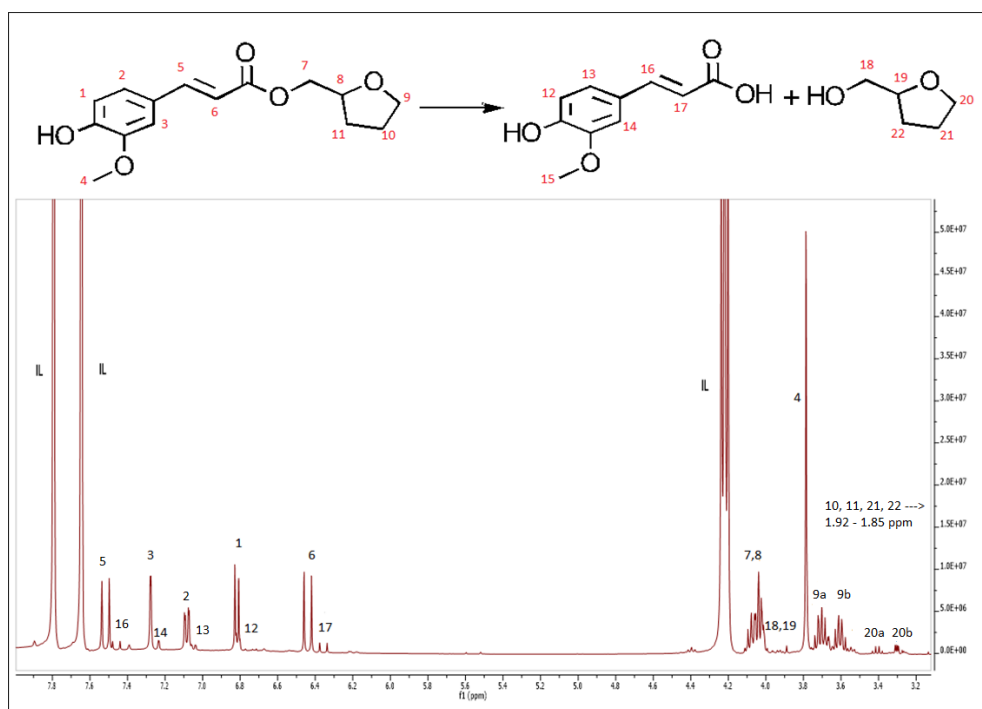
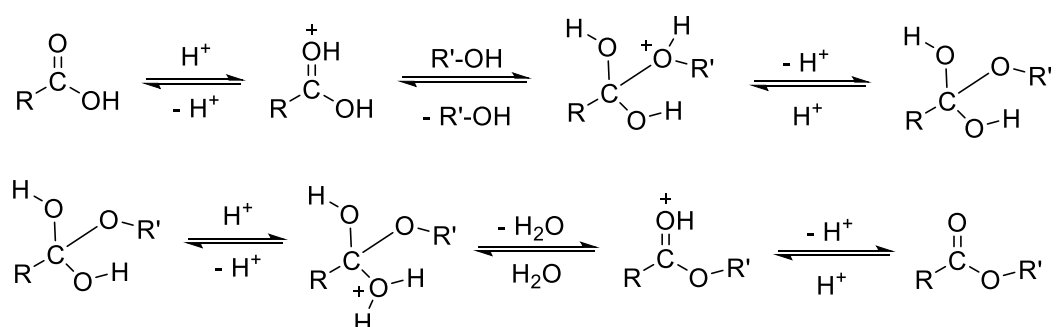


Figure 3.10 ^1H NMR of the hydrolysis of THFF in aqueous $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80°C after 2 hr.

3.1.5 Ester Hydrolysis Mechanisms

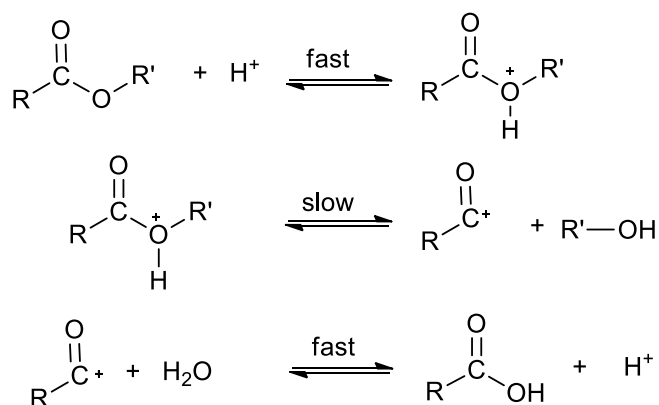
A possible esterification and hydrolysis mechanism was first proposed by Watson in 1935 (Scheme 3.1).¹⁸⁴ The carbonyl-oxygen of the carboxylic acid is first protonated before undergoing nucleophilic addition by an alcohol molecule followed by sequential deprotonation and re-protonation.



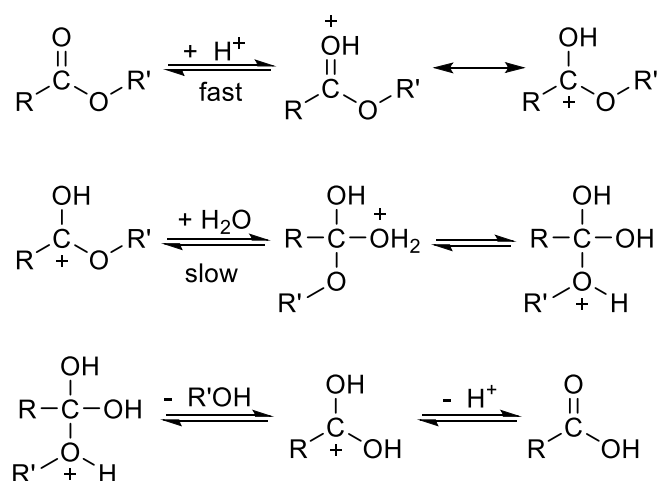
Scheme 3.1 The acid-catalysed carboxylic acid esterification and ester hydrolysis mechanism proposed by Watson in 1935.

In 1941, Day and Ingold suggested eight possible mechanisms for ester hydrolysis depending on the reaction conditions: acid or base catalysed; alkyl or acyl bond fission; with a unimolecular or bimolecular rate determining step (RDS).¹⁸⁵ They mentioned that their mechanisms are slightly different from Watson's system which they brought into their re-expressed $A_{AC}1$ mechanism.¹⁸⁶ For the $A_{AC}2$ mechanism, they suggested that the small difference with Watson's mechanism is not crucial because the systems only vary in the position of a mobile proton, and their electronic distribution. Ingold mechanisms, which he published in his classic 1953 book,¹⁸⁷ and revised in 1969,¹⁸⁸ have been cited in several organic chemistry textbooks.^{74,189,190}

Ingold pointed out that for the acid catalysed hydrolysis of ordinary esters, acyl-oxygen bond fission usually occurs, therefore A_{AC1} and A_{AC2} mechanisms are likely involved in this kind of reaction. Both mechanisms involve a fast reversible pre-equilibrium step which is the protonation by the acid, followed by either a unimolecular C-O cleavage in the RDS for A_{AC1} (Scheme 3.2) or bimolecular attack of water in the RDS for A_{AC2} (Scheme 3.3).^{74,188,190}



Scheme 3.2 A_{AC1} mechanism of acid catalysed ester hydrolysis



Scheme 3.3 A_{AC2} mechanism of acid catalysed ester hydrolysis

Ingold mentioned that the A_{AC2} mechanism was preferred for most esters in dilute aqueous solution of acids due to the relatively large concentration of water. In contrast, the A_{AC1} mechanism is favoured by the stabilisation of the conjugate acid of the ester by electron donating substituents and by steric hindrance around the reaction centre due to the presence of bulky substituents.¹⁸⁵

3.2 Aims and Objectives

The first aim of this chapter is to study the relative reactivity of the ester linkage in biomass by using model compounds, BHB and THFF and to elucidate their hydrolysis reaction mechanism with the acidic IL, $[HC_4im][HSO_4]$, with varying amounts of added sulfuric acid and different water contents. This is to give a greater understanding of the hydrolysis of the ester linkages in biomass during delignification and how the acid and water content will affect the process. The second aim is to elucidate the reaction mechanism by using the Zucker-Hammett and Bunnett-Olsen equations. This will be performed by recording the kinetics of the reactions and correlating the rates of the reactions with the Hammett acidity (H_0) function. From these equations, the role of water in the RDS will be explored. The final aim of this chapter is to use the activation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, of the reactions determined by the Eyring equation to provide more information on the molecularity of the RDS, and further interrogate the mechanism of these reactions.

3.3 Results and Discussion

3.3.1 Kinetic Studies of the Hydrolysis of the Ester Model Compounds in [HC₄im][HSO₄] with Varying Water and Acid Content

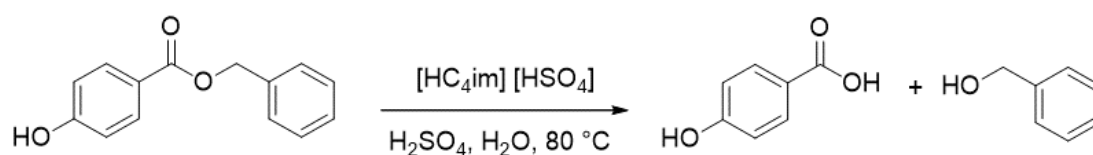
Kinetic experiments of the hydrolysis of the two ester model compounds in [HC₄im][HSO₄] were performed to study the rates of the reaction of the two linkages as well as the effect of the added sulfuric acid and water. The kinetic experiments were monitored using ¹H NMR, as described in section 3.1.4. UV-Vis measurement was found to be unsuitable as the reactant and the product absorption peaks overlapped. At least one set of ¹H NMR signals of the reactant ester are clearly distinguishable from the resultant carboxylic acid product for each of the model compounds. As the temperature of the NMR can be varied as desired, the direct *in situ* monitoring of the reaction can be performed.

Due to the high water content of the system, the water peak in the ¹H NMR spectrum occasionally overlapped with the significant peaks (the peaks being monitored of the reactant and product). Two methods were used to obtain more accurate kinetic data for each reaction. The first method is a direct monitoring, where the reactions were performed in an NMR tube with a sealed DMSO-*d*₆ capillary insert in the tube. These samples were directly monitored within the NMR set to the desired temperature. The other method involved performing the reactions in a vial on a hot plate set to the desired temperature from which aliquots were periodically taken and diluted with DMSO-*d*₆ for ¹H NMR analysis. These methods are explained in more detail in the experimental chapter.

Since the peak integration is proportional to the concentration of the reactant and product, the rates were calculated from the ratio of concentration of the remaining ester [A] with the sum of the concentration of product and the remaining ester [A₀]. For the integration of the reactant and the product, for reaction of BHB, peak of O-CH₂-Ph of the BHB at 4.43 ppm (labelled as 3 in Figure 3.9) was used against HO-CH₂-Ph of the product peak at 3.82 ppm (labelled as 9 in Figure 3.9). While for reaction of THFF, peak of HC=CH-C(O) of THFF at 6.48 ppm (labelled as 6 in Figure 3.10) was used against HC=CH-C(O) of the product peak at 6.35 ppm (labelled as 17 in Figure 3.10). As no alternative products were observed by ¹H NMR over the course of the reaction, the implicit assumption inherent to this approach of 100% selectivity to the desired product is satisfied. Based on the linearity of the ln ([A]/[A₀]) vs time graphs, all reactions for this study obeyed *pseudo*-first-order kinetics with regards to the ester. Observed rate constants, *k_{obs}* for the reactions were obtained from the gradient of the graphs.

3.3.2 Benzyl 4-hydroxybenzoate, BHB

The hydrolysis of BHB in [HC₄im][HSO₄] was performed under *pseudo*-first-order conditions with regards to the ester with different concentrations of sulfuric acid, 0–42.9% (mol ratio to the IL) and water content, 10-30% (v/v ratio to the IL) at 80 °C (Scheme 3.3).



Scheme 3.4 Hydrolysis of BHB in [HC₄im][HSO₄] with varying acid and water content at 80 °C.

The temperature of 80 °C was chosen instead of 120 °C which is used under pretreatment condition to reduce the evaporation of water from the reaction solution. One of the plots of $\ln ([A]/[A_0])$ vs time is depicted in Figure 3.11 and shows the linearity of these plots. The rest of the plots can be found in the Appendix (A.2.26 – A.2.28). The k_{obs} of the reactions were obtained from the gradient of the plots and are listed in Table 3.1.

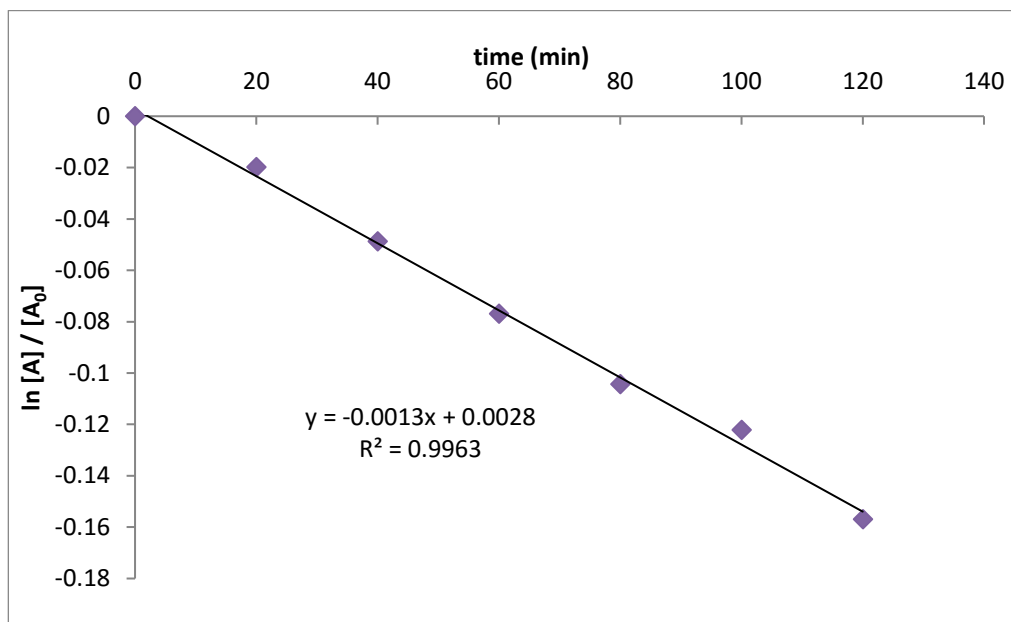


Figure 3.11 Plot of $\ln [A]/[A_0]$ vs time for the hydrolysis of BHB with $[\text{HC}_4\text{im}][\text{HSO}_4]$ in 10% water and 33.3 mol% sulfuric acid at 80 °C.

Table 3.1 k_{obs} values for the hydrolysis of BHB with $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80 °C.

Sulfuric acid mol%	$k_{obs} 10^{-3} (\text{min}^{-1})$		
	10 % H ₂ O	20 % H ₂ O	30 % H ₂ O
0	0.088	0.080	0.066
9.10	0.54	0.36	0.30
16.7	0.79	0.78	0.57
23.1	1.33	1.21	0.91
28.6	1.82	1.66	1.22
33.3	3.37	2.24	1.63
42.9	4.43	4.13	3.04

*note: mol% acid represents mol fraction of sulfuric acid and IL and % water represents v/v of water in water and IL solution.

From the k_{obs} values listed above, clear patterns can be seen where the observed reaction rates increase with increasing sulfuric acid concentration. The presence of 9.1 mol% sulfuric acid led to a 3 to 6-fold increase in rate compared to the reactions without added acid. Increasing the water content has the effect of slightly decreasing k_{obs} although this effect is subtler than that for adding acid. It is possible that the reduction in rate with increasing water could be due to the reduced acidity of the more dilute solutions. These trends can be more clearly visualised in Figure 3.12.

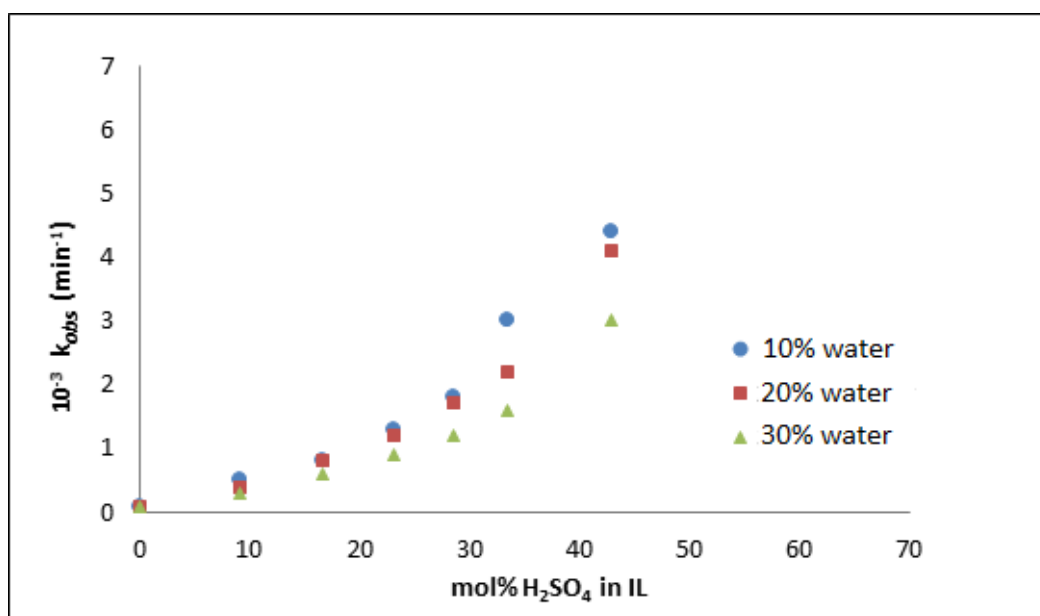


Figure 3.12 Relationship between the reaction rates of the hydrolysis of BHB in [HC₄im][HSO₄] and the acid and water content. **note: mol% acid represents mol fraction of sulfuric acid and IL and % water represents v/v of water in water and IL solution.*

Figure 3.13 illustrates the correlation of the reactions rates with the mol% sulfuric acid in total solution (IL, water and acid). Similar trends of increasing rates with increased mol% acid is observed. A different trend is observed where the rates are slightly increased with increasing water content; this is because the water reduces the viscosity of the reaction media and thus increases the diffusion rates of the reactants.¹⁹¹

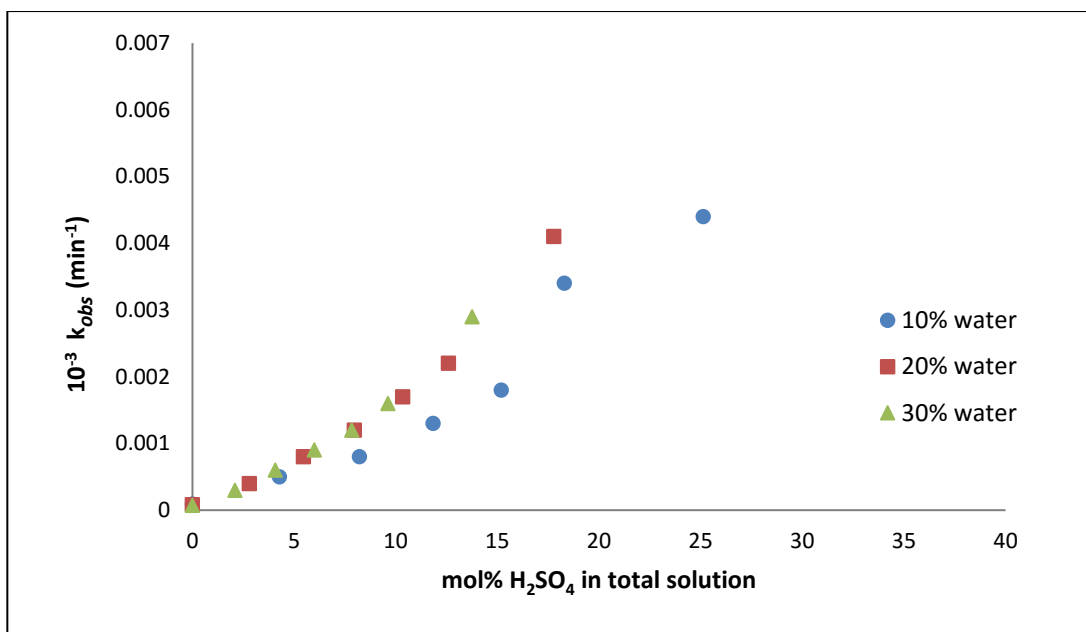
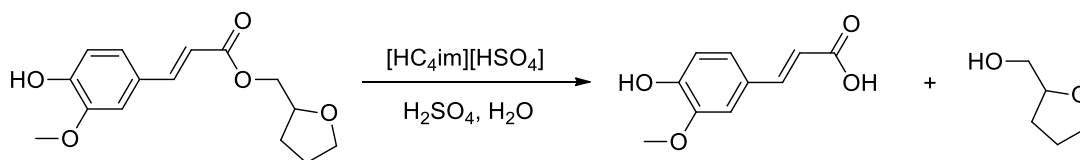


Figure 3.13 Relationship between the reaction rates of the hydrolysis of BHB in [HC₄im][HSO₄] and the acid and water content. **note: mol% acid represents mol fraction of sulfuric acid in total solution of IL, water and sulfuric acid; % water represents v/v of water in water and IL solution.*

3.3.3 Tetrahydrofurfuryl Ferulate, THFF

The hydrolysis of THFF was studied using the same conditions as were used for the hydrolysis of BHB. Similarly, to BHB, the water content was varied from 10 - 30% and the sulfuric acid added from 0 - 42.9 mol% both with respect to IL. *Pseudo*-first-order kinetic reactions were measured at 80 °C and analysed using ¹H NMR. Plotting $\ln [A]/[A_0]$ against time gave the k_{obs} (an example is shown in Figure 3.14; the remainder are depicted in the Appendix A.2.29 – A.2.31). The k_{obs} values under these conditions are shown in Table 3.2.



Scheme 3.5 Hydrolysis of THFF in $[\text{HC}_4\text{im}][\text{HSO}_4]$ with varying acid and water content at 80 °C.

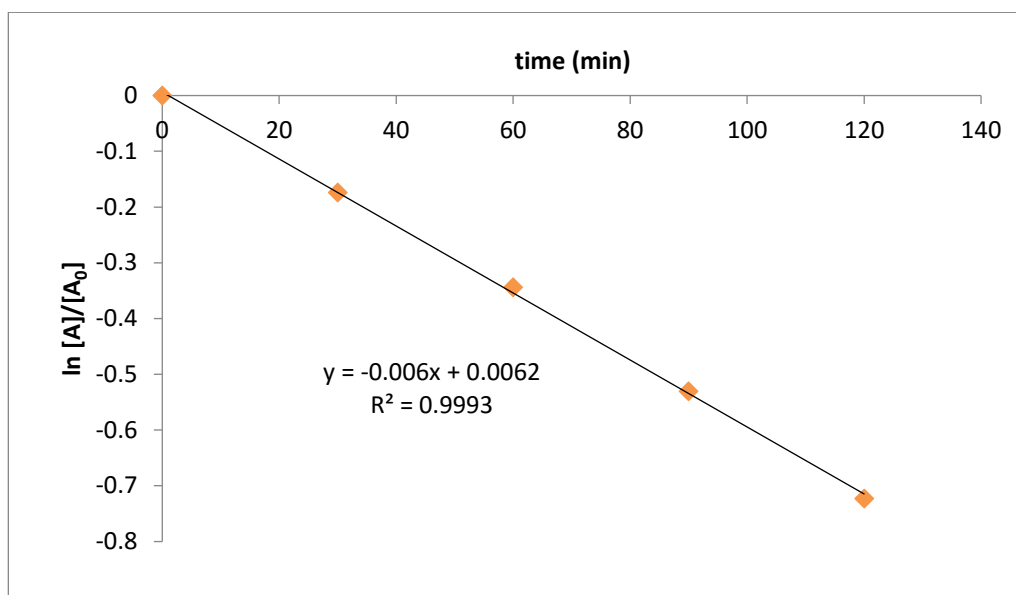


Figure 3.14 Plot of $\ln [A]/[A_0]$ vs time of the hydrolysis of THFF with $[\text{HC}_4\text{im}][\text{HSO}_4]$ in 20% water and 23.1 mol% sulfuric acid at 80 °C.

Table 3.2 k_{obs} values of the hydrolysis of THFF in $[\text{HC}_4\text{im}][\text{HSO}_4]$ with varying acid and water content at 80 °C.

Sulfuric acid mol%	$10^{-2} k_{\text{obs}} (\text{min}^{-1})$		
	10% H ₂ O	20% H ₂ O	30% H ₂ O
0	0.087	0.083	0.072
9.10	0.52	0.39	0.33
16.7	0.75	0.60	0.49
23.1	1.02	0.85	0.71
28.6	1.56	1.15	1.02
33.3	1.64	1.42	1.22
42.9	2.12	2.03	1.79

*note: mol% acid represents mol fraction of sulfuric acid and IL and % water represents v/v of water in water and IL solution.

From Figure 3.15, the same trends were observed where the k_{obs} values increased with increasing acid concentration, but slightly decreased with increasing water content. The reaction with 10% water and 42.9 mol% sulfuric acid was the fastest while that with 30% water without added acid was the slowest. From the plot, the rates are decreasing with increasing water content. The water content changes the rates presumably because the acid is more dilute at the same ‘mol%’ as it is with reference to the IL not the system as a whole.

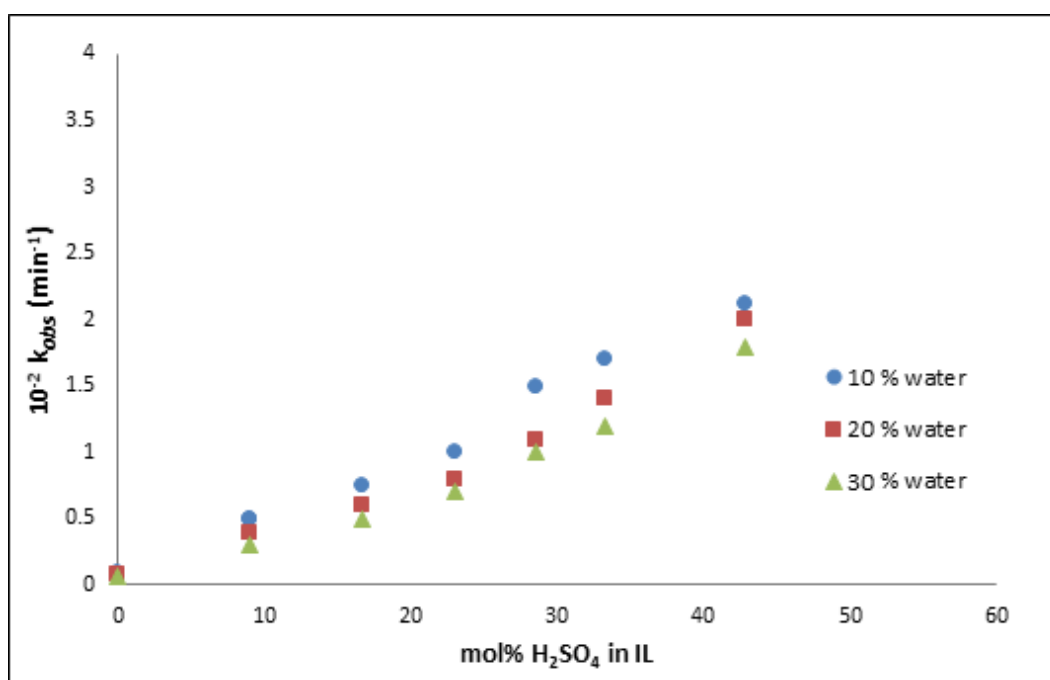


Figure 3.15 Relationship between the reaction rates of the hydrolysis of THFF in [HC₄im][HSO₄] with acid and water content. **note: mol% acid represents mol fraction of sulfuric acid and IL and % water represents v/v of water in water and IL solution.*

To see the correlation of mol% acid as in whole solution with the reactions rates, k_{obs} vs mol% was plotted in Figure 3.16. A similar trend to the benzoate is observed, where the rates are increasing with increasing mol% acid and water content. As previously

mentioned, this is presumably due to the reduced viscosity when more water being added to the system, thus increased the diffusion rates.

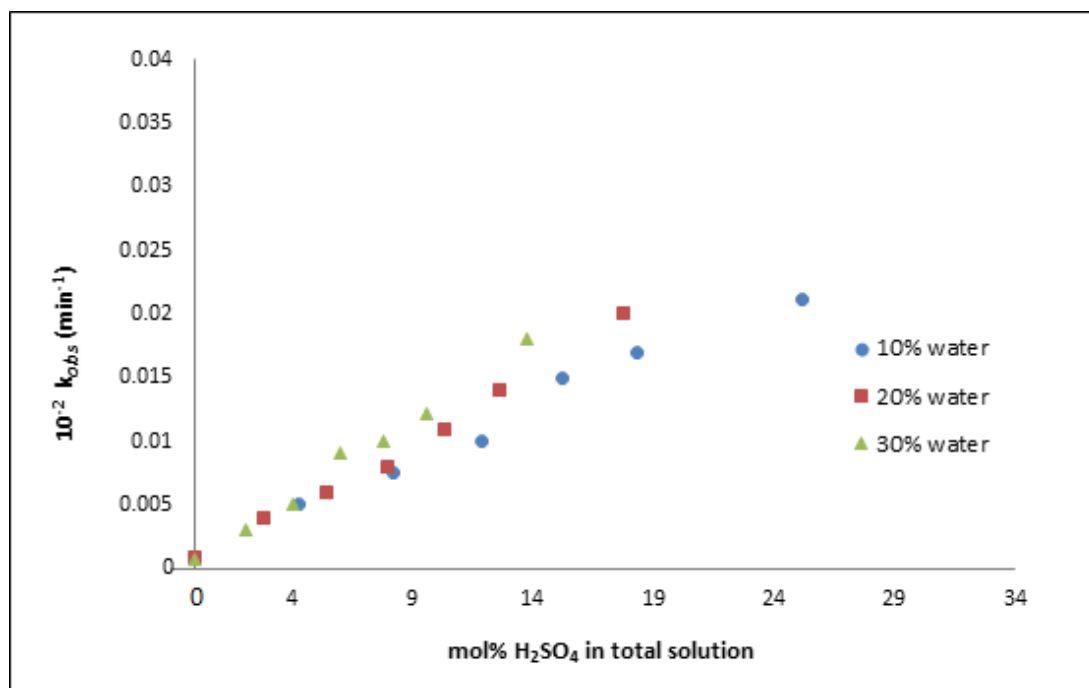


Figure 3.16 Relationship between the reaction rates of the hydrolysis of THFF in [HC₄im][HSO₄] with acid and water content. **note: mol% acid represents mol fraction of sulfuric acid in total solution of IL, water and sulfuric acid; % water represents v/v of water in water and IL solution.*

Overall, the hydrolysis rates of this compound are an order of magnitude faster than BHB. This result could be due to electronic effects, where the ferulate (having methoxy and hydroxyl group in the *meta* and *para* positions respectively) is more electron rich than the benzoate. The higher basicity of the ferulate could also account for the faster rates as the effective concentration of protonated intermediate would be greater.

It is apparent that the acidity of the medium affects the reaction rate for both of the esters that have been investigated. To explore this more quantitatively, the reaction rates need to be compared to the activity of H⁺ which may not necessarily vary linearly with concentration given the medium is predominantly non-aqueous. To get further

information on this, the Hammett acidity of each solution was measured and used to compare with the reaction rates observed.

3.3.4 Hammett Acidity Function

The Hammett acidity function (H_0) is an extension of Brønsted-Lowry acidity and the pH scale to the acidity of very concentrated acid solutions including superacids and non-aqueous systems. This acidity scale uses the measurement of ionisation or protonation equilibria of a particular set of indicators or bases to determine the proton activity in an acidic solution.¹⁹² For an uncharged base,



Thus, H_0 is defined as;

$$H_0 = -\log \frac{[BH^+]}{[B]} + pK_{BH^+} \quad (3.1.2)$$

Where $[B]$ and $[BH^+]$ are the concentration of the base and conjugate acid, pK_{BH^+} is the pK_a of the conjugate acid BH^+ . This equation also equivalent to:

$$H_0 = -\log \frac{a_{H^+} + \gamma_B}{\gamma_{BH^+}} \quad (3.1.3)$$

Where a_{H^+} represents the activity of H^+ and γ_B and γ_{BH^+} are molar concentration activity coefficients. In ideal dilute aqueous solutions, γ_B and γ_{BH^+} are approximately unity and a_{H^+} becomes the concentration of H^+ . Thus, as the solution approaches infinite dilution, all the species' activity coefficients approach unity and H_0 becomes approximately equal to pH.

The H_0 acidity function has been used to measure the acidity of ILs. Xing and co-workers have measured H_0 of a series of sulfonic acid functionalised ILs with pyridinium cations.¹⁹³ Recently, colleagues in the Welton and Hallett research groups have used UV-Vis and NMR spectroscopy to measure the acidity of the IL mixtures with acids, such as $[\text{HSO}_4]^-$ ILs with sulfuric acid.⁸³

For this study, the H_0 values of the reaction solutions were measured using UV-Vis spectroscopy using 2- and 4-nitroaniline as the Hammett bases. The absorbance of the solution where there is no IL present (A_0) was used as the reference to calculate the H_0 values using equation 3.1.4.

$$H_0 = -\log \left[\frac{A_0 - A}{A} \right] + \text{p}K_{\text{BH}^+} \quad (3.1.4)$$

Where, A_0 is the absorbance of the blank solution in CH_2Cl_2 (without IL-sulfuric acid-water mixture) and A is the absorbance of the measured solution with IL-sulfuric acid-water mixtures. The experimental details are described in the experimental chapter, 6.3.1. Table 3.3 shows the H_0 values for the mixtures and Figure 3.17 shows the correlations of H_0 with water and mol% sulfuric acid.

Table 3.3 H_0 values of $[\text{HC}_4\text{im}][\text{HSO}_4]$ mixture with water and sulfuric acid.

H_2SO_4 (mol%)	H_0 values		
	% Water		
	10	20	30
0	2.49	1.93	1.79
9.10	1.73	1.04	1.00
16.7	0.28	0.53	0.61
23.1	-0.37	0.38	0.60
28.6	-0.71	0.06	-0.08
33.3	-1.24	-0.89	0.15
42.9	-0.85	-0.62	-0.11

**note: mol% acid represents mol fraction of sulfuric acid and IL and % water represents v/v of water in water and IL solution.*

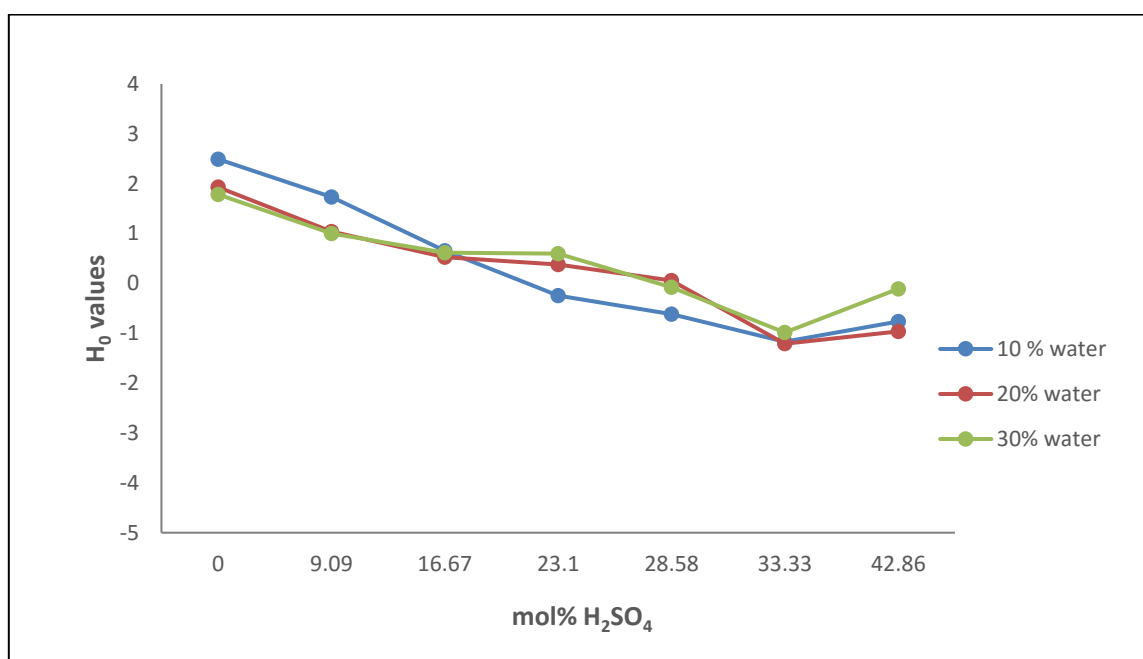


Figure 3.17 Correlation between H_0 and mol% sulfuric acid in 10, 20 and 30 wt% water mixture of $[\text{HC}_4\text{im}][\text{HSO}_4]$. **note: mol% acid represents mol fraction of sulfuric acid and IL and % water represents v/v of water in water and IL solution.*

The H_0 values are decreasing with the increasing of mol% acid while water content shows an erratic effect. There are no significant differences for H_0 values of 20% and

30% water except at 42.9 mol% acid. The H_0 values decreased with the increasing of water content at 0 to 16.7 mol% acid but then increased with the increasing of water at 23.1 to 33.3 mol% acid. These H_0 values are comparable to the previous measurement of the same water-acid-IL system for $[C_4C_1im][HSO_4]$ shown in Figure 3.18. H_0 values for neat $[C_4C_1im][HSO_4]$ and $[HC_4im][HSO_4]$ measured in our lab are 1.96 and 1.73 respectively. As comparison, for 20% of water in the IL, the H_0 value for $[C_4C_1im][HSO_4]$ is 2.81 while the value for $[HC_4im][HSO_4]$ is 1.93.

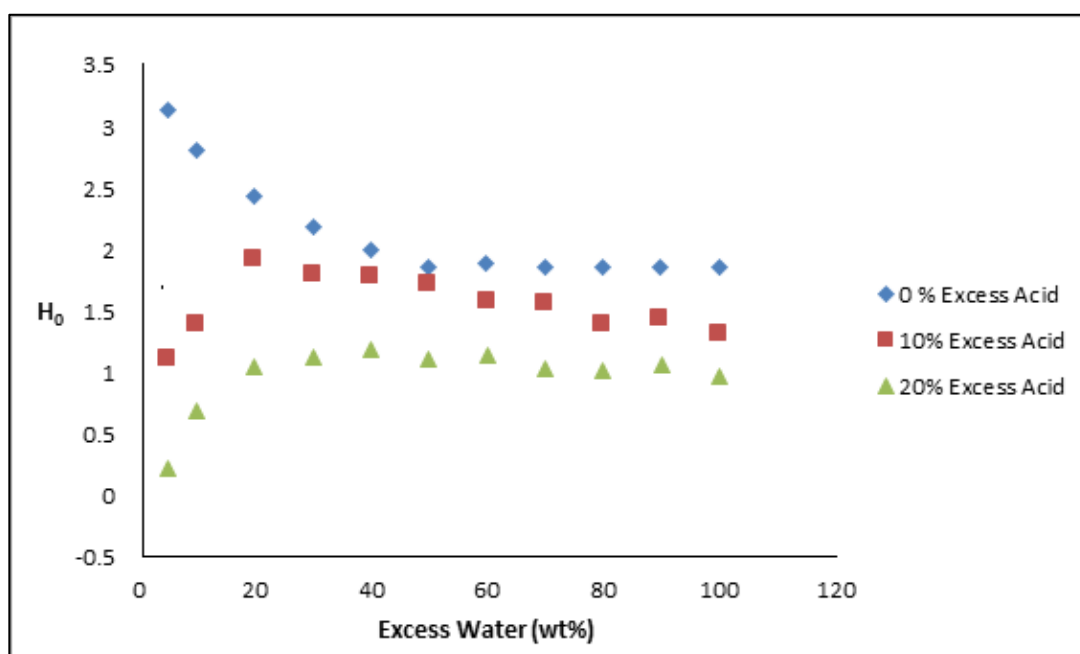


Figure 3.18 H_0 values of $[C_4C_1im][HSO_4]$ water and sulfuric acid mixture.⁴²

Acknowledgements This acidity measurement was done together with the assistance of Hanim Saupi, a fellow PhD student in the Welton research group.

3.3.5 Mechanistic Insights

3.3.5.1 Zucker-Hammett Hypothesis

Hammett and co-workers noted that there may be a correlation between the reaction rate and the acidity function for acid catalysed reaction when the protonation of the substrate occurs prior to the RDS.^{192,194} That is, if a reaction proceeds through the following mechanism:



where r_2 is the RDS:

$$r_2 = k_2 [SH^+] \quad (3.2.3)$$

and r_1 is at equilibrium so that:

$$K_a = \frac{a_S a_{H^+}}{a_{SH^+}} \longrightarrow [SH^+] = \frac{a_{H^+} \gamma_S}{K_a \gamma_{SH^+}} [S] \quad (3.2.4)$$

and if the protonation of the neutral substance is chemically similar to the indicator base used during the H_0 measurement of the acid so that:

$$[SH^+] = \frac{a_{H^+} \gamma_S}{\gamma_{SH^+} K_a} \frac{[S]}{K_a} \approx \frac{a_{H^+} \gamma_B}{\gamma_{BH^+} K_a} \frac{[S]}{K_a} \quad (3.2.5)$$

Then, the rate of the reaction becomes:

$$r_2 = k_2 [SH^+] \approx k_2 \frac{a_{H^+} \gamma_B}{\gamma_{BH^+} K_a} \frac{[S]}{K_a} \quad (3.2.6)$$

While the observed reaction rate constant reaction is:

$$k_{\text{obs}} = \frac{k_2}{K_a} \frac{a_{\text{H}^+} \gamma_{\text{B}}}{\gamma_{\text{BH}^+}} \quad (3.2.7)$$

And if we recall that H_0 is:

$$H_0 = -\log \frac{a_{\text{H}^+} \gamma_{\text{B}}}{\gamma_{\text{BH}^+}} \quad (3.2.8)$$

Then combining equation 3.2.8 and 3.2.7 yields:

$$\log k_{\text{obs}} = \text{constant} + \log \frac{a_{\text{H}^+} \gamma_{\text{B}}}{\gamma_{\text{BH}^+}} = \text{constant} - H_0 \quad (3.2.9)$$

Thus, a reaction following an A1 mechanism where water or other nucleophiles are not involved in the RDS (equation 3.2.2) produces a linear line in plot $\log k_{obs}$ against $-H_0$. The $\log k_{obs}$ and $-H_0$ values corresponding to the hydrolysis conditions of BHB in $[HC_{4im}][HSO_4]$ utilising the three different water contents and varied acidity are shown in Table 3.4. The $\log k_{obs}$ of the reactions were plotted against $-H_0$ in Figure 3.19.

Table 3.4 $\log k_{obs}$ and $-H_0$ values for the hydrolysis of BHB with $[HC_{4im}][HSO_4]$ at 80 °C.

Sulfuric acid mol%	10 wt% H ₂ O		20 wt% H ₂ O		30 wt% H ₂ O	
	$-H_0$	$\log k_{obs}$	$-H_0$	$\log k_{obs}$	$-H_0$	$\log k_{obs}$
0	-2.49	-4.05	-1.93	-4.00	-1.79	-4.10
9.10	-1.73	-3.30	-1.04	-3.40	-1.00	-3.52
16.7	-0.66	-3.10	-0.53	-3.10	-0.61	-3.22
23.1	0.24	-2.89	-0.38	-2.92	-0.60	-3.05
28.6	0.61	-2.74	-0.06	-2.77	0.08	-2.92
33.3	1.17	-2.47	1.21	-2.66	0.90	-2.80
42.9	0.76	-2.36	0.96	-2.39	0.11	-2.57

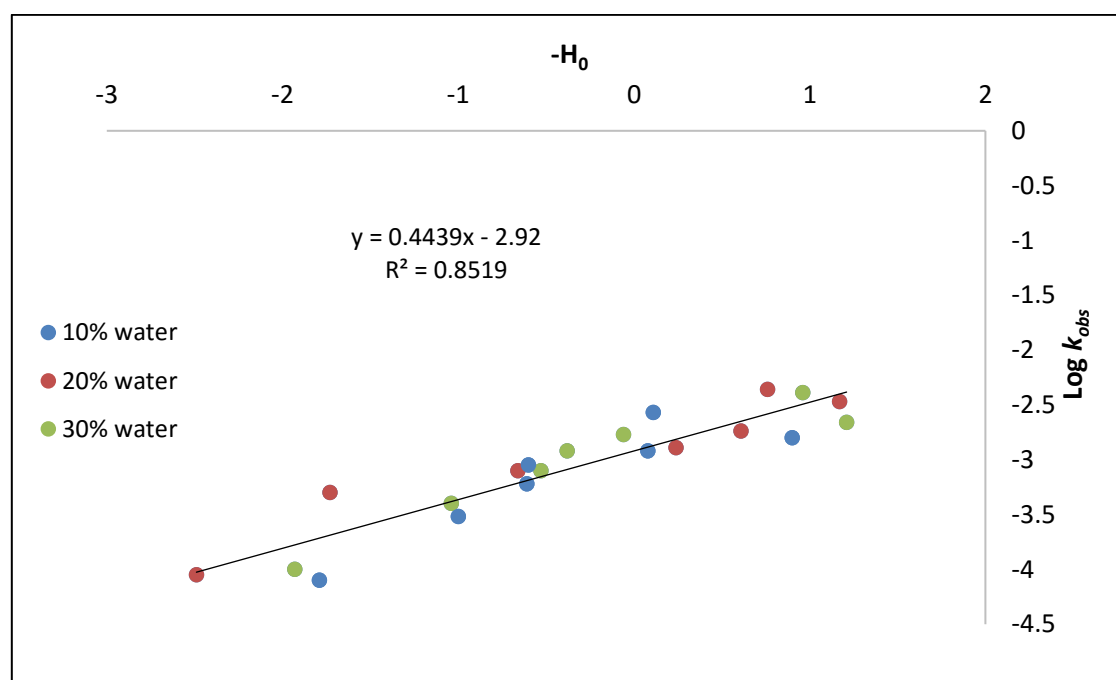


Figure 3.19 Plot $\log k_{obs}$ against $-H_0$ for the hydrolysis of BHB within $[HC_{4im}][HSO_4]$ at 80 °C.

The resulting plot in Figure 3.20 showed that the correlation between $\log k_{obs}$ and $-H_0$ is not linear and the slope value is 0.44. This value is not in agreement with the Zucker-Hammett's A1 mechanism hypothesis requirement which, the line should be linear with slope value is 1. Separate calculation of slope values of each reaction with 10%, 20% and 30% water were also done and they are 0.40, 0.46 and 0.52 respectively. This result suggests that A1 mechanism is not favourable in this reaction. This plot was also tested for the other hydrolysis of the second model compound, THFF in $[HC_4im][HSO_4]$ at the same condition. Table 3.5 shows the $\log k_{obs}$ and H_0 values of the reaction and the plot of $\log k_{obs}$ vs $-H_0$ is shown in Figure 3.20.

Table 3.5 $\log k_{obs}$ and $-H_0$ values for hydrolysis of THFF with $[HC_4im][HSO_4]$ at 80 °C.

Sulfuric acid mol%	10 wt% H ₂ O		20 wt% H ₂ O		30 wt% H ₂ O	
	$-H_0$	$\log k_{obs}$	$-H_0$	$\log k_{obs}$	$-H_0$	$\log k_{obs}$
0	-2.49	-3.30	-1.93	-3.30	-1.79	-3.10
9.10	-1.73	-2.30	-1.04	-2.41	-1.00	-2.52
16.7	-0.66	-2.12	-0.53	-2.22	-0.61	-2.31
23.1	0.24	-2.00	-0.38	-2.10	-0.60	-2.15
28.6	0.61	-1.82	-0.06	-1.96	0.08	-2.00
33.3	1.17	-1.77	1.21	-1.85	0.90	-1.92
42.9	0.76	-1.67	0.96	-1.70	0.11	-1.74

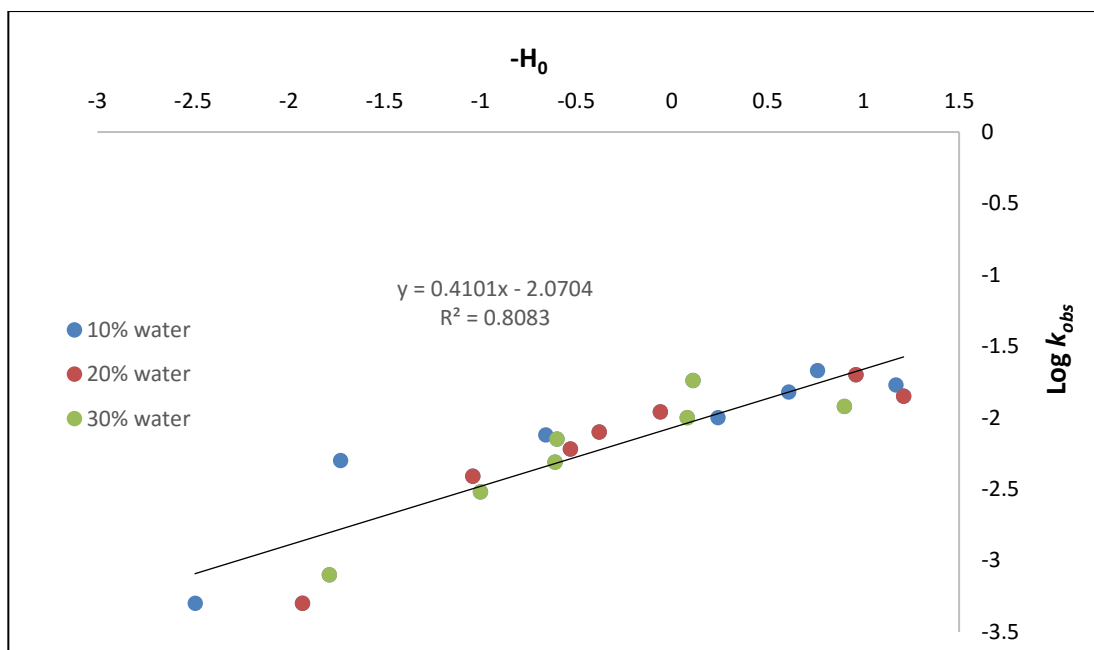


Figure 3.20 Plot $\log k_{obs}$ against $-H_0$ for the hydrolysis of THFF within $[\text{HC4im}][\text{HSO}_4]$ at 80°C .

The same trend is observed with this reaction, where the plot does not show a good straight line and the slope value is below 1. The individual slopes of each 10%, 20% and 30% water reactions were calculated as 0.37, 0.44 and 0.47 respectively. This again suggests that the reaction did not occur via the A1 mechanism like the Zucker-Hammett hypothesis suggested. However, this hypothesis in which an A1 reaction will give a linear plot of $\log k_{obs}$ vs $-H_0$ with a unity slope is found to be unreliable as the A_{SE2} mechanism can also give linear correlation for the same plot.^{195, 189} However, since the two resulting plots do not show straight lines, and the slopes are below than 1, this implies that the reactions did not occur via A1 or A_{SE2} mechanism.

Zucker-Hammett also suggested that for reactions that proceed via an A2 mechanism, the rate of the reaction will vary proportionally with $[\text{H}^+]$.¹⁹⁶ This hypothesis is supported by several studies of ester hydrolyses that are well-established to proceed

through an A2 mechanism which showed that in aqueous solution, the logarithms of the rate constants change linearly with $\log [H^+]$ with slopes of unity. Chmiel and Long found the relationship between the observed rate constants of the hydrolysis reactions of methyl benzoate and two monoglyceryl esters of benzoic and anisic acids are significantly more linear with $[H^+]$ than h_0 (antilog $-H_0$).¹⁹⁷ Bell, Dowding and Noble found similar results in their studies of ethyl acetate and methyl formate hydrolysis in hydrochloric and sulfuric acid.¹⁹⁸

According to ester hydrolysis studies performed by Yates and Cox¹⁹⁹ and Bunnett and Olsen,^{200,201} the $[H^+]$ is the molarity of the strongest acid in the mixture, thus the $[H^+]$ values in the reactions with the mixture of IL and sulfuric acid will be determined by the concentration of sulfuric acid. In the reactions without added sulfuric acid, the $[H^+]$ will be determined by the concentration of the $[HSO_4]^-$ anion. Therefore, it is sensible to treat these in two different plots.

Table 3.6 Log k_{obs} and log $[H^+]$ values for hydrolysis of BHB with $[HC_{4im}][HSO_4]$ at 80 °C.

Sulfuric acid mol%	10% H ₂ O		20% H ₂ O		30% H ₂ O	
	Log $[H^+]$	Log k_{obs}	Log $[H^+]$	Log k_{obs}	Log $[H^+]$	Log k_{obs}
0	0.71	-4.05	0.66	-4.10	0.62	-4.15
9.10	-0.30	-3.30	-0.35	-3.40	-0.39	-3.52
16.7	-0.01	-3.10	-0.06	-3.10	-0.10	-3.22
23.1	0.15	-2.89	0.11	-2.92	0.07	-3.05
28.6	0.27	-2.74	0.22	-2.77	0.19	-2.92
33.3	0.35	-2.47	0.31	-2.66	0.27	-2.80
42.9	0.50	-2.36	0.46	-2.39	0.43	-2.57

The $\log k_{obs}$ of the BHB hydrolysis in $[\text{HC}_{4im}][\text{HSO}_4]$ without added acid were plotted against $\log [\text{H}^+]$ (Figure 3.21). This gives a straight line with a slope just greater than unity (1.22). The reactions with added sulfuric acid give a similar trend with a linear relationship that has a slope of 1.22 (Figure 3.22). The individual slopes of reactions of 10%, 20% and 30% water were calculated as 1.23, 1.21 and 1.14 respectively. This is consistent with the presence of an A2 mechanism as outlined in the previously mentioned studies.

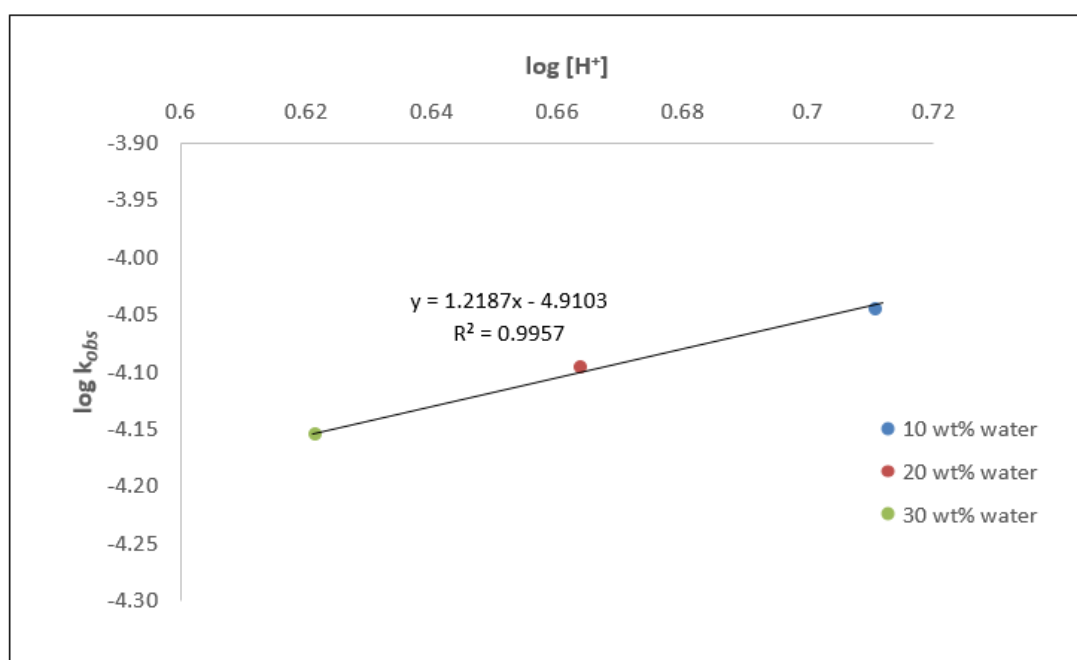


Figure 3.21 Plot of $\log k_{obs}$ vs $\log [\text{H}^+]$ for the hydrolysis of BHB within $[\text{HC}_{4im}][\text{HSO}_4]$ without added sulfuric acid at 80 °C.

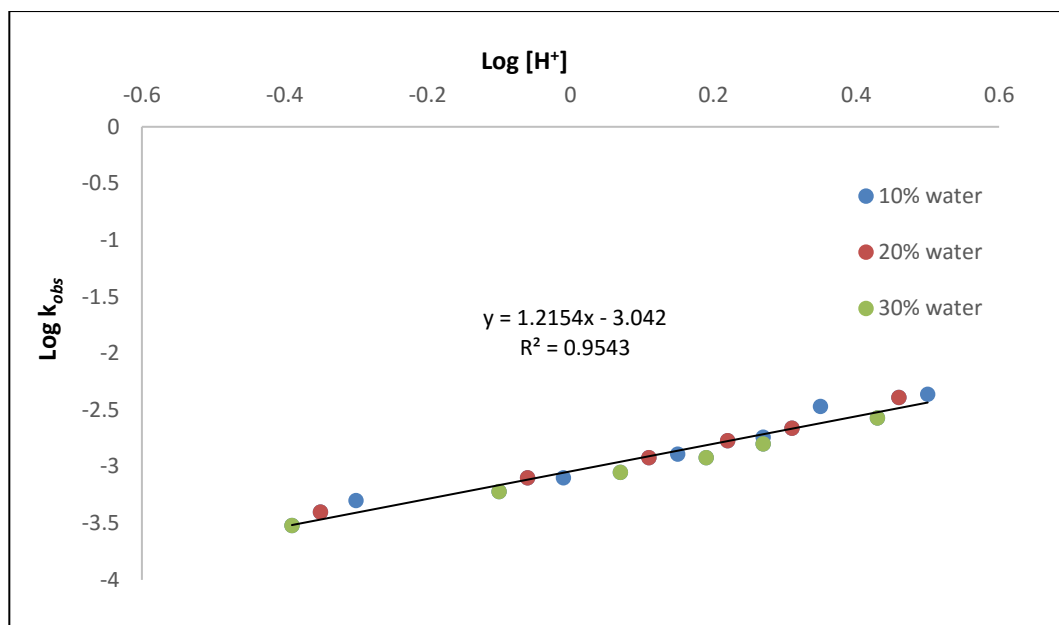


Figure 3.22 Plot of $\log k_{obs}$ vs $\log [H^+]$ for the hydrolysis of BHB within $[HC_4im][HSO_4]$ with added sulfuric acid at 80 °C.

The rate constants for the hydrolysis of the second compound, THFF were treated with the same theory and the plots of $\log k_{obs}$ vs $\log [H^+]$ of both reactions in neat IL without added acid, and those with added sulfuric acid (Figure 3.23 and 3.24), give straight lines with slopes of 1.22 and 1.00 respectively. The individual slopes of reactions of 10%, 20% and 30% water with added acid were calculated as 0.83, 0.96 and 0.89 respectively.

Table 3.7 $\log k_{obs}$ and $\log [H^+]$ values for the hydrolysis of THFF with $[HC_4im][HSO_4]$ at 80 °C.

Sulfuric acid mol%	10% H ₂ O		20% H ₂ O		30% H ₂ O	
	Log [H ⁺]	Log k _{obs}	Log [H ⁺]	Log k _{obs}	Log [H ⁺]	Log k _{obs}
0	0.71	-3.05	0.66	-3.10	0.62	-3.15
9.10	-0.30	-2.30	-0.35	-2.41	-0.39	-2.52
16.7	-0.01	-2.12	-0.06	-2.22	-0.10	-2.31
23.1	0.15	-2.00	0.11	-2.10	0.07	-2.15
28.6	0.27	-1.82	0.22	-1.96	0.19	-2.00
33.3	0.35	-1.77	0.31	-1.85	0.27	-1.92
42.9	0.50	-1.67	0.46	-1.70	0.43	-1.74

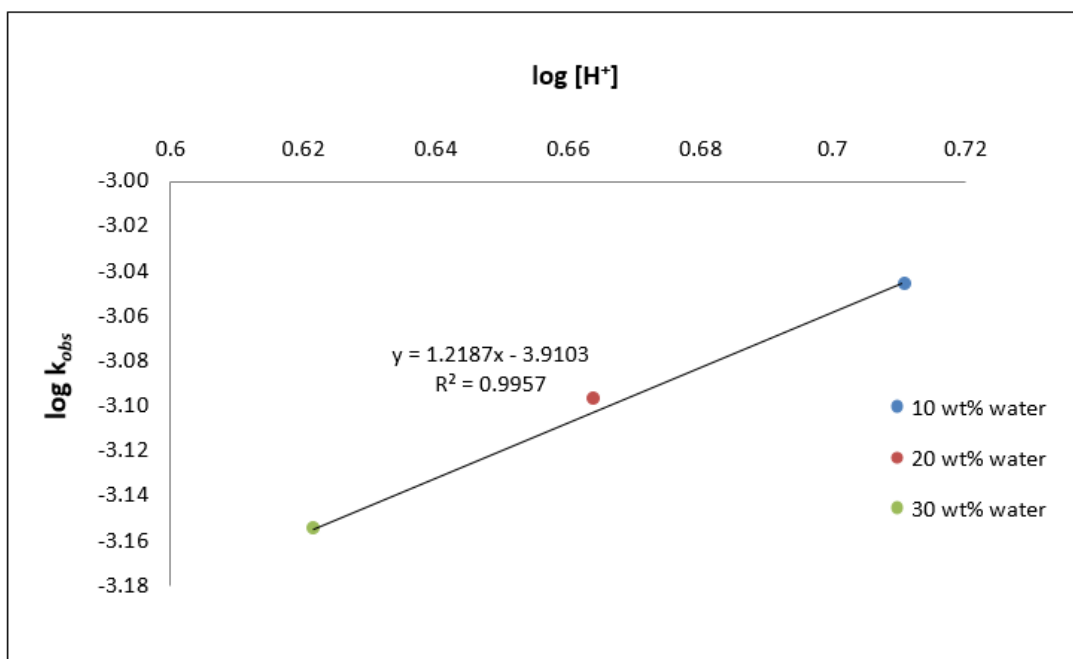


Figure 3.23 Plot of $\log k_{obs}$ vs $\log [H^+]$ for the hydrolysis of THFF within $[HC_4im][HSO_4]$ without added sulfuric acid at 80 °C.

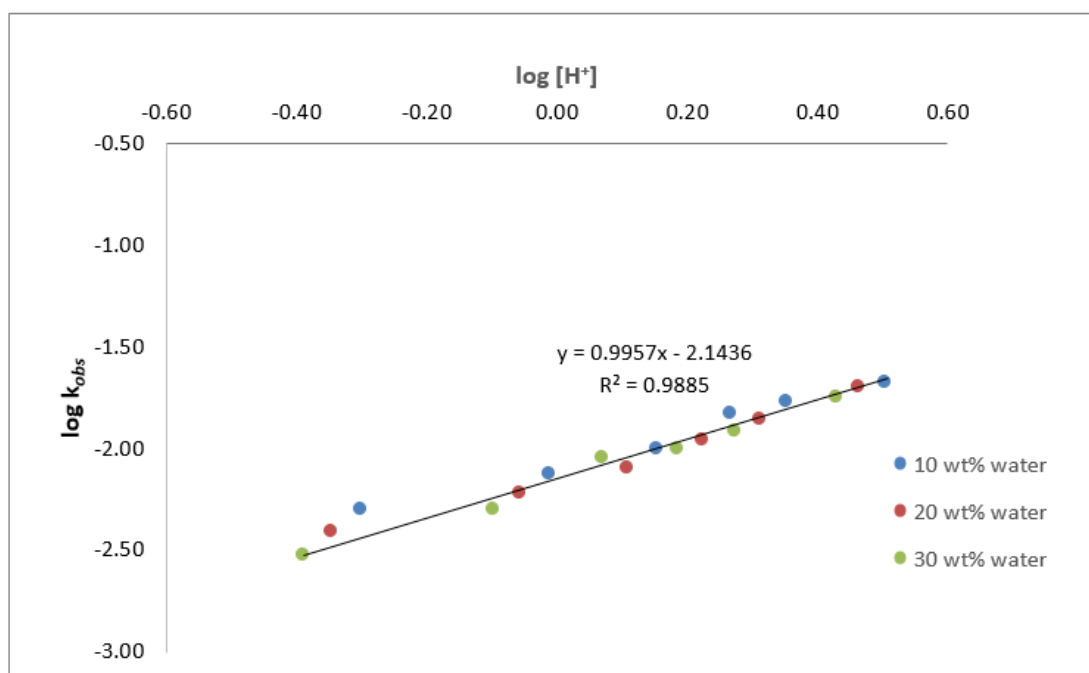


Figure 3.24 Plot of $\log k_{obs}$ vs $\log [H^+]$ for the hydrolysis of THFF within $[HC_4im][HSO_4]$ with added sulfuric acid at 80 °C.

As we can determine from the four plots, the hydrolysis rates of these two esters in aqueous mixture of $[\text{HC}_4\text{im}][\text{HSO}_4]$ and sulfuric acid vary linearly with $\log [\text{H}^+]$. This behaviour is similar to the bimolecular hydrolysis of methyl benzoate in aqueous perchloric acid (1 to 4 M), α -glyceryl monobenzoate and monoanisoate in aqueous perchloric acid (0.04 to 6 M), α -glyceryl esters of benzoic, anisic and 3,4,5-trimethoxybenzoic acids in aqueous solutions of sulfuric acid (0 to 1 M).¹⁹⁷ The slopes of these lines, ranging from 1.00 to 1.23, are in the same range as those of the A2 type ester hydrolysis of ethyl acetate and methyl formate in hydrochloric and sulfuric acid which were 1.00 to 1.60.¹⁹⁸ Another similar case is the hydrolysis of γ -butyrolactone in aqueous solutions of perchloric and hydrochloric acids where the reaction was expected to follow the A2 mechanism. In these reactions it was shown that the rate coefficients were proportional to $[\text{H}^+]$ with the plot of $\log k_t$ vs $\log [\text{H}^+]$ giving slopes of 1.00 and 1.08 while being non-linear in h_0 .²⁰² In contrast, the rate constants for the hydrolysis of β -propiolactone varied linearly with H_0 but not with $[\text{H}^+]$, which was claimed as evidence of an A1 mechanism.²⁰³ All of these reactions support the Zucker-Hammett A2 hypothesis, thus the similar results obtained here imply that both esters in this study, BHB and THFF are hydrolysed via the A2 mechanism in aqueous solutions of $[\text{HC}_4\text{im}][\text{HSO}_4]$ with or without the addition of sulfuric acid.

3.3.5.2 Bunnett-Olsen criterion

Bunnett and Olsen proposed an extended version of the Zucker-Hammett hypothesis to increase its applicability to a larger number of acid catalysed reactions. This theory

suggested that there is a linear free energy relationship between $\log ([SH^+]/[S]) + H_0$ and $H_0 + \log [H^+]$ where S is a base protonated by an aqueous acid solution and $H_0 + \log [H^+]$ represents the activity function of amine bases used for the measurement of H_0 .²⁰¹

$$\log \frac{[SH^+]}{[S]} + H_0 = \Phi(H_0 + \log [H^+]) + pK_{SH^+} \quad (3.3.1)$$

Here, ϕ is the hydration parameter, which represents the response of the equilibrium between S and SH^+ to changes in the acid concentration. For kinetic measurements, a similar equation can be applied;

$$\log k_{obs} + H_0 = \Phi(H_0 + \log [H^+]) + k_2^0 \quad (3.3.2)$$

Where k_{obs} is the *pseudo*-first-order rate constant and k_2^0 is the second-order rate constant at infinite dilution in water. In this case, ϕ signifies the reaction rate response to the changing of acid concentration. The value of ϕ usually lies between -1 to 1 and, based on the determination of ϕ across 160 sets of kinetic data. Bunnett and Olsen categorised the ϕ values of the selected calibration reactions according to their reaction mechanisms, and derived the proposed classification of ϕ values and its significance (Table 3.8).^{201,200}

Table 3.8 Bunnett-Olsen ϕ values and their related mechanism

ϕ value	Mechanism
< 0.0	A1, water not involved in RDS
0.22 to 0.56	A2, water involved as nucleophile in RDS
> 0.58	A2, water involved as proton transfer agent in RDS

This equation is still used in the study of hydrolysis reactions in moderately and strongly acidic media. Fernandez *et al.* have studied the acidic hydrolysis of esters in microemulsions and by using the Bunnett-Olsen equation they found that the mechanism of the reaction changed from A2 to A1 as the water content decreased. This was attributed to the association of water with the surfactant counter-ion at low concentrations of water, reducing its availability to react.²⁰⁴ Cox and Yates also supported the use of the Bunnett-Olsen equation in less well-studied media.¹⁹⁹

For this study, two plots of $\log k_{obs} + H_0$ vs $H_0 + \log [H^+]$ were prepared for each compound. Figures 3.25 and 3.26 represent the Bunnett-Olsen plots for BHB while Figures 3.27 and 3.28 are for THFF. This is because the calculation of $[H^+]$ for the reactions without added sulfuric acid and with the addition of sulfuric acid is different for both cases, as has been discussed previously. The hydrolysis of BHB in aqueous $[HC_4im][HSO_4]$ gave a nearly perfect straight line with almost unity slope, $\phi = 1.02$. The same trend was observed for the reactions with the addition of sulfuric acid, with the same ϕ value of 1.02. These positive ϕ values which support the existence of an A2 mechanism, in agreement with the previous hypothesis.

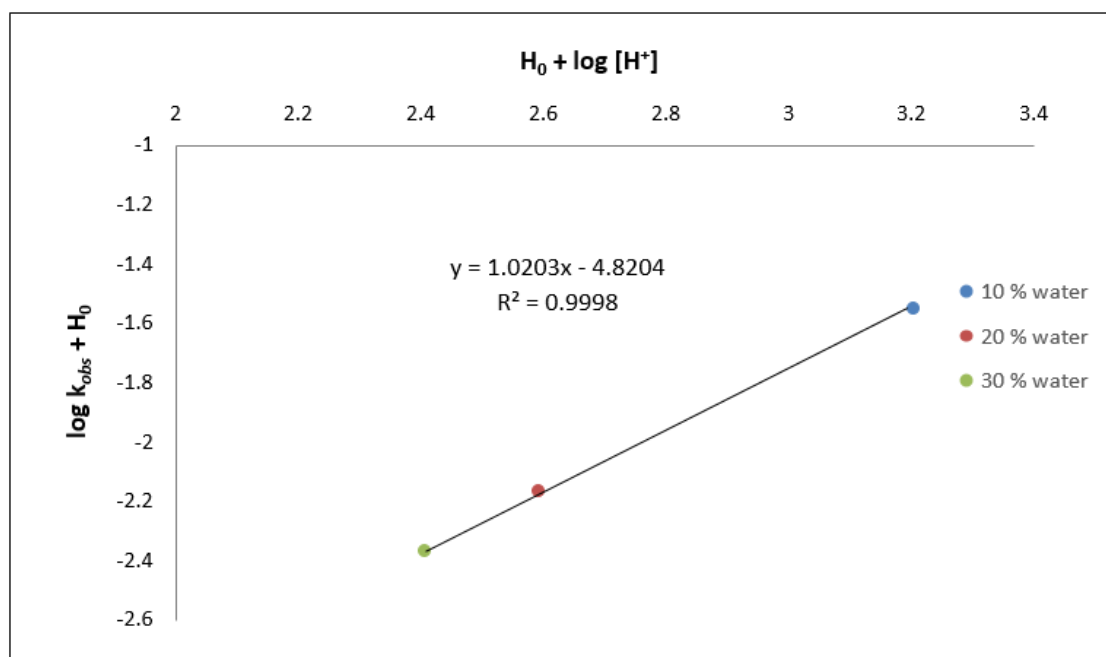


Figure 3.25 Bunnett-Olsen plot for the hydrolysis of BHB in aqueous $[HC_4im][HSO_4]$ without added sulfuric acid at 80 °C.

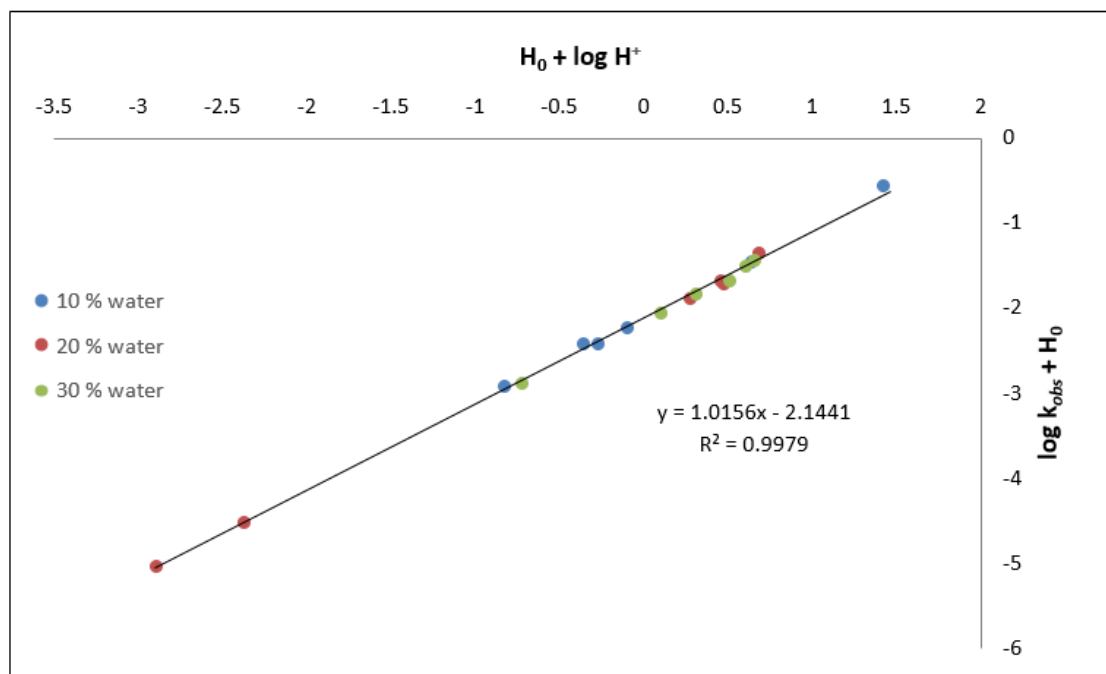


Figure 3.26 Bunnett-Olsen plot for the hydrolysis of BHB in aqueous $[HC_4im][HSO_4]$ with added sulfuric acid at 80 °C.

The same trends were observed for the THFF hydrolysis in both reactions, in the IL without sulfuric acid and those with added sulfuric acid. Both cases give a ϕ value of 1.02. This indicates that the ferulate model compound, THFF, also underwent hydrolysis via the same A2 mechanism as the benzoate, BHB.

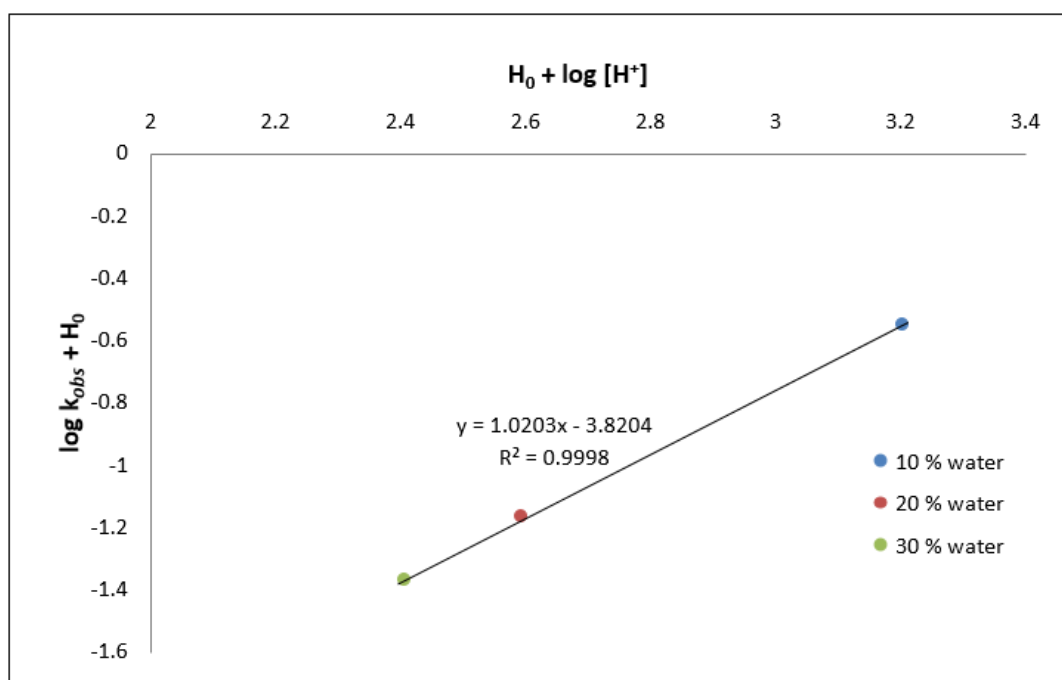


Figure 3.27 Bunnett-Olsen plot for the hydrolysis of THFF in aqueous $[HC_4im][HSO_4]$ without added sulfuric acid at 80 °C.

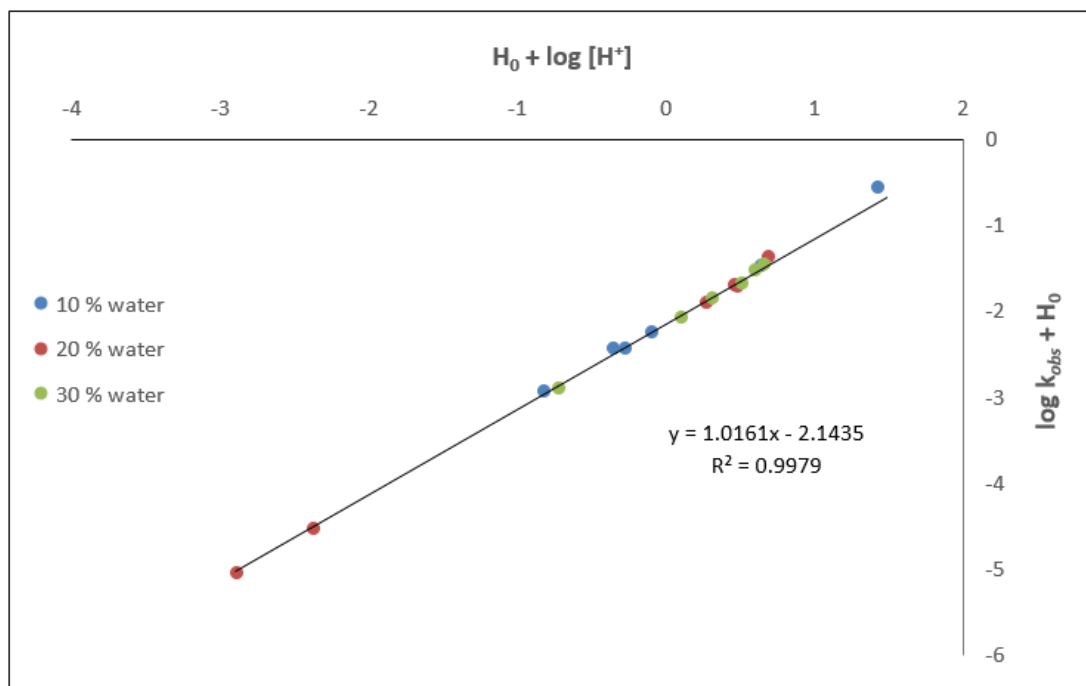


Figure 3.28 Bunnett-Olsen plot for the hydrolysis of THFF in aqueous $[HC_4im][HSO_4]$ with added sulfuric acid at 80 °C.

The large values of ϕ values signify that A2 mechanism was favoured in these reactions.

This is similar to previous ester hydrolysis reactions, listed in Table 3.9.

Table 3.9 ϕ values and mechanism of present work and selected ester hydrolysis from literature.

Reaction	ϕ	Proposed mechanism	Ref
Methyl benzoate (aq. $HClO_4$)	0.98	A2	201
α -glyceryl monobenzoate (aq. $HClO_4$)	0.99	A2	201
Ethyl acetate (aq. H_2SO_4)	0.84	A2	201
Methyl 2-benzoylbenzoate (aq. H_2SO_4)	0.66	A2	205
4-Nitrophenylacetate (aq. HCl)	0.74	A2	204
4-Nitrophenylacetate (microemulsion of water/NaOT/isooctane)	1.38	A2	204
4-Nitrophenyllaurate (microemulsion of water/NaOT/isooctane)	1.74	A2	204
BHB (aq. $[HC_4im][HSO_4]$)	1.01	A2	present work
BHB (aq. $[HC_4im][HSO_4] + H_2SO_4$)	1.07	A2	present work
THFF (aq. $[HC_4im][HSO_4]$)	1.36	A2	present work
THFF (aq. $[HC_4im][HSO_4] + H_2SO_4$)	1.00	A2	present work

As Bunnett-Olsen suggested that water acts as a base and nucleophile in the RDS for ϕ values larger than 0.58 and this effect has been borne out by other authors that have applied this equation and have found comparable ϕ values, it implies -that the hydrolysis of BHB and THFF in aqueous $[\text{HC}_4\text{im}][\text{HSO}_4]$ with or without the addition of sulfuric acid proceeds via a bimolecular mechanism, where the water acts as a base and nucleophile in the RDS. As Bunnett and Olsen have highlighted, this equation is merely empirical and must be used with caution, thus this proposed mechanism will be further interrogated by enumerating the activation parameters, as discussed in the next section.

3.3.6 Activation Parameters of the Reaction using the Eyring Equation

Another experimental criterion that makes it possible to distinguish between unimolecular and bimolecular mechanisms in acid catalysed reactions is the entropy of activation, $\Delta S^\ddagger$. $\Delta S^\ddagger$ provides insight into the molecularity or arrangement of atoms in the transition state with respect to the loss or gain of translational, rotational or vibrational degrees of freedom compared to the initial state.²⁰⁶

According to Whalley²⁰⁷ and Schaleger and Long,²⁰⁸ the thermodynamics of the transition states of acid/base reactions may be used as model comparison for other reactions that have similar equilibria.²⁰⁸ They collected substantial amounts of kinetic data, mainly hydrolysis reactions, and compared the entropies of activation obtained for each reaction to distinguish the mechanism of the reaction. Some of these data are listed in Table 3.10. They established that $\Delta S^\ddagger$ for an A1 reaction typically has values between 0 and 42 $\text{JK}^{-1}\text{mol}^{-1}$ while for A2 reactions the values are typically between -60 to -120 $\text{JK}^{-1}\text{mol}^{-1}$. This is in agreement with the theory that $\Delta S^\ddagger$ can provide information on the

molecularity of the RDS of the reaction. The bimolecular reaction will have negative values as the entropy decreases upon reaching the transition state due to association of two molecules to form a single activated complex. Thus $\Delta S^\ddagger$ for A2 hydrolysis reactions should have lower values than A1 reactions due to the involvement of the water molecule in the transition state. The association of these molecules means that translational and rotational degrees of freedom are lost in the transition state compared to the initial state where the motion of water and the ester are independent.

$\Delta S^\ddagger$ values can be obtained from the Eyring equation which is based on transition state theory. Consider a bimolecular reaction, the rate of the reaction will be;

$$r = k [A][B] \quad (3.4.1)$$

$$\text{and } k [A][B] = \nu [A][B]K^\ddagger \quad (3.4.2)$$

where, k is rate constant, ν is frequency of vibration and $K^\ddagger$ is equilibrium constant describing the equilibrium between the initial state and the activated complex.

The frequency of vibration given by;

$$\nu = k_B T / h \quad (3.4.3)$$

where k_B is Boltzman's constant, T is temperature in Kelvin and h is Plank's constant.

This equation can be simplified to;

$$k = \nu K^\ddagger \quad (3.4.4)$$

and inserting equation 3.4.3 into 3.4.4;

$$k = \frac{k_B T}{h} K^\ddagger \quad (3.4.5)$$

The thermodynamic equation is described by;

$$\Delta G^\ddagger = -RT \ln K^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (3.4.6)$$

Where $\Delta G^\ddagger$ is the Gibbs energy of activation, R is the gas constant (8.314 JK⁻¹mol⁻¹)

$\Delta H^\ddagger$ is the enthalpy of activation, and $\Delta S^\ddagger$ is the entropy of activation. From equation

3.4.6, $\ln K^\ddagger$ can be described by;

$$\ln K^\ddagger = -\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R} \quad (3.4.7)$$

Recall the equation 3.4.5 and combine with the equation 3.4.7 to yield the Eyring equation;

$$k = \frac{k_B T}{h} e^{-\frac{\Delta H^\ddagger}{RT}} e^{\frac{\Delta S^\ddagger}{R}} \quad (3.4.8)$$

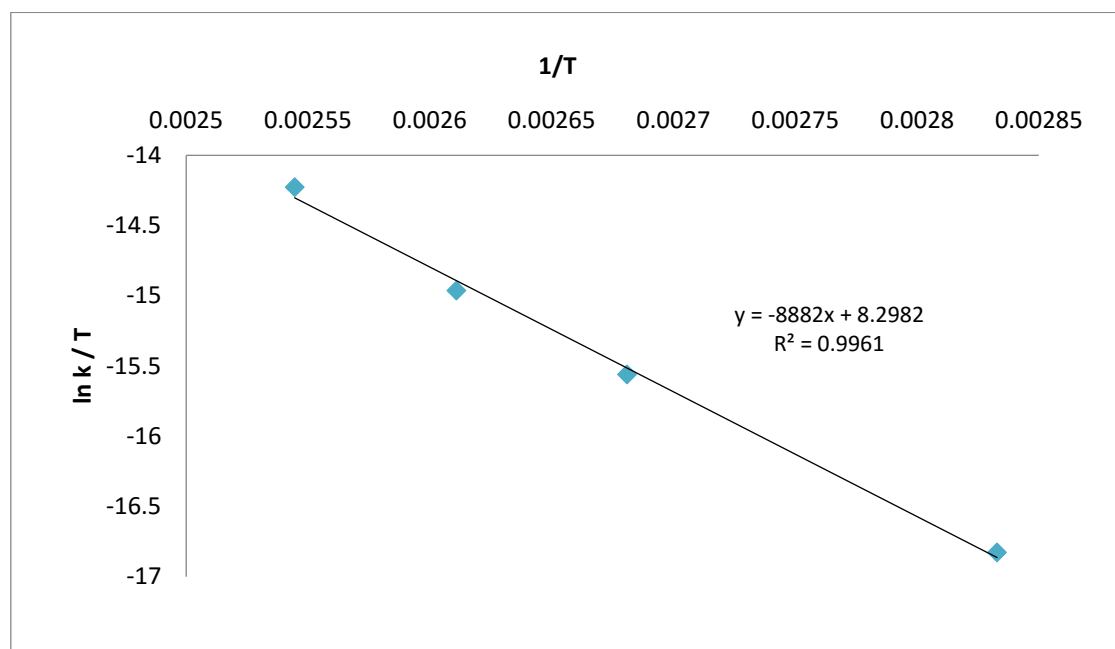
In the linear form, the equation can be described by;

$$\ln \frac{k}{T} = -\frac{\Delta H^\ddagger}{R} \frac{1}{T} + \ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R} \quad (3.4.9)$$

Thus plotting $\ln k/T$ vs $1/T$ will give $-\Delta H^\ddagger/R$ as the slope with $\ln k_B/h + \Delta S^\ddagger/R$ as the intercept. The hydrolysis of BHB and THFF were performed in [HC₄im][HSO₄] with 20% water at 80, 100, 110 and 120 °C to enable the enumeration of activation parameters through the use of the Eyring equation. The kinetic data of the reactions are listed in Table 3.10 and their Eyring plots are shown in Figures 3.29 and 3.30.

Table 3.10 Eyring plot data for the hydrolysis of BHB in aqueous [HC₄im][HSO₄].

Temperature, K	k x 10 ⁻⁴	ln k/T	$\Delta H^\ddagger$	$\Delta S^\ddagger$
353	0.17	-16.83		
373	0.65	-15.56	73.85 kJ/mol	-128.53
383	1.21	-14.96	19.72 kCal	
393	2.60	-14.23		

**Figure 3.29** Eyring plot for the hydrolysis of BHB in aqueous [HC₄im][HSO₄].**Table 3.11** Eyring plot data for the hydrolysis of THFF in aqueous [HC₄im][HSO₄].

Temperature, K	k x 10 ⁻³	ln k/T	$\Delta H^\ddagger$	$\Delta S^\ddagger$
353	0.17	-14.52		
373	1.04	-12.78	80.22 kJ/mol	-88.13
383	1.96	-12.18	19.17 kCal	
393	3.04	-11.77		

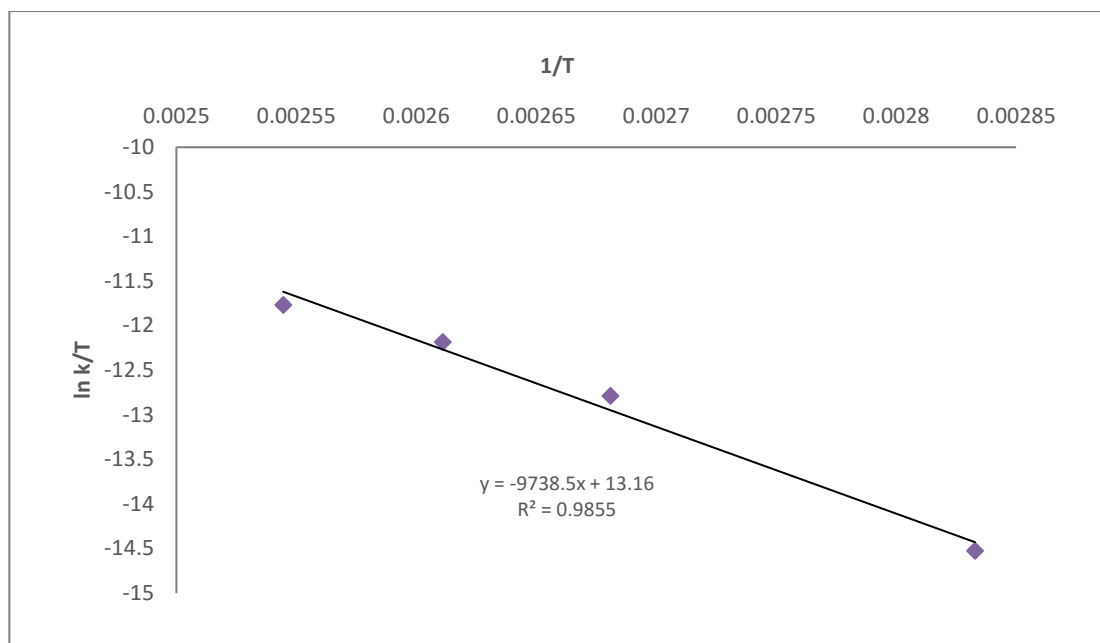


Figure 3.30 Eyring plot for the hydrolysis of THFF in aqueous [HC₄im][HSO₄].

From the resulting Eyring plots, the $\Delta S^\ddagger$ values calculated from the slope values are -128.5 and -88.13, which indicate a bimolecular mechanism. The large negative values show the loss of translational and rotational freedom of the nucleophilic water molecule in the transition state. These values are comparable with the previous A2 hydrolysis reactions (Table 3.12). The $\Delta H^\ddagger$ for both compounds are similar, which are 73.85 and 80.22 kJ⁻¹ mol⁻¹, respectively indicating that both compounds proceed through the same mechanism.

Table 3.12 Entropy change of activation and mechanism of selected hydrolysis reactions from literatures and this study.^{205,207,208}

Substrate	$\Delta S^\ddagger$ (JK ⁻¹ mol ⁻¹)	Mechanism	Ref
Ethyl acetate	-96.2	A2	207
Ethyl benzoate	-110.5	A2	207
Methyl pseudo-2-benzoylbenzoate	-81.2	A2	205
t-Butyl acetate	59.4	A1	208
γ -Propiolactone	39.3	A1	208
γ -Valerolactone	-102.9	A2	208
BHB	-128.5	A2	present work
THFF	-100.3	A2	present work

3.4 Conclusion

In this chapter, the reactivity of the ester linkage in biomass during pretreatment was studied by investigating the hydrolysis of two model compounds, BHB and THFF in [HC₄im][HSO₄]. The effects of the water content and acidity on the reaction were also determined by this kinetic study. From the kinetic data, the rates of the hydrolysis of the two esters increase with increasing acid concentration and slightly decreased with increasing water content. Overall the hydrolysis of the benzoate is one order of magnitude lower than the ferulate and this is due to the electronic effects where BHB is less basic compared to the ferulate. It was found that the hydrolysis of these two esters occurred via an A2 mechanism, where the water is involved in the RDS. These mechanisms were determined using the Zucker-Hammett and Bunnett-Olsen equations,

and the $\Delta S^\ddagger$ values obtained from Eyring plots. All three methods are in agreement regarding the bimolecular mechanism.

This finding therefore provides insight on the reactivity of the ester linkage in biomass and also the effects of water and acidity on the delignification process when the hemicellulose is separated from the lignin components. It is apparent that to achieve faster cleavage of hemicellulose from lignin, higher acid concentrations and moderate water contents in the IL are required.

Chapter 4

4 Transesterification in $[\text{HC}_4\text{im}][\text{HSO}_4]$

4.1 Background of the Study

4.1.1 Transesterification

Transesterification is a classic organic reaction that has various applications in laboratory practices and in industry such as pharmaceuticals, cosmetics, polymers, and fuels.²⁰⁹ Similar to esterification, transesterification can be catalysed by acids, such as sulfuric, sulfonic, phosphoric and hydrochloric acid or bases such as metal alkoxides, acetates, oxides and carbonates.⁷⁴ For example, natural triglycerides can be transesterified into fatty acid methyl or ethyl esters by using heterogeneous catalysts such as calcium, manganese, and zinc oxide.²¹⁰ The use of conventional liquid acids and bases often poses drawbacks in synthesis and environmental concerns, such as poor separation and purification, equipment corrosion, and production of waste. Due to that reason, solid acids have been used as an alternative to tackle these problems. However, solid acids have limitations of poor mass-transfer causing low activity, long reaction times, and deactivation.²¹¹ Biocatalysts are another sustainable alternative that are widely used in transesterification processes.²¹² Despite their high efficiency, their short

lifetimes, long reaction times and relatively massive expense compared to sulfuric acid and sodium hydroxide make them restricted to certain industrial applications.²¹³

Transesterification is one of the important processes that has been applied extensively in the biorefinery.^{214,215} Oil-rich biomass such as vegetable oil can be converted via transesterification to produce biodiesel.^{216,217} Biodiesel is among the important alternative fuels that can contribute to a sustainable environment. Since biodiesel is derived from renewable sources, it could be among the solutions to tackle the problem of diminishing of petroleum reserves. Within this field, lots of efforts and studies have been done, especially involving ILs to develop better processes and production.^{88,142,218} In biodiesel production, transesterification with simple alcohol is used to liberate glycerol and the biofuel esters that are isolated from triglycerides (Figure 4.1).

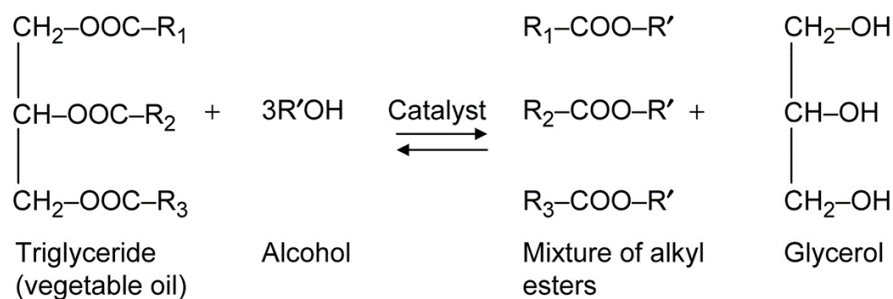


Figure 4.1 Transesterification process to produce glycerol and alkyl esters.²¹³

4.1.2 ILs in Transesterification as Solvent

As discussed in the Introduction chapter 1.6, ILs' unique physical properties make them famous as “designer solvents”. The ILs can be tuned to meet the process requirements, during the reaction and the work-up, such as separation of the products, recycling of the catalyst and the solvent, and waste handling. This is due to the adjustability of their

hydrophobicity, selectivity, and polarity. ILs have been found to be effective as the solvent and support for biocatalytic reactions.²¹⁹ Various ILs have been used in enzyme-catalysed transesterification.^{220,213} Notably, lipase has exhibited an increase in catalytic activity in transesterification in ILs due to the hydrophobicity and polarity of the ILs used.²²¹ A study of the lipase-catalysed methanolysis of soya bean oil has been done in several ILs (Figure 4.2). The result shows that the product, fatty acid methyl ester (FAMES) was most produced in [C₂C₁im][OTf] which was slightly higher than using *tert*-butanol as an additive.²²²

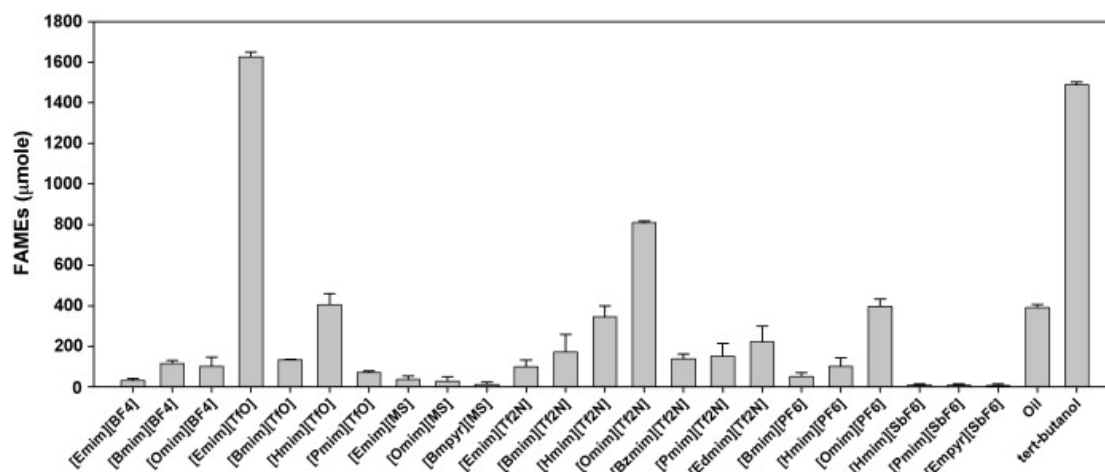


Figure 4.2 Lipase-catalysed methanolysis of soya bean oil with several additives.²²²

Another similar study also showed high conversion with [C₄C₁im][NTf₂] supported with lipase, due to the fact that the glycerol adsorption onto the IL support shifted the reaction equilibrium towards the product.²²³

Transesterification of β -ketoesters catalysed by sulfamic acid were found to be more selective in imidazolium chloride ILs compared to the reactions in CH₂Cl₂ or hexane. The authors mentioned about how the chloride ILs acted as dual solvent and catalyst for

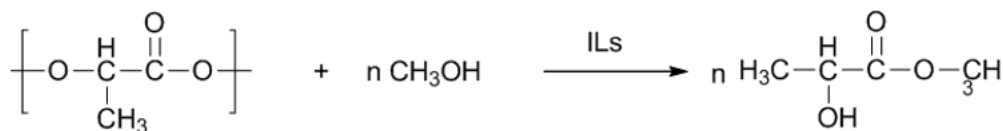
the reaction but no detailed explanation was presented upon this finding.²²⁴ Previous study investigated the effect of polarity of the solvents in acid catalysed transesterification of methylmethoxy acetate with benzyl alcohol in [C₄C₁im][NTf₂] and [C₄C₁im][OTf] and other organic solvents. Using the Kamlet-Taft parameters, it was found that the solvent basicity is the dominant parameter in determining acid-catalysed transesterification rate and the reactions were faster in low basicity solvents.⁸¹

4.1.3 ILs as Catalysts in Transesterifications

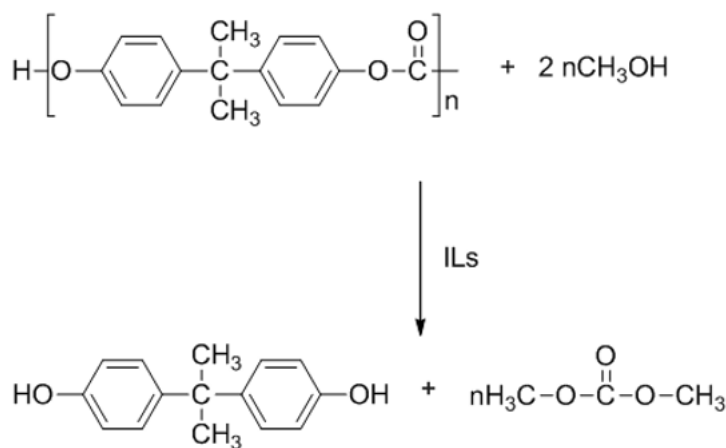
ILs have been found to be successful in catalysing many reactions such as Michael reactions, Friedel-Crafts alkylations, acylations and esterifications.^{225,226,227} Many studies have been done on ILs as catalysts for transesterification reactions, and most of the studies exhibit Brønsted acidic and basic ILs as the single catalyst.^{144,145,228} In producing biodiesel, this approach is profoundly important to make a product that is free of contamination from residual catalyst. Wu *et. al.* investigated various Brønsted acidic ILs as catalysts in the conversion of cottonseed oil to biodiesel via transesterification with methanol.¹⁴⁴ The 1-(4-sulfonic acid)-butylpyridinium hydrogen sulfate ([C₄(SO₃H)Pyr][HSO₄], which had the highest values of Brønsted acidity was found to produce the highest yield, 95% using 12 equivalents of methanol. They also found that the catalytic activity of the IL was comparable to the conventional catalyst for this reaction; H₂SO₄. Not only producing very high yield, sulfonic acid functionalised ILs also can be reused up to 7-9 times in catalysing conversion of Jatropha and waste vegetable oils.^{142,228}

Chemical recycling of polymers such as polyester and polycarbonate also involves transesterification or alcoholysis as a route for depolymerisation (Scheme 4.1 and 4.2).

ILs have been used as the catalyst and always exhibit good catalytic effects in this process.



Scheme 4.1 Methanolysis of polylactic acid in ILs



Scheme 4.2 Methanolysis of polycarbonate in ILs

Recently, [C₄C₁im]Cl, [C₄C₁im][OAc] and [C₄C₁im][HSO₄] were found to be effective catalysts for the methanolysis of polylactate acid, PLA to methyl lactate, ML (Table 4.1). High yield and conversion were obtained from the methanolysis of PLA in [C₄C₁im][HSO₄] and [C₄C₁im][OAc] but zero conversion in [C₄C₁im]Cl.²²⁹ High conversion and yield were observed in [C₄C₁im]Cl and [C₄C₁im][OAc] for the methanolysis of polycarbonate, PC (Table 4.1).^{230,231}

Table 4.1 Methanolysis of PC and PLA in several ILs.

ILs	PC ^{226,227}		PLA ²²⁵	
	Conversion (%)	BPA Yield (%)	Conversion (%)	ML Yield (%)
Blank (without IL)	0	0	0	0
[C ₄ C ₁ im] Cl	100	95.6	0	0
[C ₄ C ₁ im][OAc]	100	96.0	97.2	92.5
[C ₄ C ₁ im][HSO ₄]	-	-	90.2	87.9

A series of [HSO₄]⁻ ILs were synthesised and studied for their catalytic activity for transesterification of β -ketoester with 1-butanol (Table 4.2).²³² The ILs were used in a catalytic amount, 5 mol% in solvent free condition. *N*-methyl-2-pyrrolidonium hydrogen sulfate, [C₁pyrr][HSO₄] was found to exhibit the highest catalytic activity where the conversion and yield of the reaction were 98% and 79%, respectively. Further in the same study, [C₁pyrr][HSO₄] was tested as a catalyst for other transesterification reactions, and showed that it is capable to transesterify aliphatic, aromatic and cyclic β -ketoesters with several aliphatic and aromatic alcohols with high yields.

Table 4.2 Transesterification of β -ketoester with 1-butanol (1.5 equivalent to ester) at 80 °C after 3 h.²³²

Catalyst	Conversion (%)	Selectivity (%)	Yield (%)
[C ₄ C ₁ im][p-TSA]	75	93	70
[C ₄ C ₁ im][HSO ₄]	81	90	73
[HC ₁ im][HSO ₄]	83	89	74
[C ₁ pyrr][HSO ₄]	80	98	79
Amberlyst-15	78	79	62
Montmorillonite-K10	35	71	25

From the findings mentioned above, again $[\text{HSO}_4]^-$ ILs have shown great potential as combined catalyst and solvent in the transesterification process, whether in polymer and biomass transformations or in other organic synthesis applications. Despite, many studies reported on the use of $[\text{HSO}_4]^-$ IL as a catalyst in esterification, detailed information about how this IL behaves and acts in transesterification reactions was yet to be reported. In this chapter, the capability of $[\text{HC}_4\text{im}][\text{HSO}_4]$ as catalyst and solvent will be explored and studied in transesterification reactions of ester model compounds and compared with the *aprotic* $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ IL. By investigating this, further understanding of the catalytic activity of $[\text{HSO}_4]^-$ ILs will be revealed in order to improve the transesterification process in recycling of polyesters or production of biodiesel. Finally, it is also to be hoped that the outcome of this experiment will give preliminary insight on the possibility of performing transesterification during the pretreatment of lignocellulosic biomass in this IL as it has already shown the high effectiveness in delignification of a variety of lignocellulosic biomass.^{1,9}

4.1.4 Model compounds

The first model compound chosen for this study was benzyl 4-hydroxybenzoate, BHB (Figure 4.3) as it is soluble in $[\text{HSO}_4]^-$ ILs. Its structure not only represents the lignin-carbohydrate complex as discussed in the previous chapter (3.1.3) but also similar to the PC monomer structure. As has already been established in the previous chapters, the selection of this compound is also due to easy monitoring of the reaction conversion by ^1H NMR.

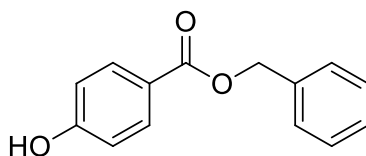


Figure 4.3 Benzyl 4-hydroxybenzoate, BHB

Ethyl lactate was used in this study to compare its reactivity in $[\text{HSO}_4]^-$ ILs with BHB (Figure 4.4). This compound is similar to the PLA repeating unit structure, lactic acid and is expected to give a faster rate as its structure is simple and more basic than the benzoate.

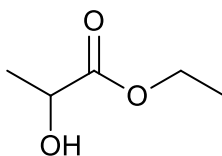


Figure 4.4 Ethyl lactate

4.2 Aims and Objectives

This chapter aimed to study the ability of $[\text{HC}_4\text{im}][\text{HSO}_4]$ IL to act as catalyst and solvent in transesterification of BHB with methanol and ethylene glycol. Methanol was chosen in this study as most of the chemical recycling of polyesters is based on methanolysis. In addition, this chapter also aim to investigate if a side reaction of alcohol with the $[\text{HSO}_4]^-$ anion could take place and interrupt the reaction conversion and yield.

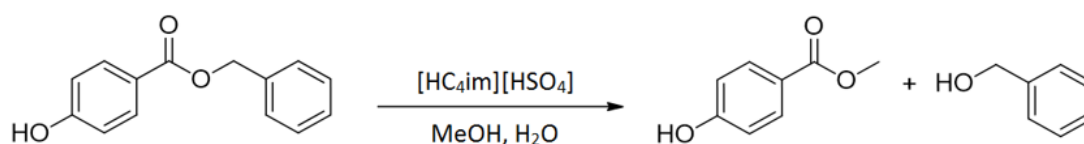
The influence of alcohol molar ratio, water content, and IL concentration will be investigated. This needs to be done in order to identify the optimum conditions towards obtaining the highest yield. Overall, this chapter aims to provide a better understanding

of transesterification in $[\text{HSO}_4]^-$ ILs as well as to give better insights into their promising applications in depolymerising polyesters and biopolymers.

4.3 Results and Discussions

4.3.1 Transesterification of Benzyl 4-hydroxybenzoate, BHB with Methanol and $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80 °C

Transesterification reactions of BHB with methanol were done in aqueous $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80 °C (Scheme 4.3). This condition is similar with the ester hydrolysis and alcohol substitution experiments in the previous chapters. The reactions were analysed using ^1H NMR spectroscopy (Figure 4.5). The yields of the reactions after 24 h were calculated from the relative integration of the methyl signal in product, methyl 4-hydroxybenzoate, and the substrate while the conversions were calculated from the relative integration of the methyl signal in benzyl alcohol and the substrate. The details of the experiments are described in the experimental sections (6.4).



Scheme 4.3 Transesterification of BHB with methanol in $[\text{HC}_4\text{im}][\text{HSO}_4]$

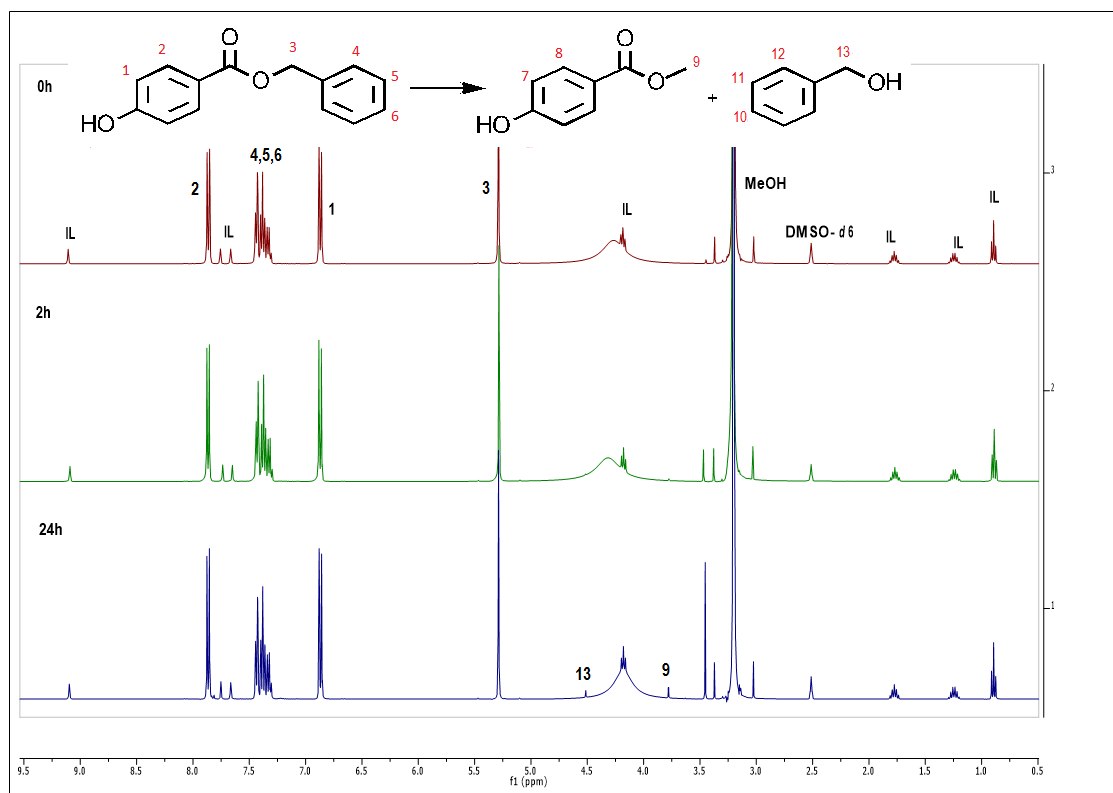


Figure 4.5 ¹H NMR of transesterification of BHB in [HC₄im][HSO₄] with methanol at 80 °C after 2 and 24 h.

The first reactions were done in [HC₄im][HSO₄] with 20 wt% water. The influence on the reaction of two different concentrations of IL, 0.1% and 10% were done to study the IL's function whether it acted better as catalyst, solvent, or both.

Table 4.3 Reaction of BHB with methanol in [HC₄im][HSO₄] with 20 wt% water at 80 °C.

Entry	BHB (mol eq.)	Methanol (mol eq.)	IL (mol eq.)	Conversion (%)	Yield (%)
1	1	5	0.1	2	N.D
2	1	5	10	4	1

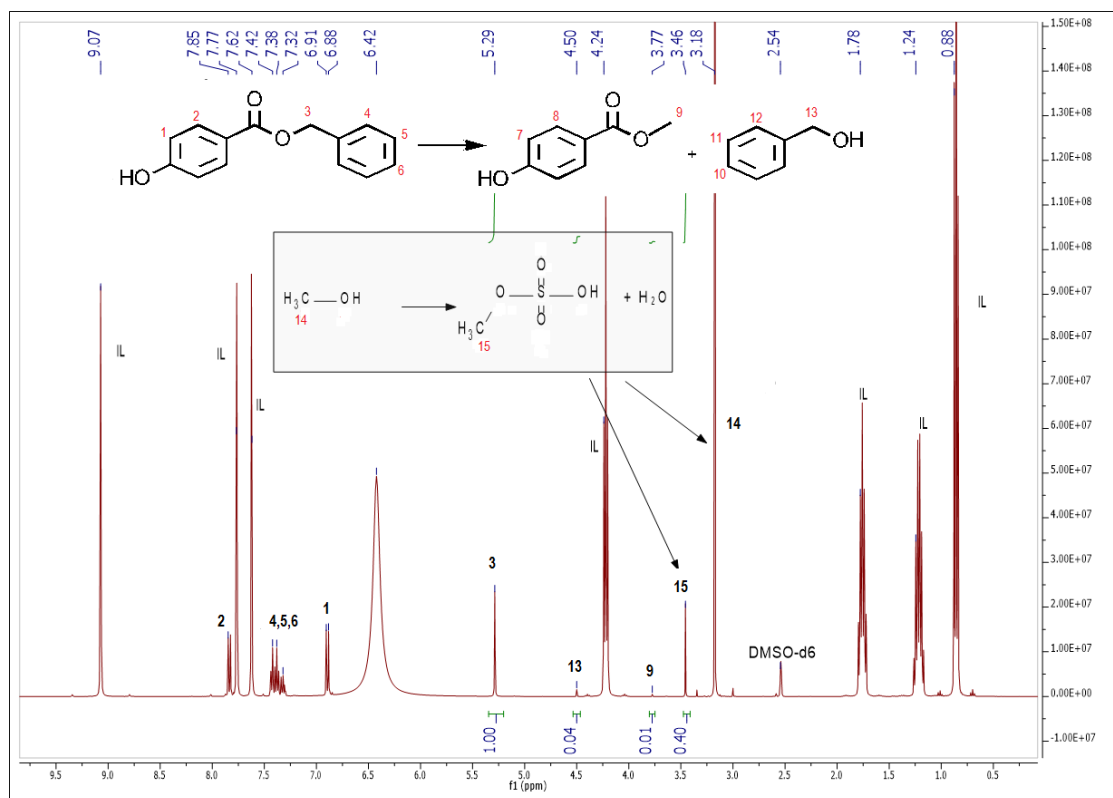


Figure 4.6 ^1H NMR of transesterification of BHB in aqueous $[\text{HC}_4\text{im}][\text{HSO}_4]$ (20 wt% water) with methanol at 80 °C after 24 h.

Unexpectedly, both reactions were found to show no conversion after 2 h. Even after 24 h the conversions were very low, 2% and 4% respectively and the yields are below 1% (Table 4.3). There are new two peaks assigned for the products: a CH_3 peak in methyl 4-hydroxybenzoate at 3.78 ppm and a CH_2 peak in benzyl alcohol at 4.52 ppm. In addition, there is another distinctive new peak observed at 3.44 ppm. This was assigned as the CH_3 peak for $\text{CH}_3\text{-OSO}_3\text{H}$ which is believed to be the product of a side reaction, sulfation of methanol (Figure 4.6). As expected and discussed in Chapter 3, $[\text{HSO}_4]^-$ ILs can react with alcohols as the anion is nucleophilic enough to undergo a substitution reaction with the hydroxyl group.

Due to the low yields, the reactions were subsequently tested in non-aqueous solution. Even though sulfation of the methanol was anticipated, it was hoped that changing the

concentration of the IL and methanol will give effects by reducing the side reaction at the same time, increasing the yield. According to the transesterification reactions with $[\text{HSO}_4]^-$ ILs in the literature, all of them were performed in non-aqueous condition.^{229,232,144} Hence, this parameter should be tested.

4.3.1.1 Influence of water in the reaction

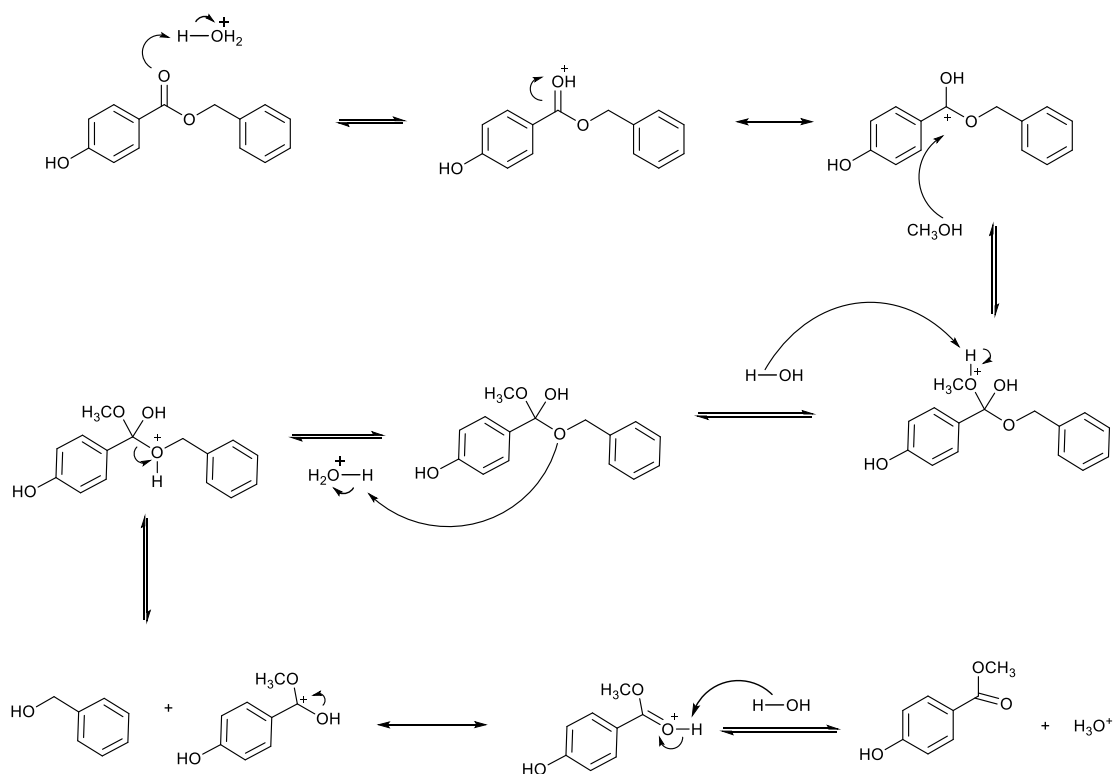
To compare with the reactions in aqueous IL, the reactions in non-aqueous conditions were further carried out with varied molar ratio of methanol and IL. After 24 h, the conversion, and yield were found to be very low, all are below 5% (Table 4.4).

Table 4.4 Transesterification of BHB with methanol in non-aqueous $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80 °C.

Entry	BHB (mol eq.)	Methanol (mol eq.)	IL (mol eq.)	Conversion (%)	Yield (%)
3	1	5	10	1	1
4	1	10	1	2	2
5	1	10	10	2	1
6	1	10	0.2	5	3
7	1	10	0.75	2	2

It was found that the conversions in aqueous IL are slightly higher than the reactions in non-aqueous solution. To compare the water effect, reaction 2 (from Table 4.3) which has similar molar ratio of ester:methanol:IL (1:5:10) with reaction 3 (Table 4.4), has higher conversion 5% compared to 1% in reaction 3. In contrast, the yield of the reaction 3 was higher than reaction 2, 1% and 2%, respectively. This could be due to the water molecules improving the protonation of the ester by increasing the availability of H_3O^+ ions (Scheme 4.4). The water only aided the hydrolysis of the ester instead of promoting

the transesterification. Even though methanol was in excess than water, 1:10 of molar ratio, this did not help the reaction force to move forward to product.

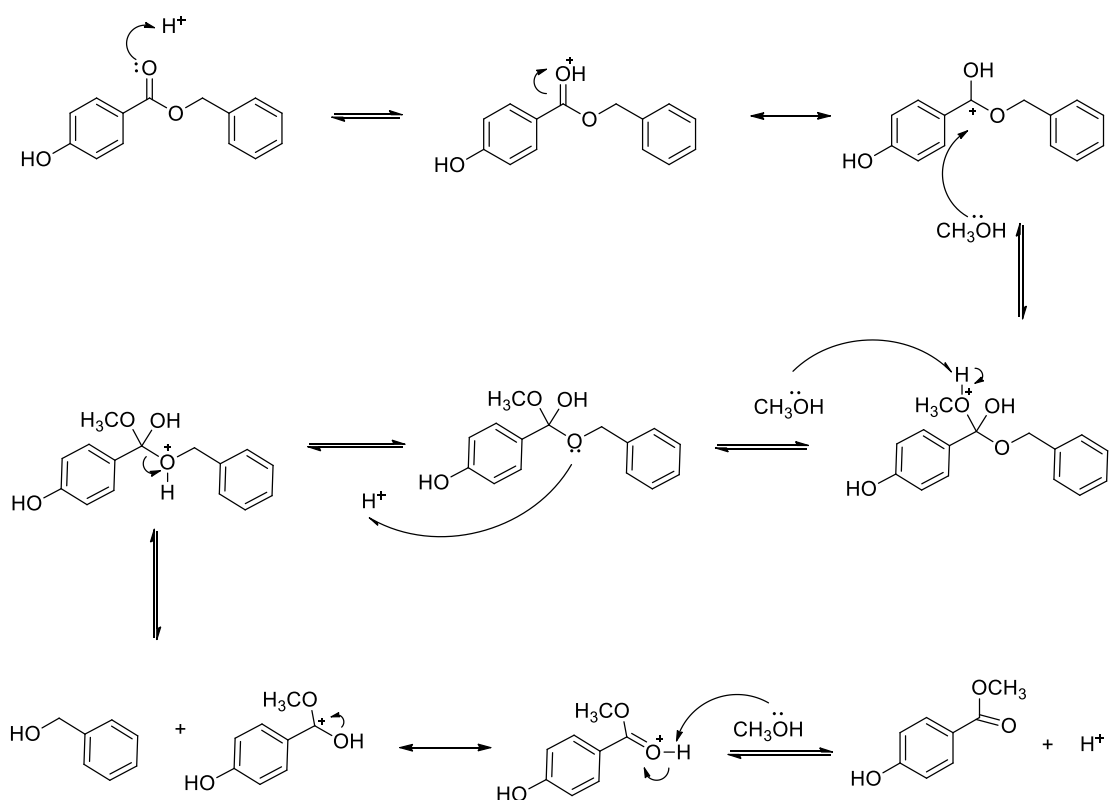


Scheme 4.4 Mechanism of transesterification of BHB in aqueous [HC₄im][HSO₄] with methanol.

This is in agreement with the literature on the transformation of vegetable oils to biodiesel. Acid-catalysed transesterification of vegetable oils was found to be inhibited by the presence of water. Reduced yield and slower rate were observed when the water content is high in these systems, especially when the free fatty acids (FFA) content in the feedstock is high, which will lead to esterification of FFA with the alcohol thus this side reaction will produce more water in the system.^{233,234} Canakci and Van Gerpen reported that for acid catalysed transesterification of soy bean oil, the ester conversion only reached 8% when the water content of the oil was at 5 wt%. They also showed that the water content should be below 0.5 wt% to achieve higher than 90% ester yield

through their reaction conditions (60 ° C, methanol to oil molar ratio 6:1, 3 wt% sulfuric acid and 96 h).²³⁵

In the non-aqueous solution, the yields are low but slightly higher compared to the reactions in aqueous IL. One of the reasons is possibly because the sulfation of the methanol is greater in non-aqueous solution, 24% compared to in aqueous solution, 6%. This could diminish the accessibility of methanol to drive the reaction forward. A proposed mechanism in non-aqueous solution is shown in Scheme 4.5. In addition, the by-product of methanol sulfation is water; this again could inhibit the reaction to yield the methyl ester (Scheme 4.6).



Scheme 4.5 Mechanism of transesterification of BHB in non-aqueous [HC₄im][HSO₄] with methanol.



Scheme 4.6 Sulfation of methanol by [HSO₄]⁻ IL.

4.3.1.2 Influence of IL concentration

From Table 4.4, the influence of IL concentration on the reactions can be studied by comparing their conversion and yield. Figure 4.7 shows the conversion and yield of the three reactions with ester: IL molar ratios of 1:0.75 (5.2 mol%), 1:1 (8.3 mol%), and 1:10 (47.6 mol%), with fixed 1:10 (ester:methanol) ratio. There were no changes in conversion; all three reactions have conversion of 2%. The highest yield 2% was obtained in the reactions with the low concentration of IL, 5.2 and 8.3 mol%, while the lowest yield was obtained from the highest concentration of IL, 47.6 mol%. The reduction in amount was only small, from 2% to 1%; thus it is hard to judge the effect of the molarity of the IL on the yield of the reactions even though some literature suggests that the IL works best as a catalyst in transesterification reaction rather than as a solvent. Qureshi and co-worker reported that 5 mol% was the optimised $[\text{HSO}_4]^-$ ILs concentration that were used to catalysed β -ketoester transesterification with 1-butanol.²³²

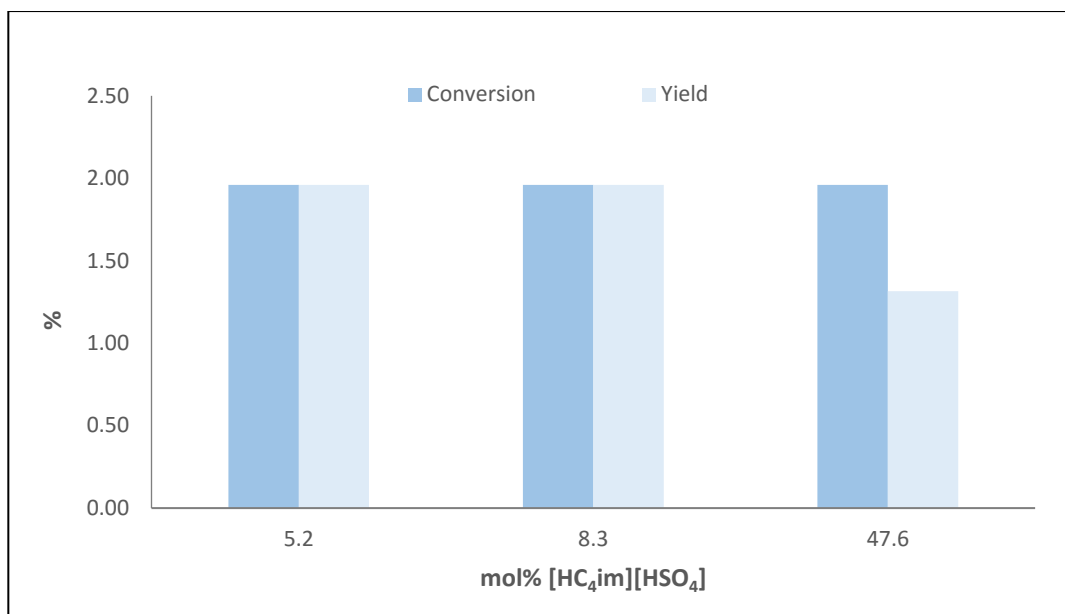


Figure 4.7 Influence of [HC₄im][HSO₄] concentration on transesterification of BHB with methanol at 80 °C.

4.3.2 Transesterification of BHB at 120 °C

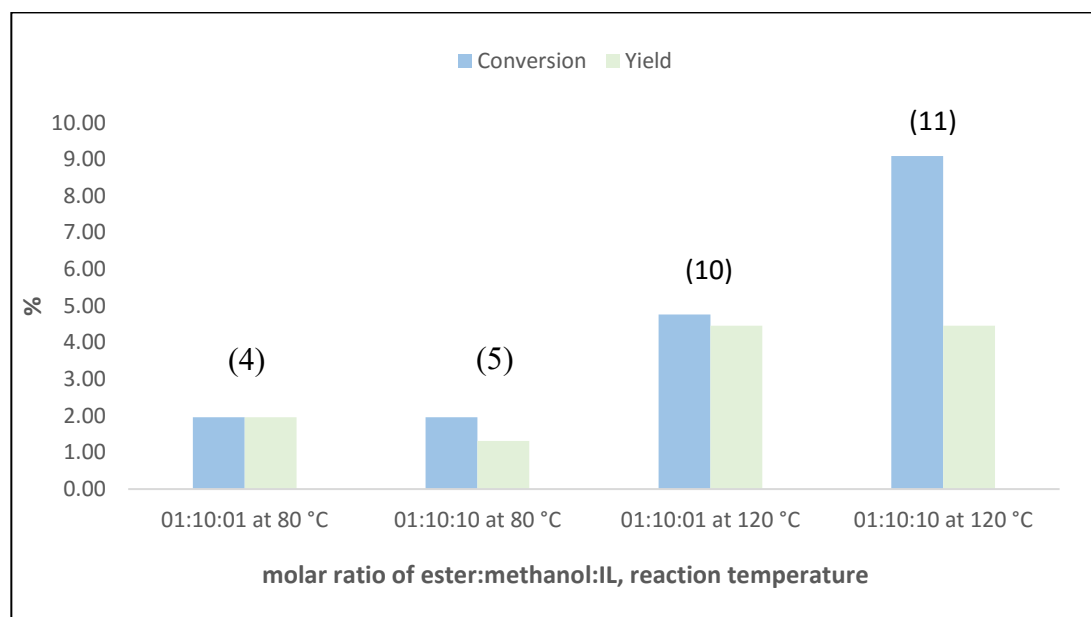
Due to the low yield, it was decided to increase the reaction temperature to 120 °C to see whether it has any substantial effect on the reaction yield or conversion. The reactions were done in closed pressure tube (sealed with Teflon lining) to avoid methanol evaporation. Table 4.5 shows the conversion and yields of the transesterification of BHB with methanol at 120 °C with varying water content and molar ratio of ester:methanol:IL. The highest conversions, 12% were obtained from the reaction with added water.

Table 4.5 Transesterification of BHB with methanol and [HC₄im][HSO₄] at 120 °C

Entry	BHB (eq)	Methanol (eq)	IL (eq)	Water (eq)	Conversion (%)	Yield (%)
8	1	10	1	10	12	10
9	1	10	10	10	12	5
10	1	10	1	0	5	5
11	1	10	10	0	9	5

4.3.2.1 Influence of reaction temperature

To compare the results with 80 °C, Figure 4.8 shows the conversions and yields of the reactions with molar ratio of ester:methanol:IL, 1:10:1 and 1:10:10 at 80 and 120 °C.

**Figure 4.8** Influence of reagents molar ratio and temperature on transesterification of BHB with methanol and [HC₄im][HSO₄].

From the resulting chart (Figure 4.8), it was found that the increase for both the conversion and the yield are about double the amount when the temperature was increased from 80 to 120 °C. For reactions 4 and 10, which have the same molar ratio of the ester:methanol:IL, slight increase of the conversion was observed, 2% to 5%, with

the yield increasing from 2% to 5%. For reactions 5 and 11 which have molar ratio of 1:10:10, from 80 to 120 °C, the conversion increased from 2% to 9% while the yield increased from 1% to 5%.

It was also found that by increasing the reaction temperature, there were another two side reactions that occurred during the reaction. This was confirmed by appearances of two new peaks at 3.85 and 4.82 ppm (Figure 4.9). The new singlet peak at 4.82 ppm belongs to the CH₂ peak for benzyl sulfate, which is the product of the side reaction of benzyl alcohol with [HSO₄][−] anion (Scheme 4.7). This is supported and described in detail in Chapter 2, Reactivity of Alcohol in Acidic ILs. The peak at 3.85 ppm is assigned to be the CH₃ peak for dimethyl sulfate. This is a product of another side reaction of methanol with methyl hydrogen sulfate (Scheme 4.8).²³⁶

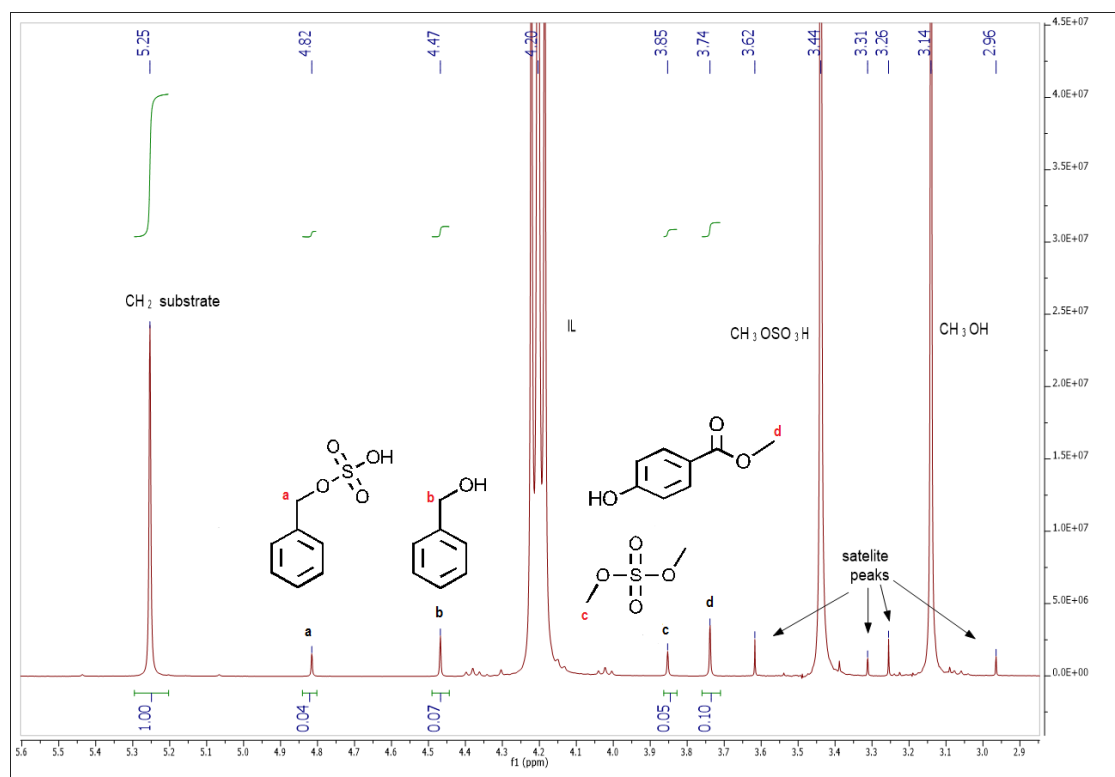
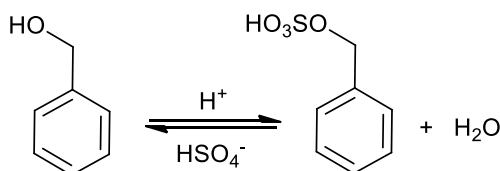
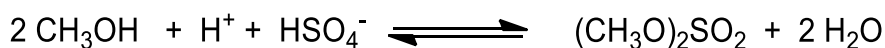


Figure 4.9 ¹H NMR of transesterification of BHB with methanol and [HC₄im][HSO₄] at 120 °C

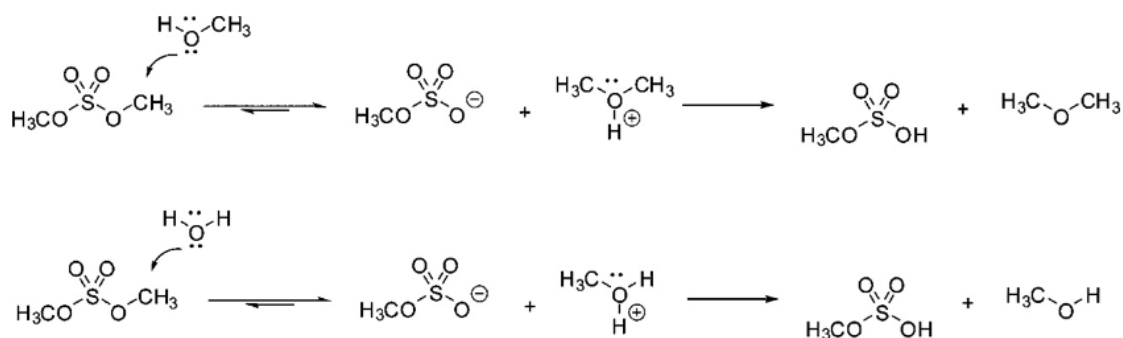


Scheme 4.7 Nucleophilic substitution reaction of $[\text{HSO}_4]^-$ anion with benzyl alcohol



Scheme 4.8 Formation of dimethyl sulfate from reaction of $[\text{HSO}_4]^-$ anion with methanol

Further side reaction of methanol and dimethyl sulfate is expected to occur in this reaction as Guzowski, Jr. et al. reported that methanol and dimethyl sulfate can esterify to produce dimethyl ether (gas).²³⁷ They also noted in the presence of water, a competing hydrolysis of dimethyl sulfate occurred (Scheme 4.9) thus increasing the formation of methyl sulfate and retarding the formation of dimethyl ether.



Scheme 4.9 Methanolysis and hydrolysis of dimethyl sulfate in methanol.²³⁷

4.3.2.2 Influence of water on the reaction

At 120 °C, the influence of water on the reaction was studied by running the reaction in two sets with molar ratio of ester:methanol:IL of 1:10:1 and 1:10:10 with water (10 mol equivalent to ester) and without water (Figure 4.10).

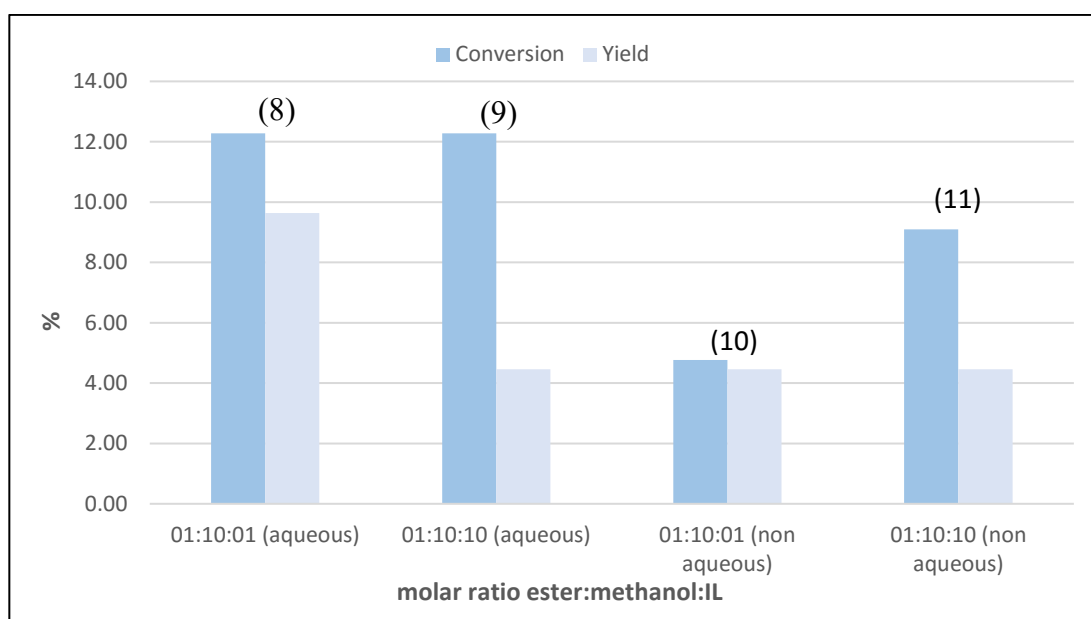


Figure 4.10 Influence of reagents molar ratio and water on transesterification of BHB with methanol and $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 120 °C.

From Figure 4.10, for the same set of molar ratio, 1:10:1, reaction 8 in aqueous solution has higher conversion of 12%, and yield 10%, compared to reaction 10 in non-aqueous solution, which has conversion and yield of 5% respectively. This is contrary to the reactions at 80 °C (Table 4.3 and 4.4), where the yield was the lowest in aqueous solution. This could be due to the presence of water inhibiting the further side reaction by hydrolysing the by-products back to methanol, thus making methanol re-available for the transesterification. For the set of molar ratios of 1:10:10, reaction 9 has slightly higher conversion, 12% compared to reaction 11 which has 9% conversion, but both reactions have the same yield of 5%. In reaction 9, the IL was in much greater amount than water, thus the hydrolysis of the by-product was retarded, and hence the low yield observed in this reaction compared to reaction 8.

From these sets of results and the reactions at 80 °C (Table 4.3 and 4.4), it was found that water improved the conversion and yield, but only if it is in greater amount than the IL. The presence of water increased the hydrolysis of the by-products and thus

diminished the consumption of methanol for esterification with $[\text{HSO}_4]^-$ anion and methanolysis with dimethyl sulfate.

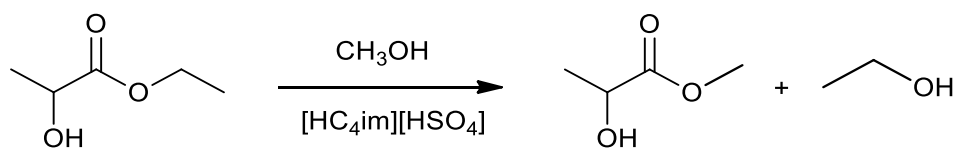
4.3.2.3 Influence of IL concentration

In Table 4.5, the influence of IL concentration was studied at 120 °C, and it was found that the effect of adding the IL in different concentrations was inconsistent and depended on the other reactants' concentrations. From Figure 4.10, the same conversion was observed in reactions of 8 and 9 while the yield was lower in reaction 9. As discussed previously, large amounts of IL increased the formation of by-products. If there is less water than IL, the hydrolysis of the by-product decreases, thus reducing the availability of methanol in the reaction.

The IL amplifies the production of the protonated methanol for protonating the ester but at the same time it reacts with the methanol to form the by-product. Hence, for the reaction in non-aqueous solution of methanol and IL, it was shown that, the higher IL concentration only improved the conversion, but did not affect the yield.

4.3.3 Transesterification of Ethyl Lactate with methanol and [HC4im] [HSO₄]

Another model compound, ethyl lactate, was used to study its reactivity in transesterification with methanol and [HC4im][HSO₄]. It was assumed that this simple aliphatic structure compound will have a higher conversion rate than the benzoate. By referring to the previous reaction, these transesterification reactions of ethyl lactate were done using the parameters that gave the highest conversion and yield in the benzoate reaction. Table 4.6 shows the conversions and yields of the reactions.



Scheme 4.10 Transesterification of ethyl lactate with methanol and [HC₄im][HSO₄]

Table 4.6 Transesterification of ethyl lactate with methanol and [HC₄im][HSO₄] at 120 °C.

Entry	Ethyl lactate	Methanol	IL	Water	Conversion (%)	Yield (%)
(12)	1	10	1	10	55	42
(13)	1	10	1	0	33	27
(14)	1	100	1	0	27	24

From Table 4.6, the conversions and yields for this compound were found to be substantially higher than BHB. This is expected as the carbonyl carbon in the aliphatic ester is more basic than that in the aromatic ester. For reaction in aqueous solution, reaction 12 the conversion and yield are higher compared to in non-aqueous methanol and IL, reaction 13. As has been discussed in section (4.3.2.3), the water improved the regeneration of methanol by hydrolysing the by-products. This compares to reaction 13, where the methanol availability is limited as it has been consumed for the side reactions. Further addition of methanol in the reaction was done to see the effect whether the greater excess amount of methanol in the reaction can help the reaction to move to its completion. The result of reaction 14 showed that the conversion and yield was slightly decreased compared to reaction 13. From the methanol CH₃ peak in ¹H NMR, it was also found that the amount of unreacted methanol after 24 h in the reaction 13 and 14 was not very much different, 43% and 55% respectively. This means the increase of methanol molar ratio from 10 to 100 did not have any significant effect to help the

reaction reach completion, but only diluted the reactants and thus decreased the rate. From the ^1H NMR, side reactions of methanol were found to have occurred and further sulfation of the product, ethanol also took place (Figure 4.11).

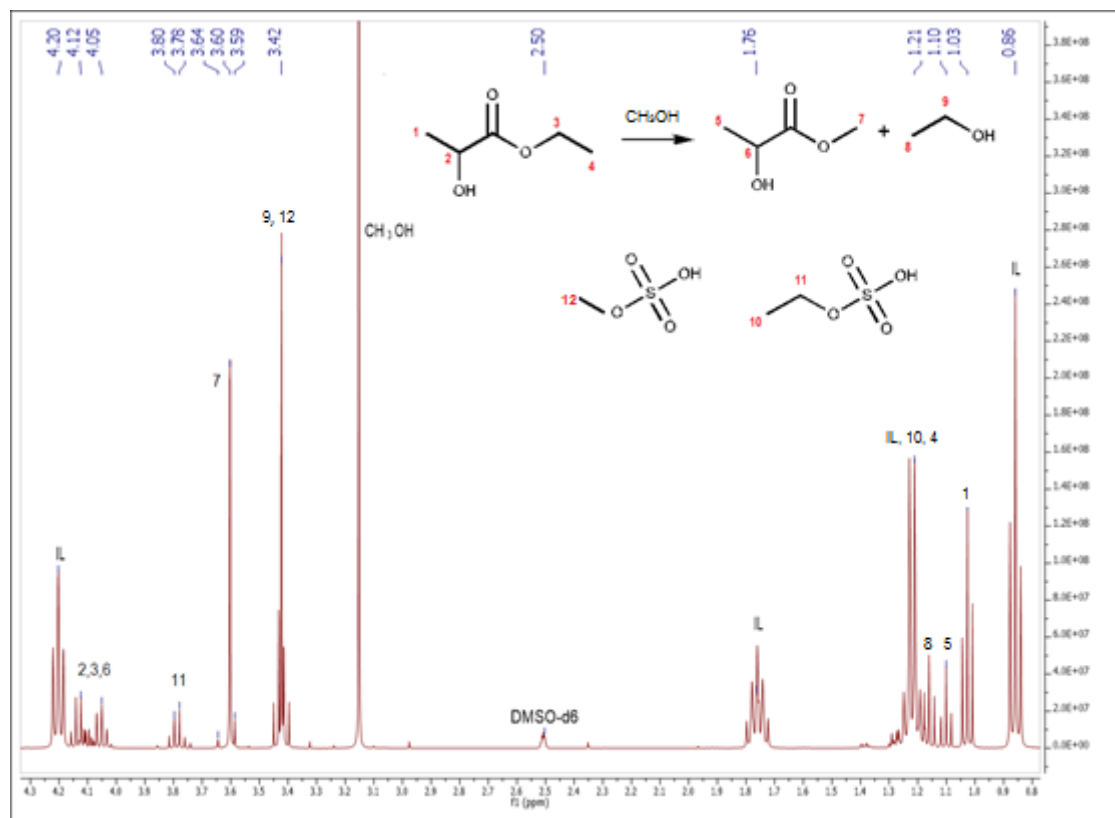


Figure 4.11 ^1H NMR of transesterification of ethyl lactate with methanol and $[\text{HC}_4\text{im}][\text{HSO}_4]$ at $120\text{ }^\circ\text{C}$

In parallel to this study, the low conversion and yield of methanolysis of ethyl lactate in $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ were also reported by MSc student from Welton's research group, Paulius Lesauskas. The highest conversions of methanolysis of ethyl lactate at $110\text{ }^\circ\text{C}$ were found for 0.49 molar equivalent of $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and 0.70 molar equivalent of $[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$ with respect to the ester (Figure 4.12). $[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$ gave higher conversions at all concentrations.

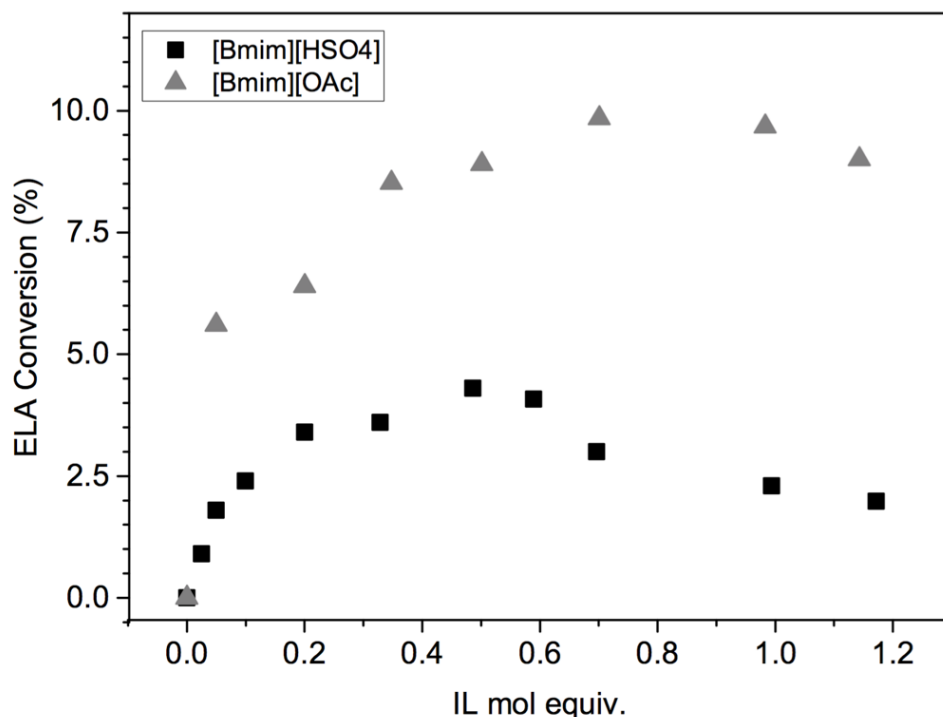


Figure 4.12 ILs concentration effects on methanolysis of ethyl lactate at 110 °C.

As mentioned previously, a few papers have reported that $[C_4C_{1im}][HSO_4]$ was found to be an effective catalyst for transesterification reactions,^{144,228,232,238} either for simple esters or for degradation of triglycerides and polyester, but only one of the papers reported the H_0 of the IL.²³⁸ For the transesterification of *sec*-butyl acetate with methanol and $[C_4C_{1im}][HSO_4]$ at 65 °C, under 0.12 MPa, and after 7 hr, the conversion was almost 60%.²³⁸ But the H_0 of the IL was 1.60, which is slightly more acidic than the $[C_4C_{1im}][HSO_4]$ used in our lab, which is standardised to be $H_0 = 1.96 - 2.0$. The similar value of H_0 of 2.08 has also been reported in other literature.¹³⁵ The lower value of H_0 may indicate that there could be a contamination of IL with sulfuric acid. The trace of sulfuric acid could be present from the synthesis method of the IL and even small amounts of sulfuric acid residue could lead to a higher conversion rate for the reaction. This could be the reason why higher conversion was reported in the literature.

4.4 Conclusions

The role of $[\text{HC}_4\text{im}][\text{HSO}_4]$ in the transesterification reaction between BHB and methanol has been successfully investigated. The influence of the parameters of the reactions such as water content, temperature, and molar ratio between ester: IL and ester:methanol were studied. In contrast with the literature which reported that other $[\text{HSO}_4]^-$ ILs to be effective as catalysts for transesterification reactions, overall reactions of BHB and ethyl lactate with $[\text{HC}_4\text{im}][\text{HSO}_4]$ were found to have low conversions and yields. The side reaction of sulfation of methanol was believed to be the main reason behind this. Increasing the reaction temperature increases the conversions and yields but promotes further and more side reactions, the formation of dimethyl sulfate and dimethyl ether. The reaction parameters' influences were found to be different at two temperatures. For the reaction at 80 °C, the water effect seems to be different to the reaction at higher temperature, 120 °C. At 80 °C, the presence of water in the reactions somehow improved the conversion of the ester but did not improve the yield. At 120 °C, the results show that the water improves the conversion, but only improves the yield if the IL was used in a smaller amount than water.

The concentration of IL effect study showed that it did not have consistent effect on the reaction conversions and yields. At 80 °C, the result showed that the IL acted best as catalyst when the smallest amount of IL used in the reaction gave the highest yield and conversion. However, at 120 °C, the largest amount of IL showed a decrease in yield. Ethyl lactate was found to react faster than BHB. Similar to the BHB reaction at 120 °C, the conversion and yield were increased by adding water to the reaction. This was observed from higher yield and conversion being obtained from the reaction in aqueous

solution rather than in the mixture of methanol and IL. Adding more methanol to balance the side effects did not improve the results but only decreased the reaction conversion and yield.

Overall, [HC₄im][HSO₄] was found to be not suitable for transesterification reactions as it reacts with alcohols, especially at high temperature. This is in contrast with many transesterification reactions with [HSO₄]⁻ ILs reported in the literature. All previous reactions were observed to give high conversions and yields but no side reactions were reported before. As mentioned before, the higher conversion in literature could be due to contamination of the ILs with sulfuric acid, but this is difficult to justify as there were no H₀ values reported. Even though some of the reactions in the literature were done under high pressure, sulfation of alcohol by [HSO₄]⁻ anion occurred very fast, especially in non-aqueous solution, as reported in Chapter 2. In Chapter 2, I also showed that [C₄C₁im][HSO₄] is reactive with alcohols, thus any [HSO₄]⁻ ILs is expected to undergo nucleophilic substitution reaction with alcohols. For this reason, it is assumed to be very difficult to achieve nearly full conversion and yield for these transesterifications of the two selected model compounds, if the side reactions with alcohol are taking place.

5 General Conclusions

In the first result chapter, $[\text{HSO}_4]^-$ ILs were successfully demonstrated to be reactive with several primary and secondary alcohols. The $[\text{HSO}_4]^-$ anion was found to be acidic and nucleophilic enough to undergo nucleophilic substitution reaction with hydroxyl group. Adding water to the reaction had the effect of reducing the yield of the hydrogen sulfated product although sufficient product formed to suggest that sulfation of cellulose is probable under Ionosolv pretreatment conditions. Hydrolysis of two ester model compounds were successfully done in $[\text{HC}_4\text{im}][\text{HSO}_4]$. By studying the rates and kinetics of the hydrolysis in varying acid and water content, it was found that in 10 - 30 wt% water and 0 – 43 mol% added sulfuric acid to the IL, the hydrolysis of the model compounds occurred *via* an A_2 mechanism where the water act as nucleophile in the RDS. Even though $[\text{HC}_4\text{im}][\text{HSO}_4]$ is acidic enough to hydrolyse the ester model compounds, this was not observed in the case of transesterification. The nucleophilic substitution reaction by the $[\text{HSO}_4]^-$ anion and methanol occurred and disrupted the formation of the transesterification products. Sulfation is greater with the increasing of reaction temperature. Contradictory findings of high yields for transesterification reactions with $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ in published papers indicate that the acidity of the acidic ILs needs to be measured prior to use.

This finding, therefore, provides insight that $[\text{HSO}_4]^-$ based ILs are not innocent to be used as reaction solvents when involving alcohol as a reactant. However, the products of this substitution reaction are definitely worth exploring. Since $[\text{HSO}_4]^-$ is a good leaving group, the product of this reaction is an excellent building block in synthesis because it can be converted to construct more complicated compounds. This could be a new approach in OH activation towards substitution reactions.

6 Experimental

All reagents were purchased from Sigma Aldrich and VWR, and were used without further purification unless otherwise stated. 1-Butylimidazole was dried with potassium hydroxide pellets overnight and distilled under reduced pressure (approximately at 120 °C and 1.6 kPa). Dimethyl sulfate was distilled over calcium oxide. Dry toluene was obtained from departmental solvent drying towers which was dried over molecular sieves.

6.1 ILs Syntheses

6.1.1 Synthesis of 1-butyliimidazolium hydrogen sulfate [HC₄im][HSO₄]

This IL was prepared according to literature procedures.⁸³ 1-Butylimidazole (146.31 g, 1.18 mol) was diluted in 150 mL of water in a 3-necked round bottom flask and cooled in an ice bath. Sulfuric acid (65.09 mL, 1.18 mol, 18.1 M) was carefully added drop wise to the flask while stirring. After the addition of the acid was completed, the reaction mixture was stirred at 40 °C for 1 h to ensure complete reaction. Next, the water was then removed by freeze-drying overnight resulting light pink viscous liquid. The coloured impurities were removed by passing it through a pre-packed Isolute™ C-18 Flash column (diluted with water, 1:3 IL:water). Finally, the IL was left to stir

vigorously at 65 °C under vacuum to dry. The resulting IL was a clear viscous liquid (256.40 g, 98%). NMR data was in agreement with the literature values.⁸³

¹H NMR (400 MHz, DMSO-d⁶) : δ 9.15 (1H, s, NCHN), 7.80 (1H, s, NCHCHN), 7.68 (1H, s, NCHCHN), 4.20 (2H, t, J = 7.2 Hz, NCH₂CH₂CH₂CH₃), 1.77 (2H, q, J = 7.6 Hz, NCH₂CH₂CH₂CH₃), 1.24 (2H, q, J = 7.6 Hz, NCH₂CH₂CH₂CH₃) and 0.90 (3H, t, J = 7.2 Hz, NCH₂CH₂CH₂CH₃) ppm.

¹³C {¹H} NMR (100 MHz, DMSO-d⁶) : δ 135.73 (NCHN), 122.49 (NCHCHN), 120.42 (NCHCHN), 48.68 (NCH₂CH₂CH₂CH₃), 31.92 (NCH₂CH₂CH₂CH₃), 19.28 (NCH₂CH₂CH₂CH₃), and 13.75 (NCH₂CH₂CH₂CH₃) ppm.

m/z (LSIMS⁺) 69 (30%, [HHim]⁺), 125 (100%, [C₄Him]⁺), 249 (5%, [(C₄Him)(C₄im)]⁺) and 347 (5%, [(C₄Him)₂(HSO₄)]⁺).

6.1.2 Synthesis of 1-butyl-3-methylimidazolium methyl sulfate, [C₄C₁im][MeSO₄]

This IL was prepared according to literatures procedures.^{83,239} Me₂SO₄ (143 mL, 1.10 mol) was carefully added drop-wise (flow rate ca. 0.5 drops/sec) to a cooled 3-necked round bottom flask (in an ice bath) containing 1-butylimidazole (135.35 g, 1.10 mol) in 300 mL of dry toluene. The reaction mixture (biphasic solution) was left to stir at room temperature overnight, followed by removal of the toluene (upper layer) by Schlenk techniques. The product (bottom layer) was dried overnight under high vacuum at 60 °C after washing with toluene (3 x 25 mL) to yield a colourless viscous liquid (270.12 g, 98%). The NMR data of the product, 1-butyl-3-methylimidazolium methyl sulfate [C₄C₁im][MeSO₄] was in agreement with the literature, and the IL was then used to produce 1-butyl-3-methylimidazolium hydrogen sulfate, [C₄C₁im][HSO₄] via hydrolysis (as described in 6.1.3).

¹H NMR (400MHz, DMSO-d⁶): δ 9.11 (1H, s, NCHN), 7.77 (1H, s, CH₃NCHCHN), 7.70 (1H, s, CH₃NCHCHN), 4.16 (2H, t, J = 7.4 Hz, NCH₂(CH₂)₂CH₃), 3.85 (3H, s,

NCH₃), 3.37 (3H, s, CH₃OS), 1.76 (2H, q, NCH₂CH₂CH₂CH₃), 1.25 (2H, m, N(CH₂)₂CH₂CH₃), 0.90 (3H, t, J = 7.4 Hz, N(CH₂)₃CH₃) ppm.

¹³C {¹H} NMR (100MHz, DMSO-d₆): δ 136.73 (N₂CH), 123.83 (NCH), 122.48 (NCH), 53.01 (CH₃OS), 48.69 (NCH₂ (CH₂)₂CH₃), 35.94 (NCH₃), 31.84 (NCH₂CH₂CH₂CH₃), 18.97 (N(CH₂)₂CH₂CH₃) and 13.47 (N(CH₂)₃CH₃) ppm.

m/z (LSIMS⁺) 139 (100%, [C₄C₁im]⁺) and 389 (4%, [(C₄C₁im)₂MeSO₄]⁺ *m/z* (LSIMS⁻) 111 (100% [MeSO₄]⁻), 361 (3% [(C₄C₁im(MeSO₄)₂]⁻)

6.1.3 Synthesis of 1-butyl-3-methylimidazolium hydrogen sulfate, [C₄C₁im][HSO₄]

This IL was prepared according to literatures procedures.^{83,239} [C₄C₁im][MeSO₄] (60 g, 0.24 mol) was mixed with 20 mL of distilled H₂O in an open-topped three-necked round bottom flask fitted with a dropping funnel and a thermometer. Approximately 2 drops of aqueous 5 M sulfuric acid were added to the solution. The resulting solution was stirred vigorously at 165 °C allowing the generated methanol and water to boil off from the solution. The solution temperature was monitored and controlled at 165-180 °C by adding water drop-wise using the dropping funnel into the solution. The progress of the hydrolysis of the methyl sulfate anion was monitored by the disappearance of its methyl peak in ¹H NMR spectrum. After the reaction was completed, the solution was allowed to cool to room temperature and then dried under vacuum at 50 °C to yield a clear viscous liquid (55.69 g, 98%).

¹H (400MHz, DMSO-d₆): δ 9.21 (1H, s, NCHN), 7.82 (1H, t, CH₃NCHCHN), 7.75 (1H, t, CH₃NCHCHN), 4.18 (2H, t, J = 7.2 Hz, NCH₂(CH₂)₂CH₃), 3.87 (3H, s, NCH₃), 1.75 (2H, m, NCH₂CH₂CH₂CH₃), 1.20 (2H, m, N(CH₂)₂CH₂CH₃) and 0.87 (3H, t, J = 7.4 Hz, N(CH₂)₃CH₃) ppm.

¹³C {¹H} NMR (100MHz, DMSO-d₆): δ 137.18 (N₂CH), 123.98 (NCH), 122.74 (NCH), 48.84 (NCH₂ (CH₂)₂CH₃), 36.06 (NCH₃), 31.88 (NCH₂CH₂CH₂CH₃), 19.16 (N(CH₂)₂CH₂CH₃) and 13.64 (N(CH₂)₃CH₃).

m/z (LSIMS⁺) 139 (100%, [C₄C₁im]⁺), *m/z* (LSIMS⁻) 97 (100%, [HOSO₃]⁻).

6.2 Nucleophilic Substitution Reaction of Alcohols with $[\text{HSO}_4]^-$ ILs

6.2.1 Reaction of alcohols in $[\text{HSO}_4]^-$ ILs

All selected alcohols were added to a solution of $[\text{C}_4\text{Him}][\text{HSO}_4]$ or $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ in 1 to 10 molar ratio (alcohol:IL, 1:10) respectively in a 25 mL round bottom flask. For the reaction with water, 20 wt% water was added to the reaction mixture. For the reactions with excess acid, 1 and 6 mol% of sulfuric acid were added to the reaction mixture. All mixtures were heated at 120 °C over 24 h and the conversion of the alcohols analysed by ^1H NMR spectroscopy.

6.2.2 Reaction of *para*-substituted benzyl alcohols in $[\text{HSO}_4]^-$ ILs: reaction kinetics procedure

All kinetic measurement of the reactions of the six types of *para*-substituted benzyl alcohols, *p*-X-PhCH₂OH (X = H, Me, OMe, CF₃, Cl, NO₂) with $[\text{HC}_4\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ were performed under *pseudo*-first order reaction conditions: i.e., the amount of IL in each reaction was in a 10:1 molar ratio to the benzyl alcohol and was assumed to be constant throughout the reaction. The changes and rates of reaction were monitored and measured by ^1H NMR. This procedure was carried out following procedure in literature.⁸⁴

The experiment was carried out by dissolving each benzyl alcohol, 0.001 mol (*ca.* 0.1 g) in 10 molar equivalents of the IL, $[\text{HC}_4\text{im}][\text{HSO}_4]$ (0.01 mol, 2.22 g) or $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ (0.01 mol, 2.36 g), in small vials which were quickly transferred into NMR tubes. DMSO-*d*₆ in a capillary was loaded in each tube. All reactions were carried out on a Bruker DRX400 MHz NMR machine at 80 °C over 2 h with 2 min measurement intervals.

6.3 Ester Hydrolysis

6.3.1 Determination of H_0 by UV-vis Spectroscopy

[HC₄im][HSO₄] with varied concentrations of sulfuric acid and water content were mixed in small vials along with 2- and 4-nitroaniline, (0.05 and 0.03 mol/L respectively) in dry CH₂Cl₂. The mixtures were then stirred before the removal of CH₂Cl₂ by evaporation. Then, their UV-vis spectra were recorded by a Perkin Elmer Lambda 25 spectrometer. The maximal absorbance of the unprotonated Hammett indicators were measured in CH₂Cl₂. The wavelength range for the measurement was set between 250 to 650 nm.

6.3.2 Synthesis of THFF

This new compound was synthesised according to the standard procedure of esterification of ferulic acid and alcohol as found in the literature.²⁴⁰ A Dean-Stark apparatus was used for removal of the water generated during the reaction.²⁴¹ A mixture of ferulic acid (4.85 g, 24.9 mmol) and tetrahydrofurfuryl alcohol (2.55 g, 24.9 mmol) was dissolved in toluene (15 mL) in a round bottom flask fitted with a condenser and the Dean-Stark distillation trap. *p*-Toluenesulfonic acid (0.1 g, 0.58 mmol) was added to the mixture and it was left to reflux overnight. After the reaction was completed (monitored by TLC), the mixture was left to cool at room temperature. After removal of toluene under reduced pressure, the crude product was diluted with water. The product was then extracted with diethyl ether (3 x 100 mL) and then washed with an aqueous solution of Na₂CO₃. The organic layer was dried over anhydrous Na₂SO₄ and the solution was then filtered before removing of the solvent under reduced pressure. The product was recrystallized from ethanol. Yield 69%.

^1H (400MHz, DMSO- d_6): 9.81 (1H, s, OH), 7.56 (1H, d, CH=CHCO, $J = 16.0$ Hz), 7.34 (1H, s, ArH), 7.10 (1H, d, ArH, $J = 8.1$ Hz), 6.81 (1H, d, ArH, $J = 8.1$ Hz), 6.48 (1H, d, CH=CHCO, $J = 16$ Hz), 4.08 (3H, m, CH₂, CH, $J = 26.7$ Hz), 3.80 (3H, s, CH₃O-Ar), 3.76 (2H, t, CH₂, $J = 21.0$ Hz), 1.92 (4H, m, CH₂).

^{13}C { ^1H } NMR (100 MHz, DMSO- d_6): 167.18 (C=O), 149.98 (C-OCH₃), 147.83 (C-OH), 142.74 (Ar-CH=CH), 127.89 (Ar), 123.13 (Ar), 115.67 (Ar), 114.99 (CH-C=O), 111.69 (Ar), 76.52 (CH-O), 65.97 (CH₂-O), 65.01 (CH₂-OC=O), 57.01 (CH₃-O), 28.23 (CH₂), 25.65 (CH₂).

m/z (ES-ToF): 279 (100%, M + Na), 177 (65%)

6.3.3 First method of kinetic measurement, *in situ* ^1H NMR

The studies of the rates of hydrolysis of two ester model compounds with [HC₄im][HSO₄] were performed under *pseudo*-first order reaction conditions, where the amount of IL in each reaction is in a 10:1 molar ratio to the esters. The changes and rates of the reaction were monitored and measured by ^1H NMR. 0.001 mol of BHB (0.23 g) and THFF (0.28 g) respectively were mixed with [HC₄im][HSO₄], (2.22 g, 0.01 mol), (with varied sulfuric acid and water contents) in small vials and transferred into NMR tubes loaded with DMSO- d_6 in a capillary. All reactions were carried out on a Bruker DRX400 MHz NMR machine at 80 °C over 18 h with 2 h measurement intervals. A delay time of 10s between each pulse was set to allow sufficient time for all protons to relax fully and for consistent and accurate integrals to be recorded.

6.3.4 Second method of kinetic measurements

0.001 mol of BHB (0.23 g) and THFF (0.28 g) respectively were mixed with [HC₄im][HSO₄], (2.22 g, 0.01 mol) (with varied sulfuric acid and water content) in reaction vials and heated at 80 °C on a heating block. Small volumes of the reaction mixture (ca 0.05 mL) were taken out at certain points (the interval time were 30, 60 and

120 minutes depending on how fast each of the reactions proceeded) and dissolved in DMSO-*d*6 (0.5 mL) to be analysed by ^1H NMR.

6.4 Transesterification

6.4.1 Transesterification of BHB and Ethyl Lactate with methanol and [HC₄im][HSO₄]

0.001 mol of BHB (0.23 g) and ethyl lactate (0.12 g) were dissolved in methanol (0.005-0.01 mol) respectively in a pressure tube with a screw-cap and Teflon lining. [HC₄im][HSO₄] with different equivalent to the ester (0.001 – 0.01 mol) was added to the tubes. Each mixture was then heated in an oil bath at different temperatures (80 and 120 °C). After 24 h, 0.05 mL of the reaction mixtures were dissolved in 0.5 mL of DMSO-*d*6 to be analysed by ^1H NMR.

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Appendix

A.1 Pseudo-first order rate equation

For a first order rate equation $r = k[A]$, the rate r is equal to the rate of loss of the concentration of the starting material A:

$$r = - \frac{d[A]}{dt} \quad (\text{A.1.1})$$

Thus,

$$r = k_{obs} [A] \quad (\text{A.1.2})$$

Rearranging equation A.1.2;

$$\frac{d[A]}{dt} = -k_{obs}[A] \quad (\text{A.1.3})$$

Solving equation A.1.3;

$$\int \frac{d[A]}{[A]} = \int -k_{obs} dt$$

$$\ln[A] = -k_{obs}t$$

In kinetic runs, the reactant concentration is always referred as fraction to its starting concentration;

$$\ln \frac{[A]}{[A_0]} = -k_{obs}t$$

A.2 Kinetic Measurements, Plot $\ln [A]/[A_0]$ vs time

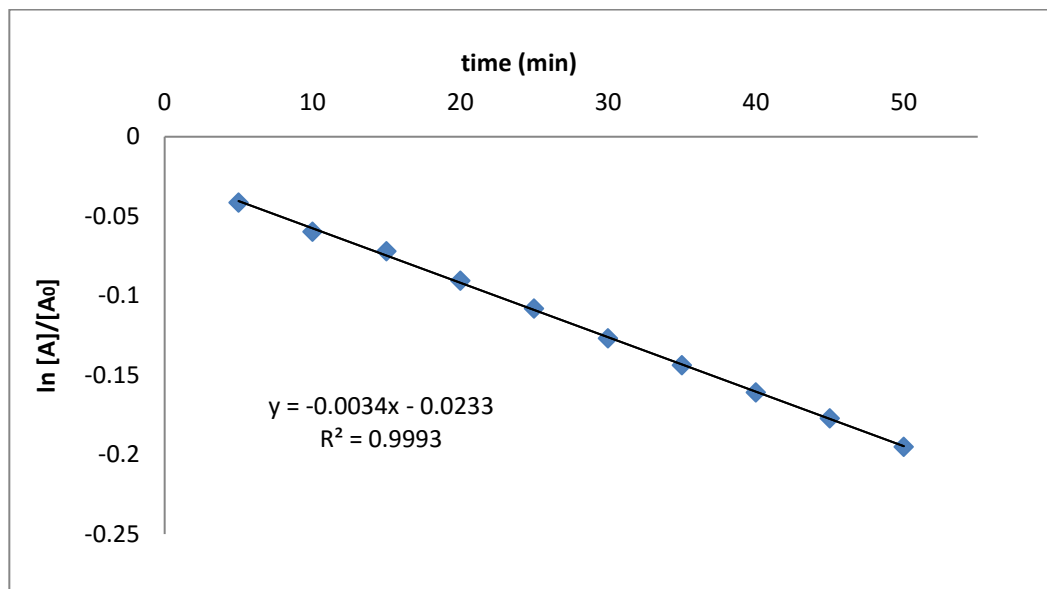


Figure A.2.1 Plot of $\ln (A/A_0)$ against time of benzyl alcohol in neat $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80 °C.

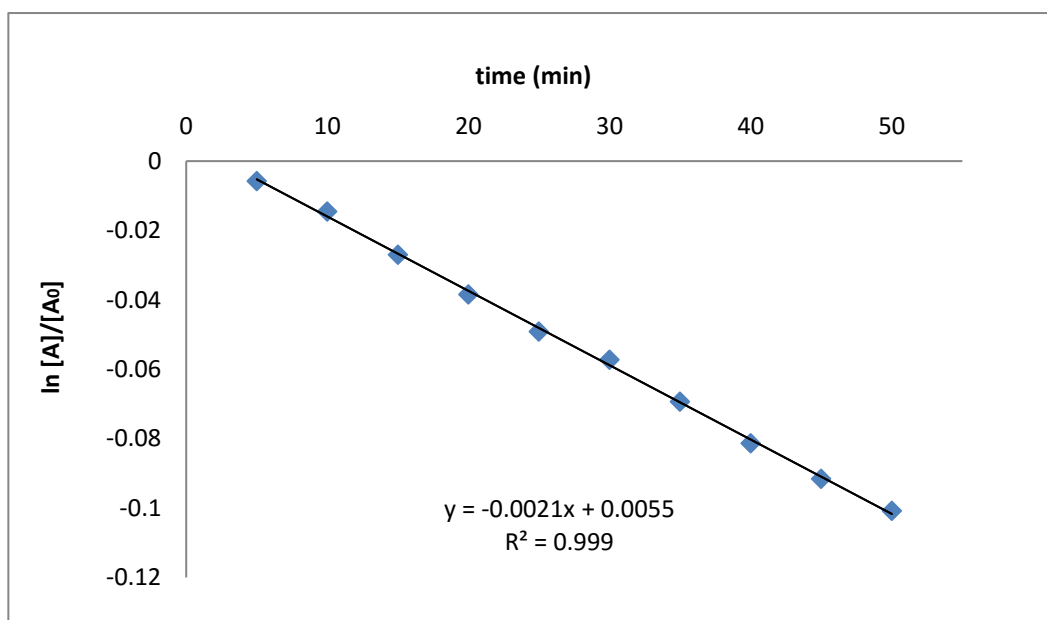


Figure A.2.2 Plot of $\ln (A/A_0)$ against time of *p*-methylbenzyl alcohol in neat $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80 °C.

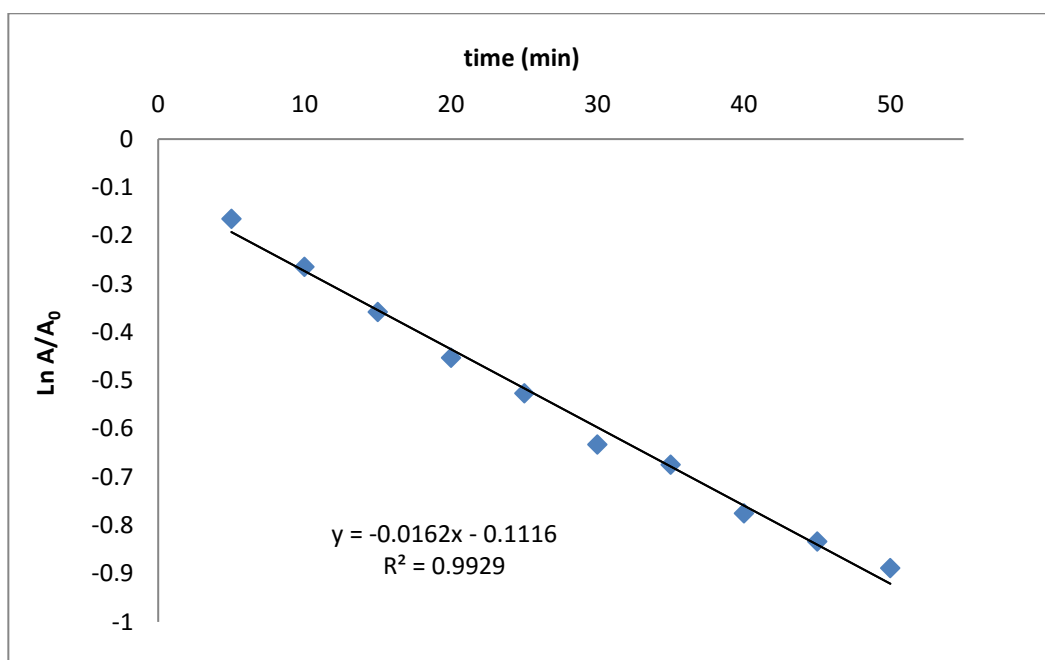


Figure A.2.3 Plot of $\ln (A/A_0)$ against time of *p*-methoxybenzyl alcohol in neat $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80 °C.

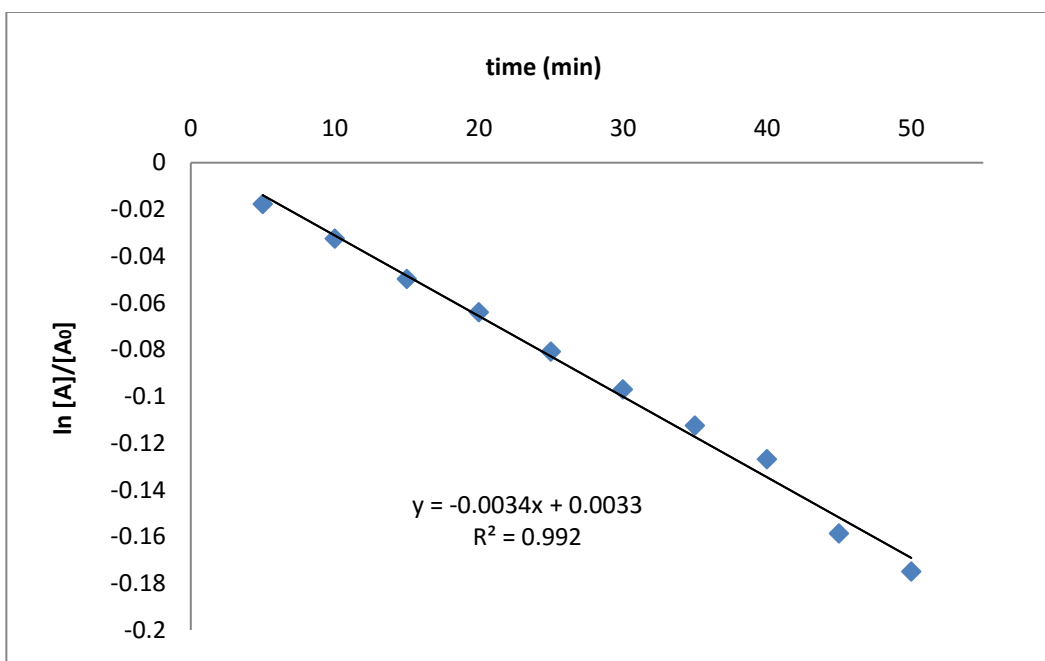


Figure A.2.4 Plot of $\ln (A/A_0)$ against time of *p*-trifluoromethylbenzyl alcohol in neat $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80 °C.

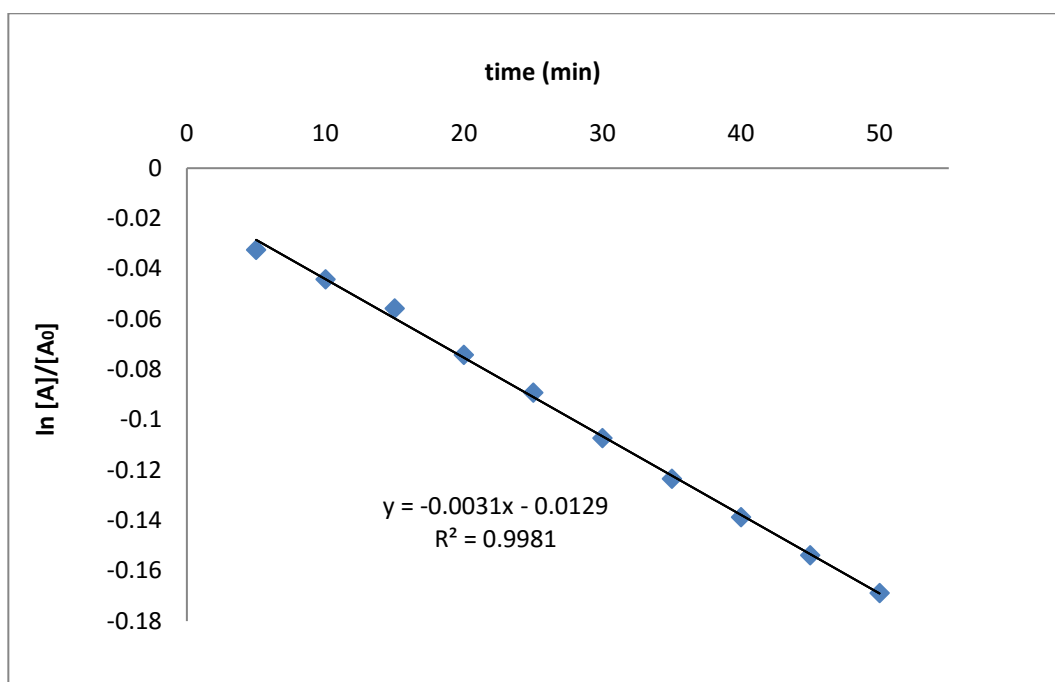


Figure A.2.5 Plot of $\ln (A/A_0)$ against time of *p*-chlorobenzyl alcohol in neat $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80 °C.

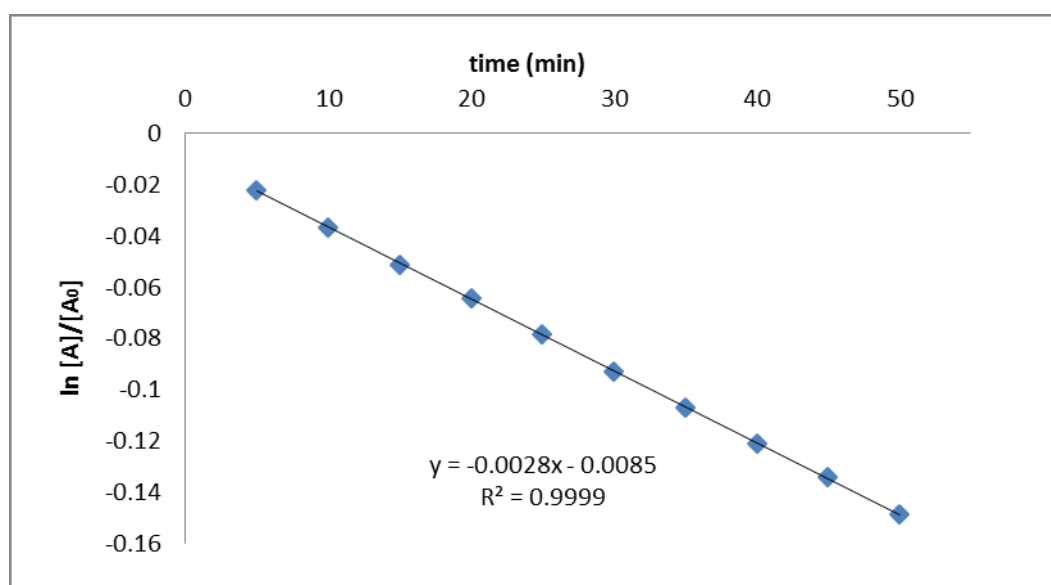


Figure A.2.6 Plot of $\ln (A/A_0)$ against time of *p*-nitrobenzyl alcohol in neat $[\text{HC}_4\text{im}][\text{HSO}_4]$ at 80 °C.

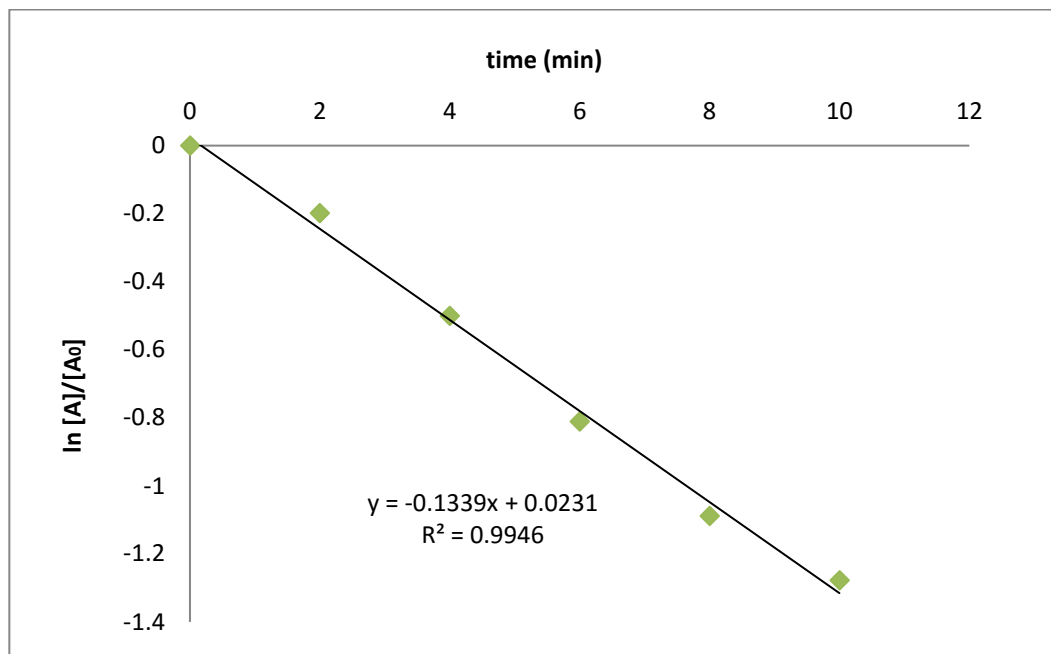


Figure A.2.7 Plot of $\ln (A/A_0)$ against time of benzyl alcohol in $[\text{HC}_4\text{im}][\text{HSO}_4] + 1 \text{ mol\% H}_2\text{SO}_4$ at 80°C .

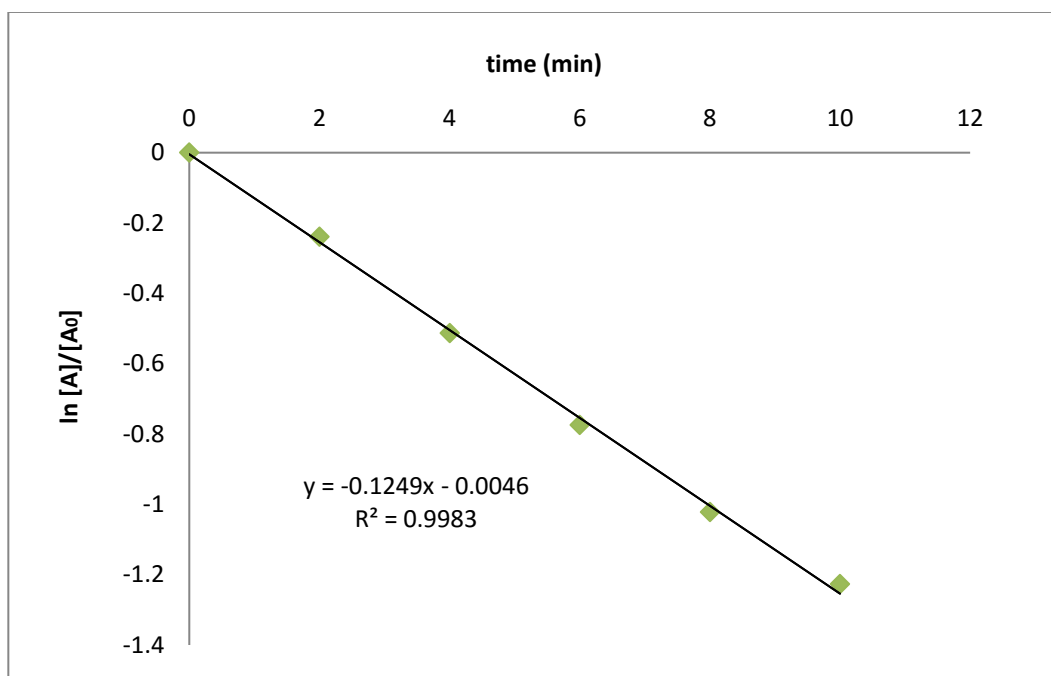


Figure A.2.8 Plot of $\ln (A/A_0)$ against time of *p*-methylbenzyl alcohol in $[\text{HC}_4\text{im}][\text{HSO}_4] + 1 \text{ mol\% H}_2\text{SO}_4$ at 80°C .

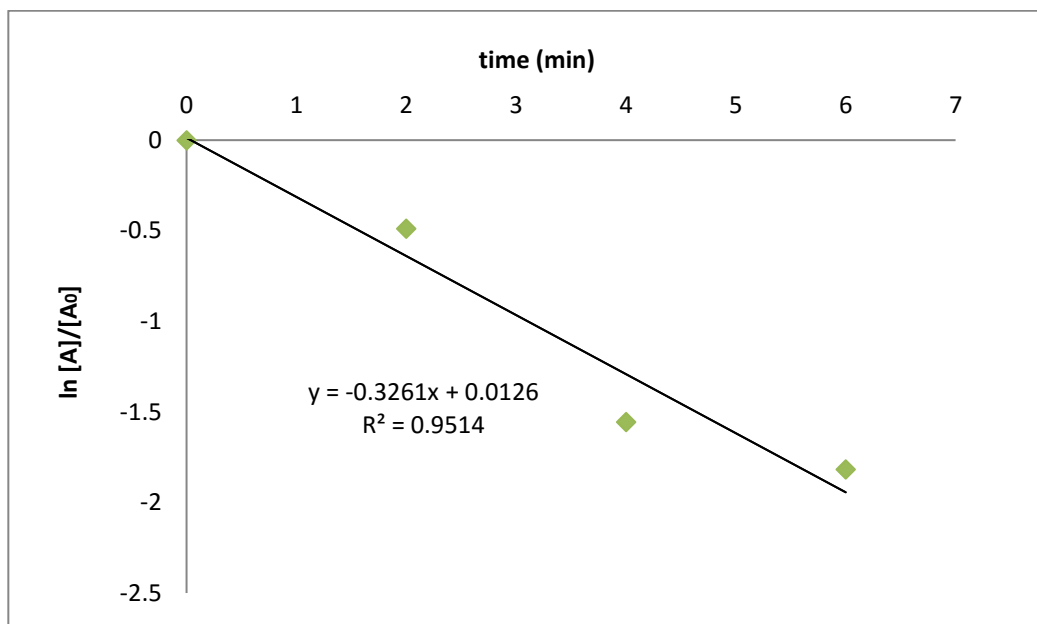


Figure A.2.9 Plot of $\ln (A/A_0)$ against time of *p*-methoxybenzyl alcohol in $[\text{HC}_4\text{im}][\text{HSO}_4] + 1$ mol% H_2SO_4 at 80 °C.

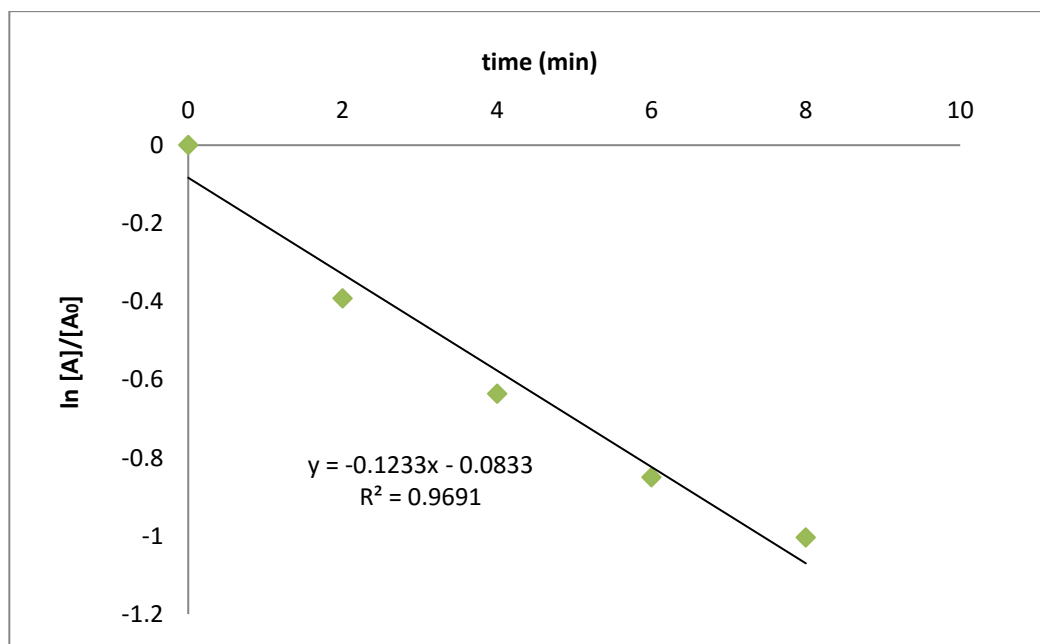


Figure A.2.10 Plot of $\ln (A/A_0)$ against time of *p*-trifluoromethylbenzyl alcohol in $[\text{HC}_4\text{im}][\text{HSO}_4] + 1$ mol% H_2SO_4 at 80 °C.

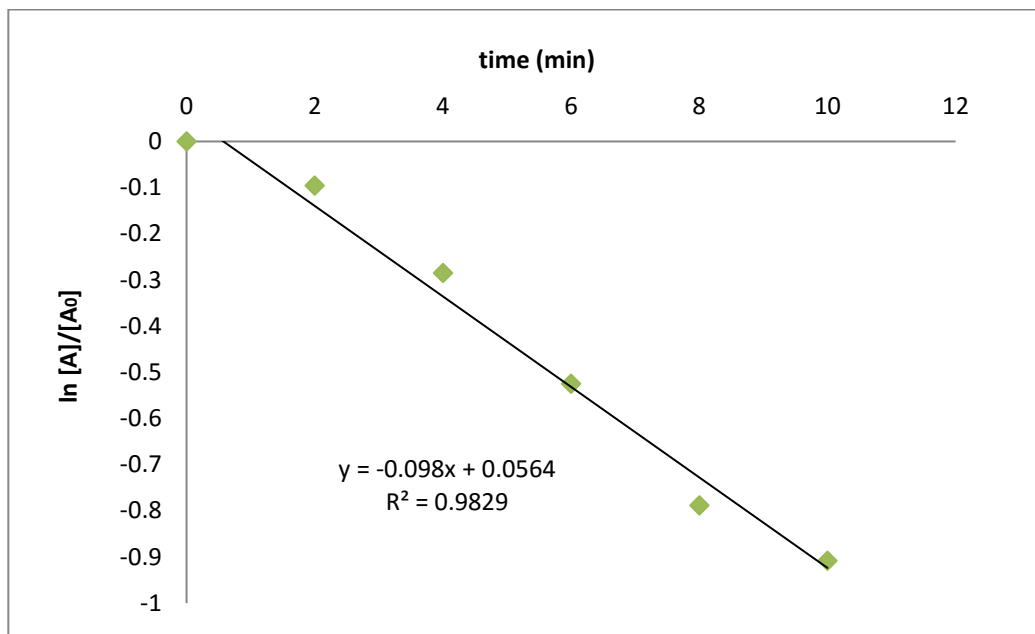


Figure A.2.11 Plot of $\ln (A/A_0)$ against time of *p*-chlorobenzyl alcohol in $[\text{HC}_4\text{im}][\text{HSO}_4] + 1$ mol% H_2SO_4 at 80 °C.

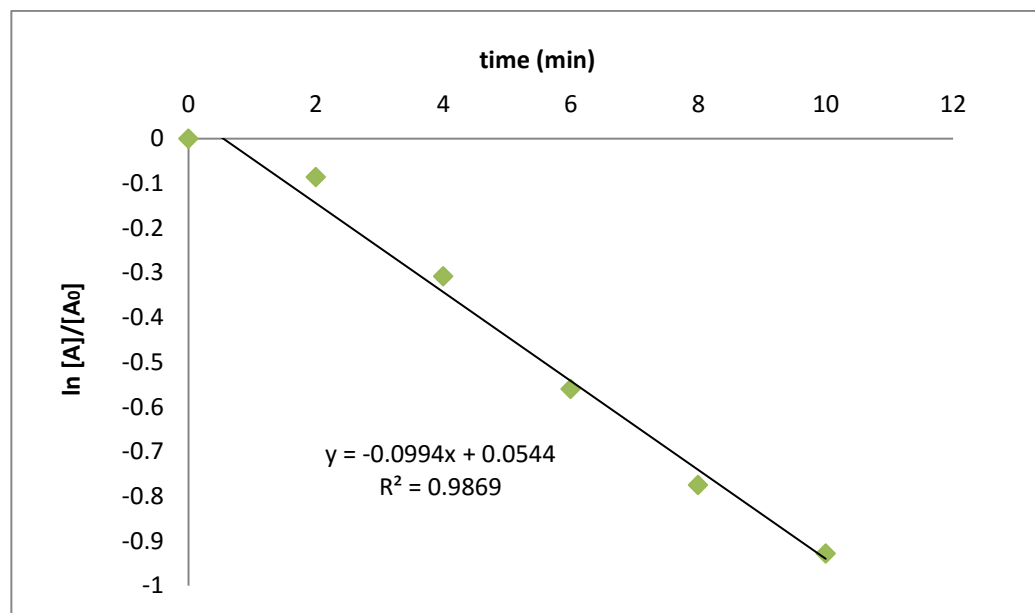


Figure A.2.12 Plot of $\ln (A/A_0)$ against time of *p*-nitrobenzyl alcohol in $[\text{HC}_4\text{im}][\text{HSO}_4] + 1$ mol% H_2SO_4 at 80 °C.

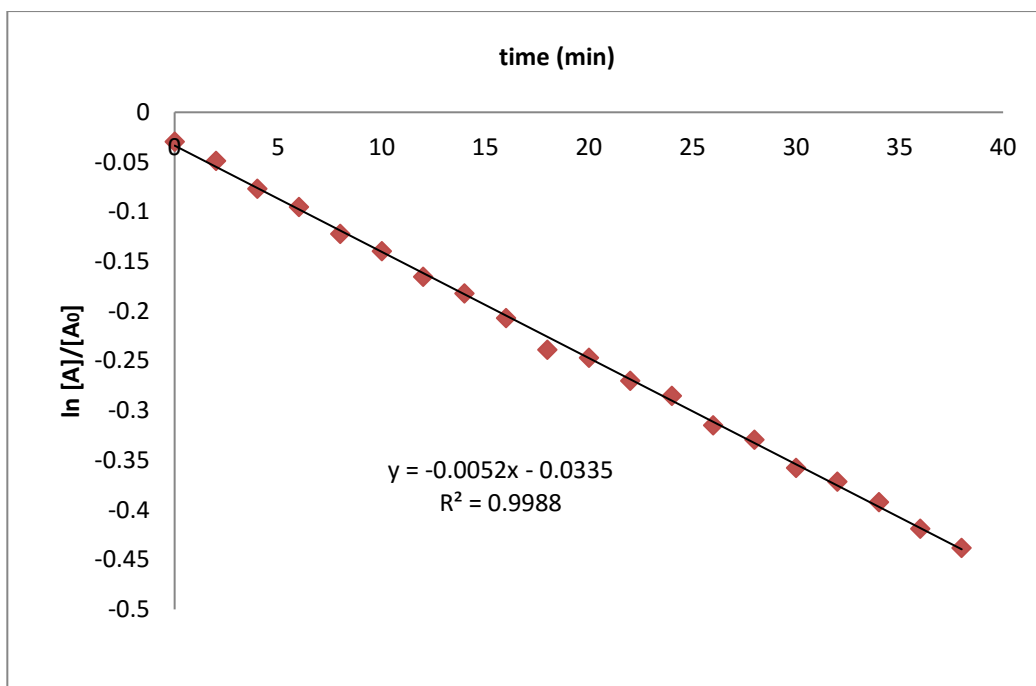


Figure A.2.13 Plot of $\ln ([A]/[A_0])$ against time of benzyl alcohol in neat $[C_4C_{1im}][HSO_4]$ at 80 °C.

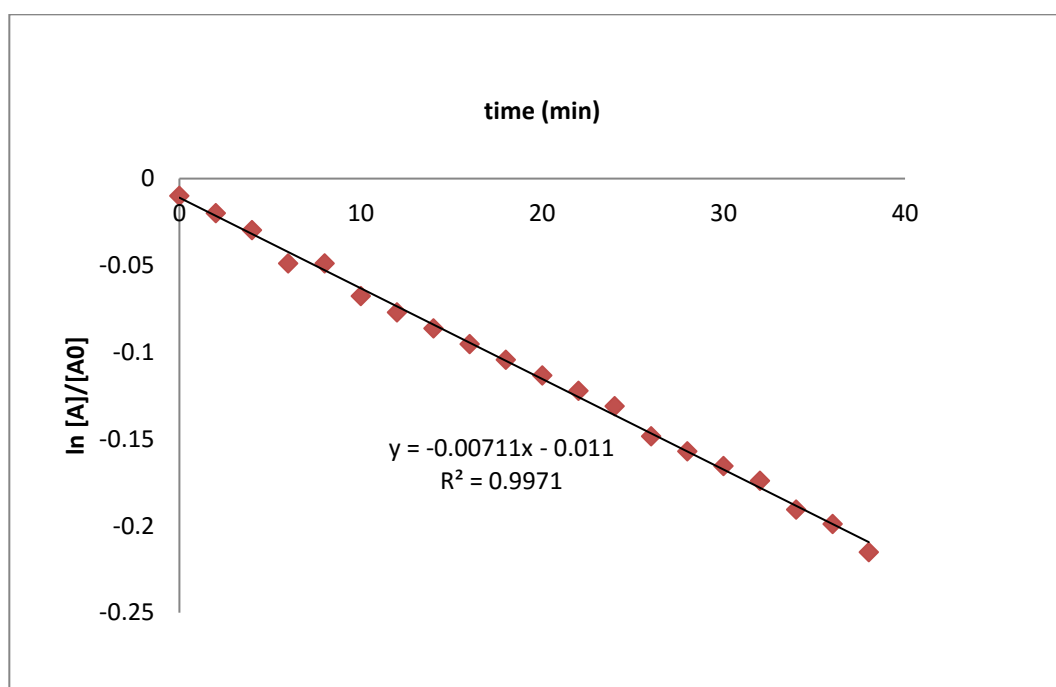


Figure A.1.14 Plot of $\ln ([A]/[A_0])$ against time of *p*-methylbenzyl alcohol in neat $[C_4C_{1im}][HSO_4]$ at 80 °C

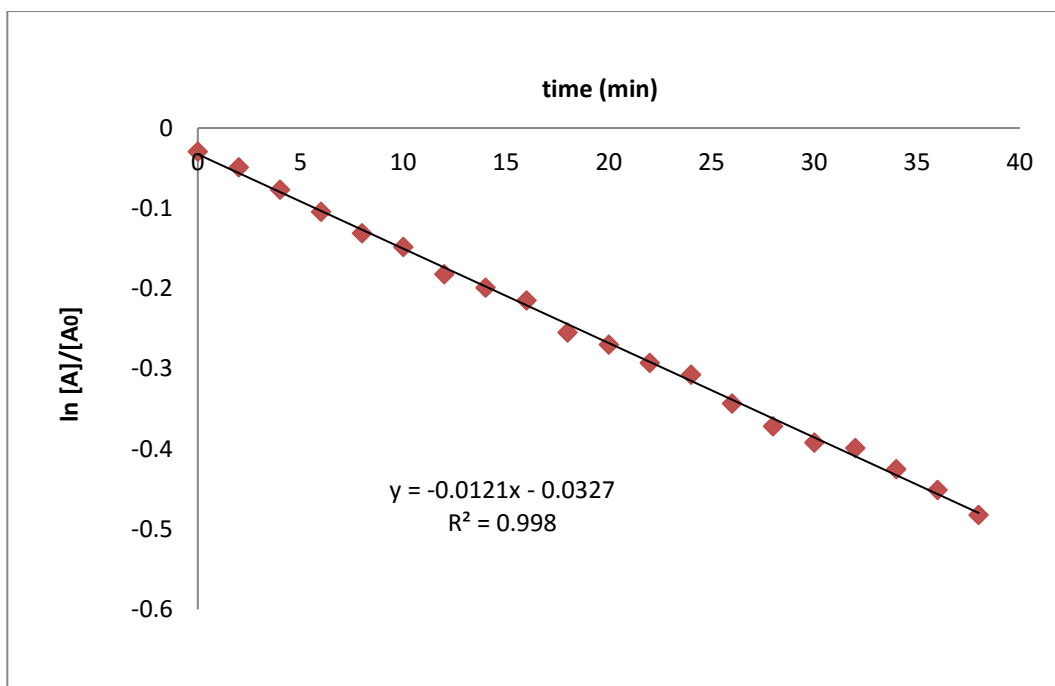


Figure A.2.15 Plot of $\ln ([A]/[A_0])$ against time of *p*-methoxybenzyl alcohol in neat $[C_4C_{1im}][HSO_4]$ at 80 °C

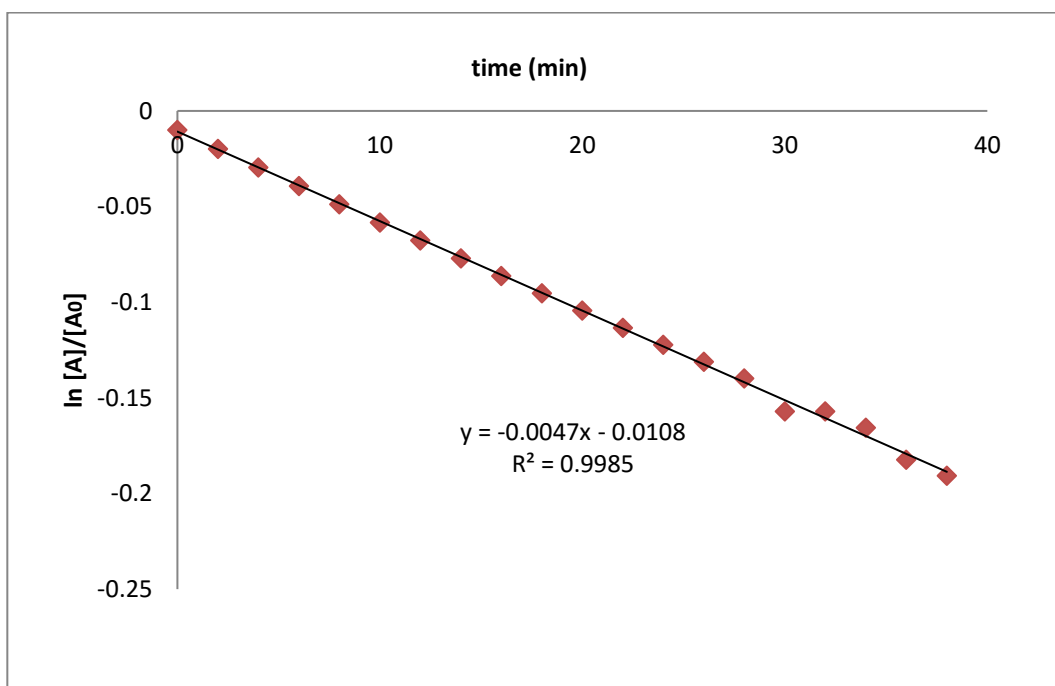


Figure A.2.16 Plot of $\ln ([A]/[A_0])$ against time of *p*-trifluoromethylbenzyl alcohol in neat $[C_4C_{1im}][HSO_4]$ at 80 °C

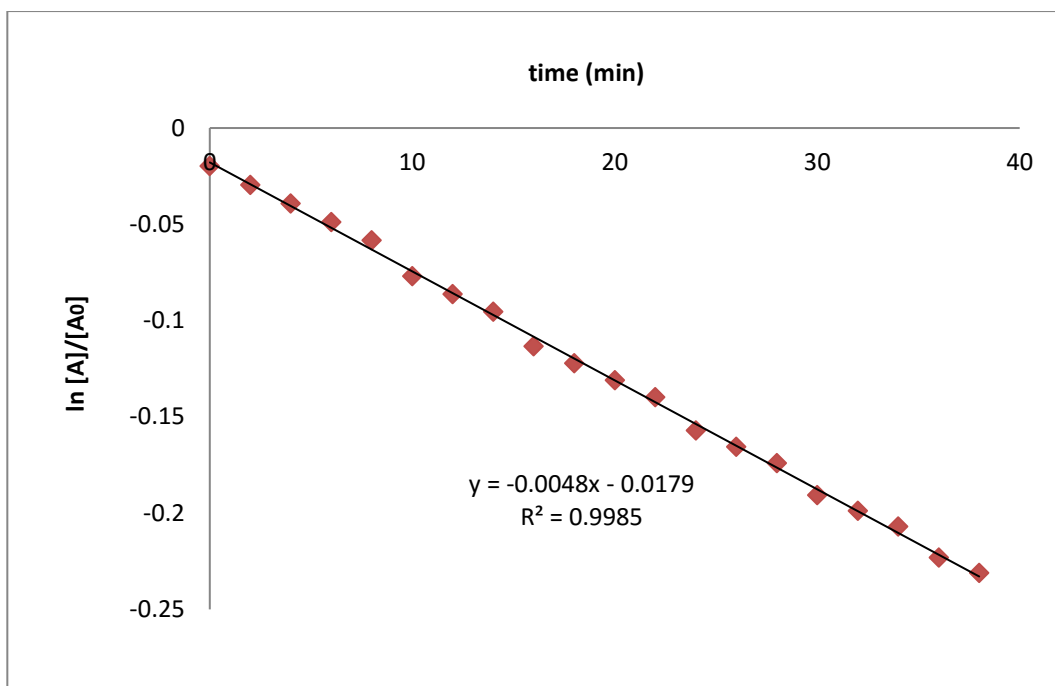


Figure A.2.17 Plot of $\ln ([A]/[A_0])$ against time of *p*-chlorobenzyl alcohol in neat $[\text{C}_4\text{C}_{1\text{im}}][\text{HSO}_4]$ at 80 °C

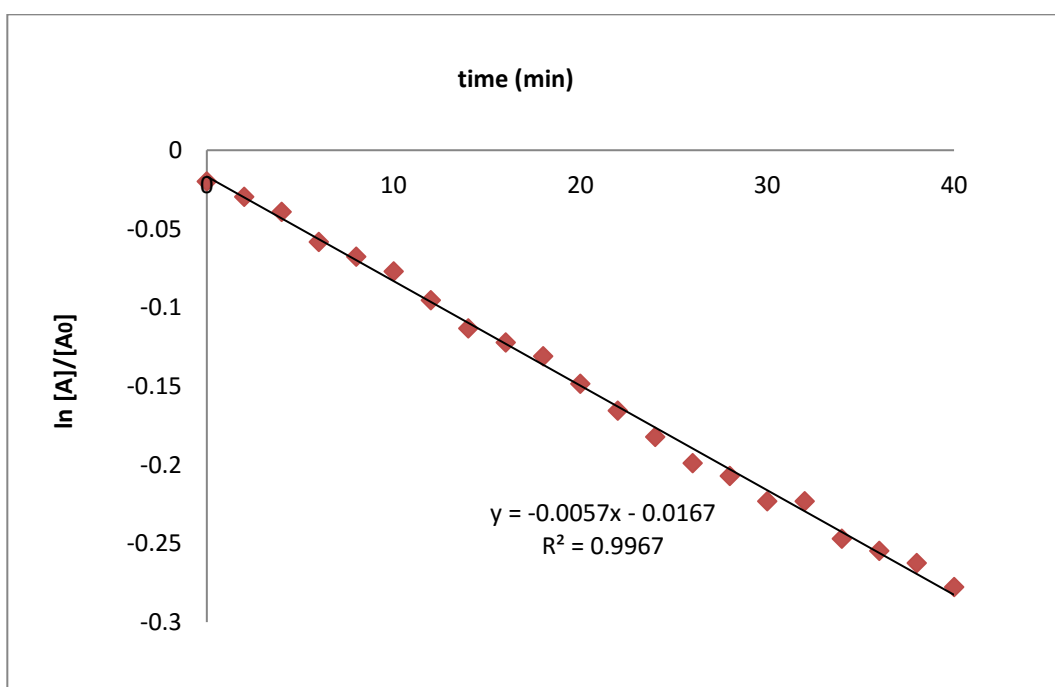


Figure A.2.18 Plot of $\ln ([A]/[A_0])$ against time of *p*-nitrobenzyl alcohol in neat $[\text{C}_4\text{C}_{1\text{im}}][\text{HSO}_4]$ at 80 °C

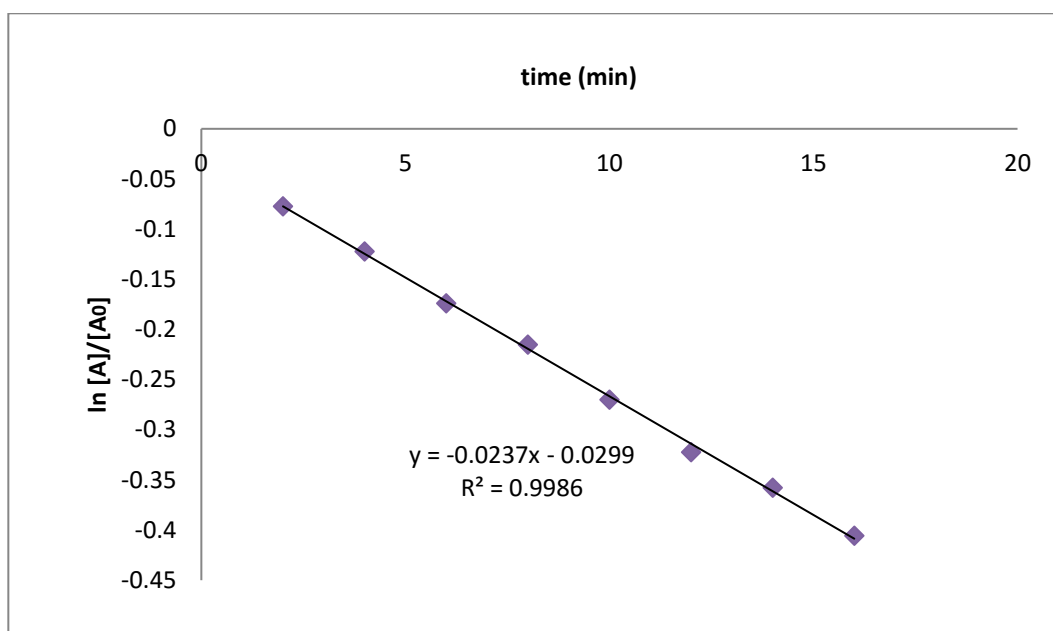


Figure A.2.19 Plot of $\ln ([A]/[A_0])$ against time of benzyl alcohol in neat $[C_4C_{1im}][HSO_4] + 1$ mol% H_2SO_4 at 80 °C

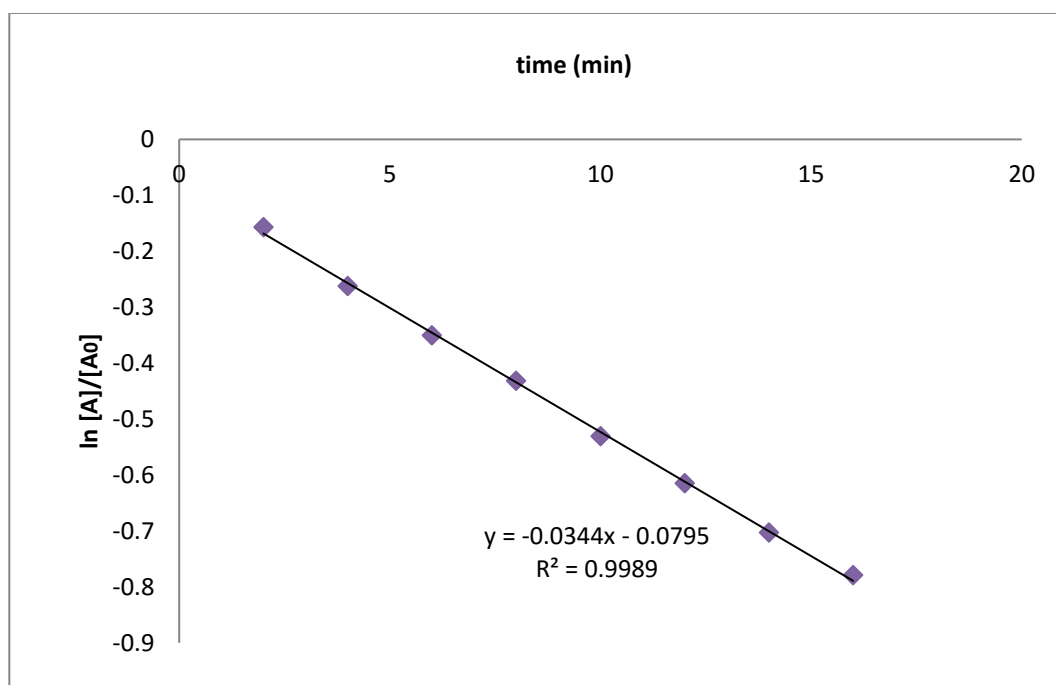


Figure A.2.20 Plot of $\ln ([A]/[A_0])$ against time of *p*-methylbenzyl alcohol in neat $[C_4C_{1im}][HSO_4] + 1$ mol% H_2SO_4 at 80 °C

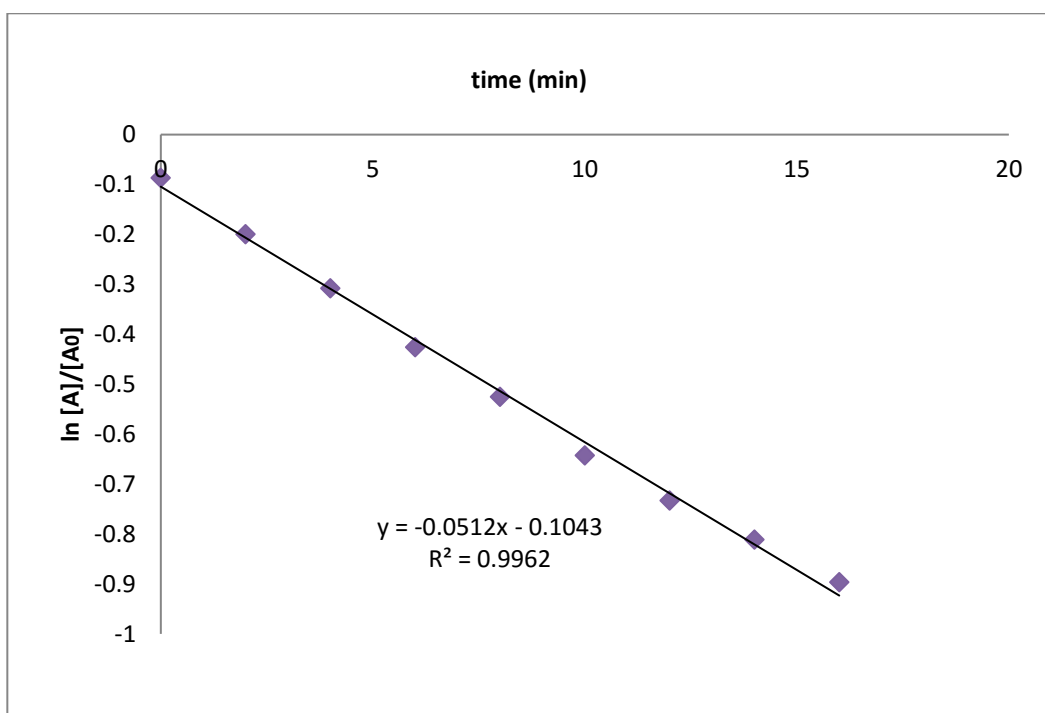


Figure A.2.21 Plot of $\ln ([A]/[A_0])$ against time of *p*-methoxybenzyl alcohol in neat $[C_4C_{1im}][HSO_4] + 1 \text{ mol\% } H_2SO_4$ at $80^\circ C$

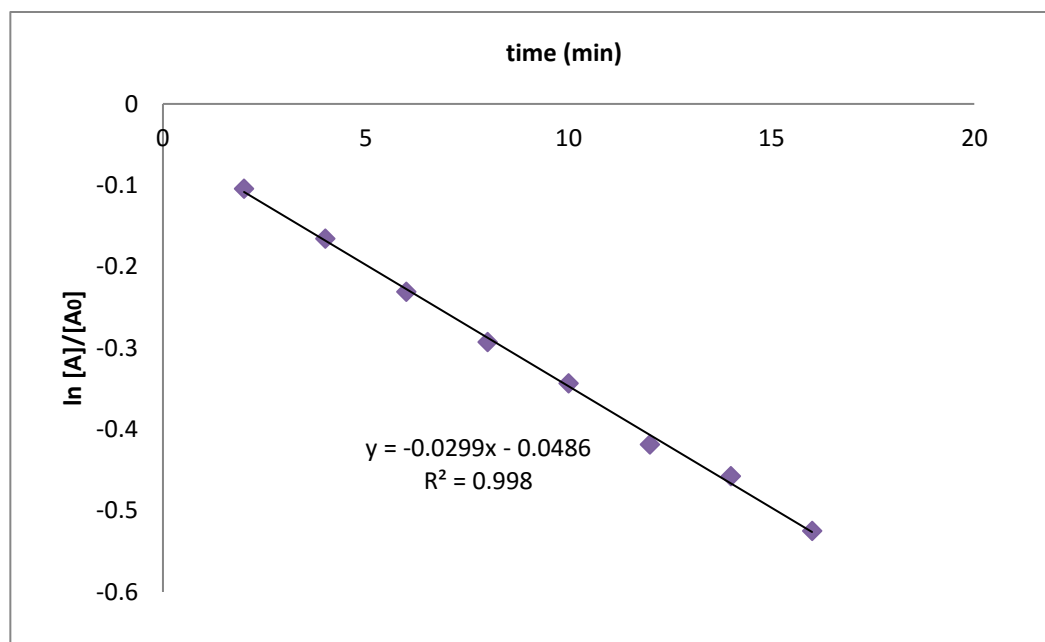


Figure A.2.22 Plot of $\ln ([A]/[A_0])$ against time of *p*-trifluoromethylbenzyl alcohol in neat $[C_4C_{1im}][HSO_4] + 1 \text{ mol\% } H_2SO_4$ at $80^\circ C$

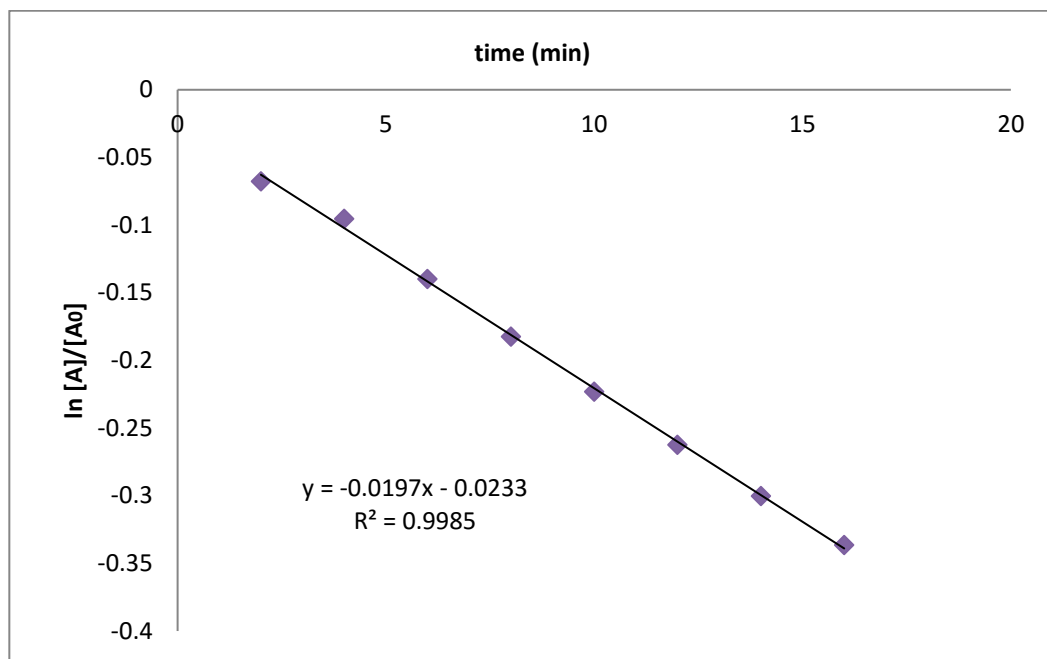


Figure A.2.23 Plot of $\ln ([A]/[A_0])$ against time of *p*-chlorobenzyl alcohol in neat $[C_4C_{1im}][HSO_4] + 1 \text{ mol\% } H_2SO_4$ at $80^\circ C$

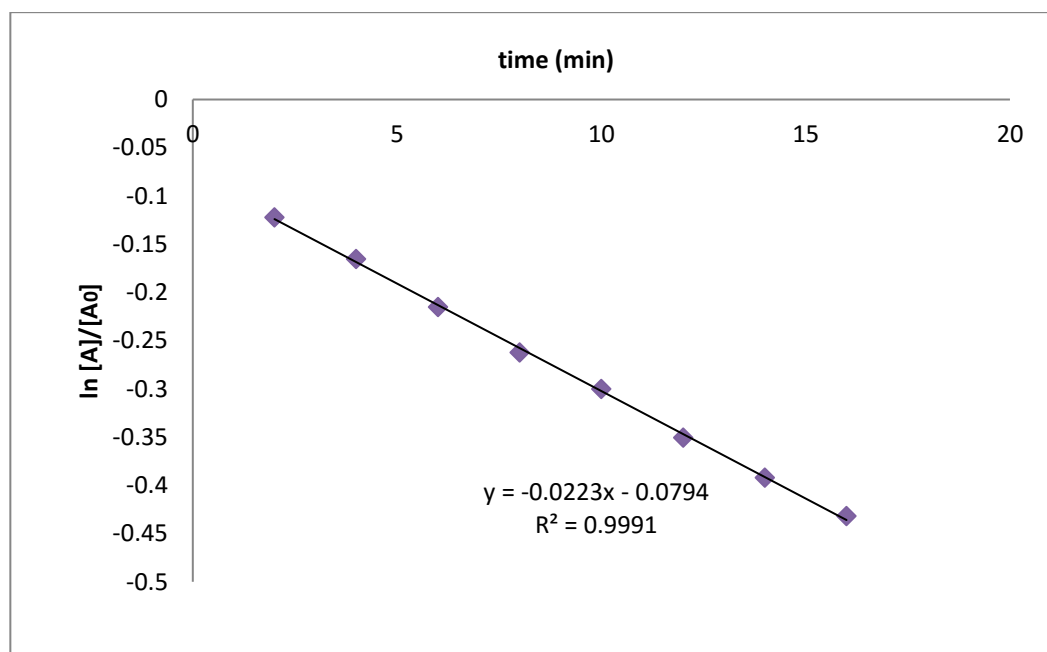


Figure A.2.24 Plot of $\ln ([A]/[A_0])$ against time of *p*-nitrobenzyl alcohol in neat $[C_4C_{1im}][HSO_4] + 1 \text{ mol\% } H_2SO_4$ at $80^\circ C$

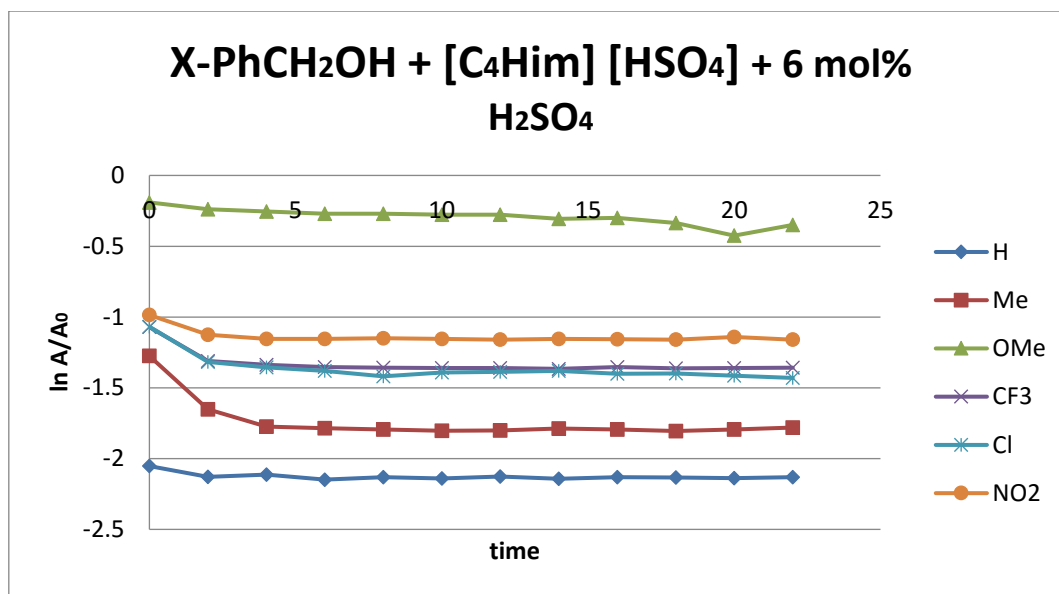


Figure A.2.25 Nucleophilic substitution reaction of *p*-X-benzyl alcohol in [HC₄im][HSO₄] + 6 mol% H₂SO₄ at 80 °C

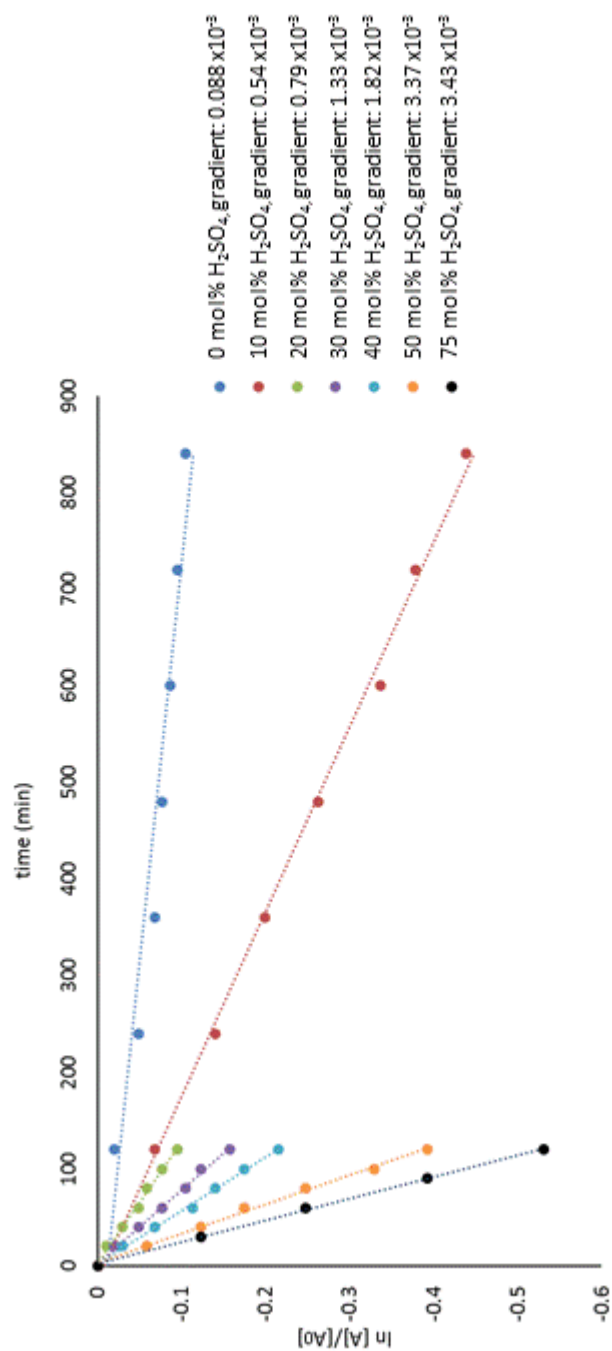


Figure A.2.26 Hydrolysis of BHB in $[\text{HC}_4\text{im}][\text{HSO}_4]$ with 10% water and varied acid content at 80 °C.

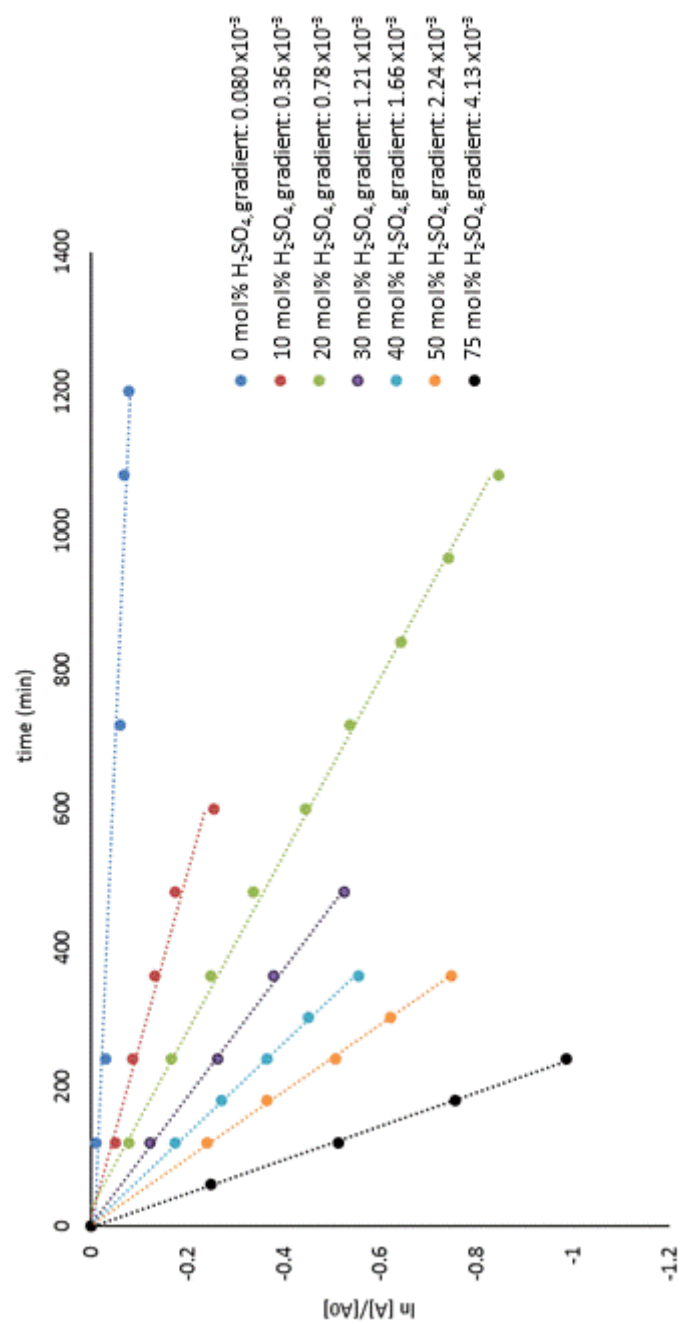


Figure A.2.27 Hydrolysis of BHB in [HC₄im][HSO₄] with 20% water and varying acid content at 80 °C.

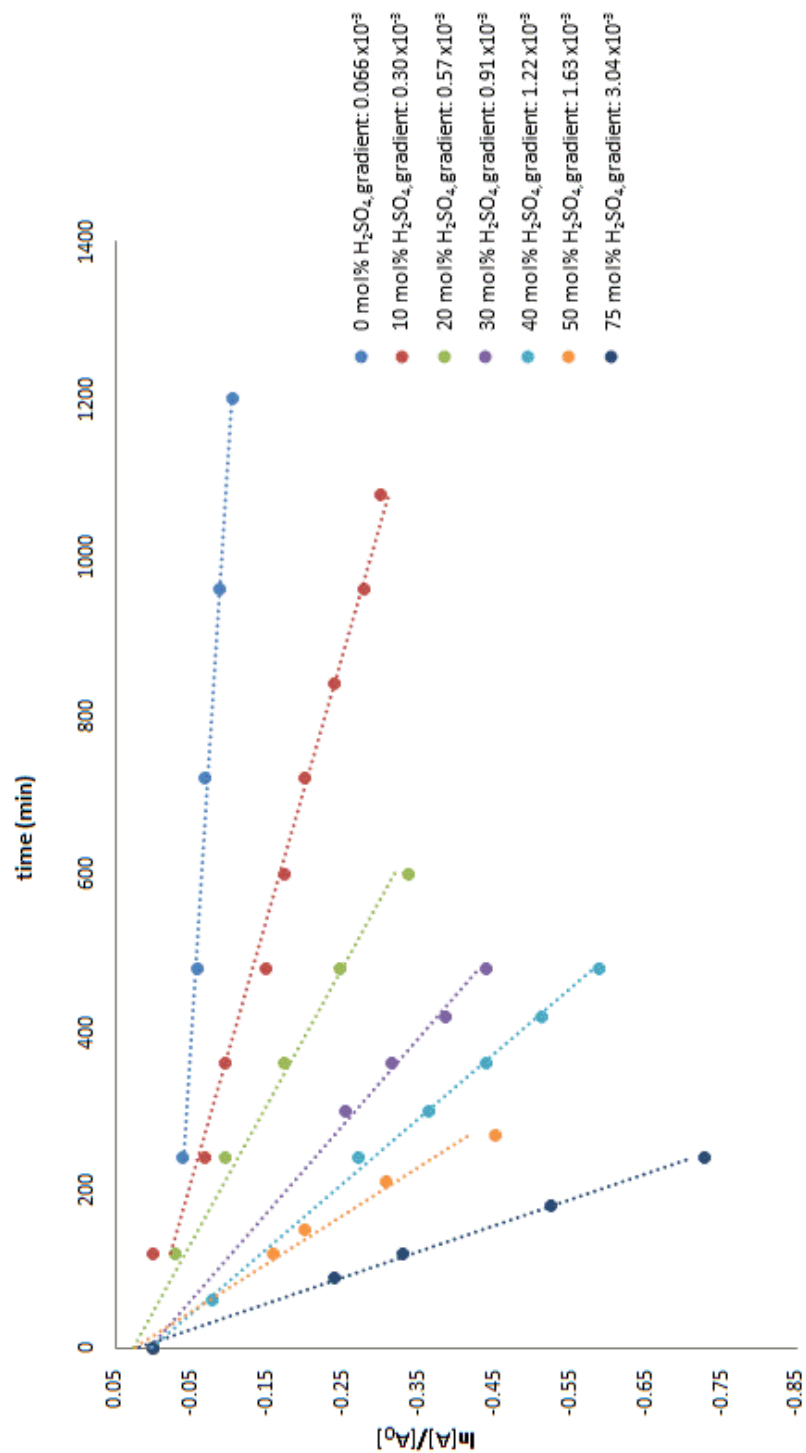


Figure A.2.28 Hydrolysis of BHB in [HC4im][HSO₄] with 30% water and varying acid content at 80 °C.

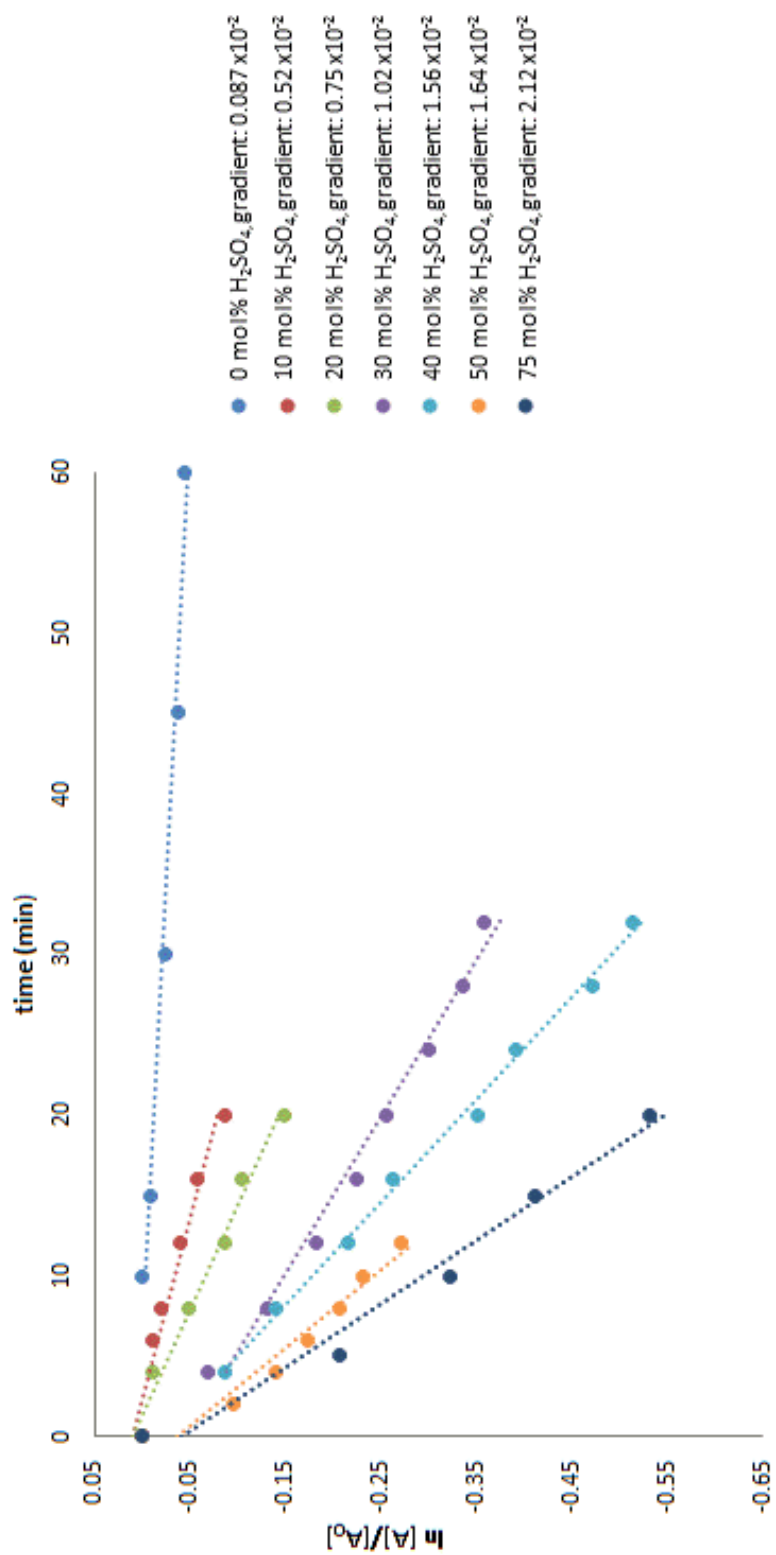


Figure A.2.29 Hydrolysis of THFF in $[\text{HC}_{4}\text{im}][\text{HSO}_4]$ with 10% water and varying acid content at 80 °C.

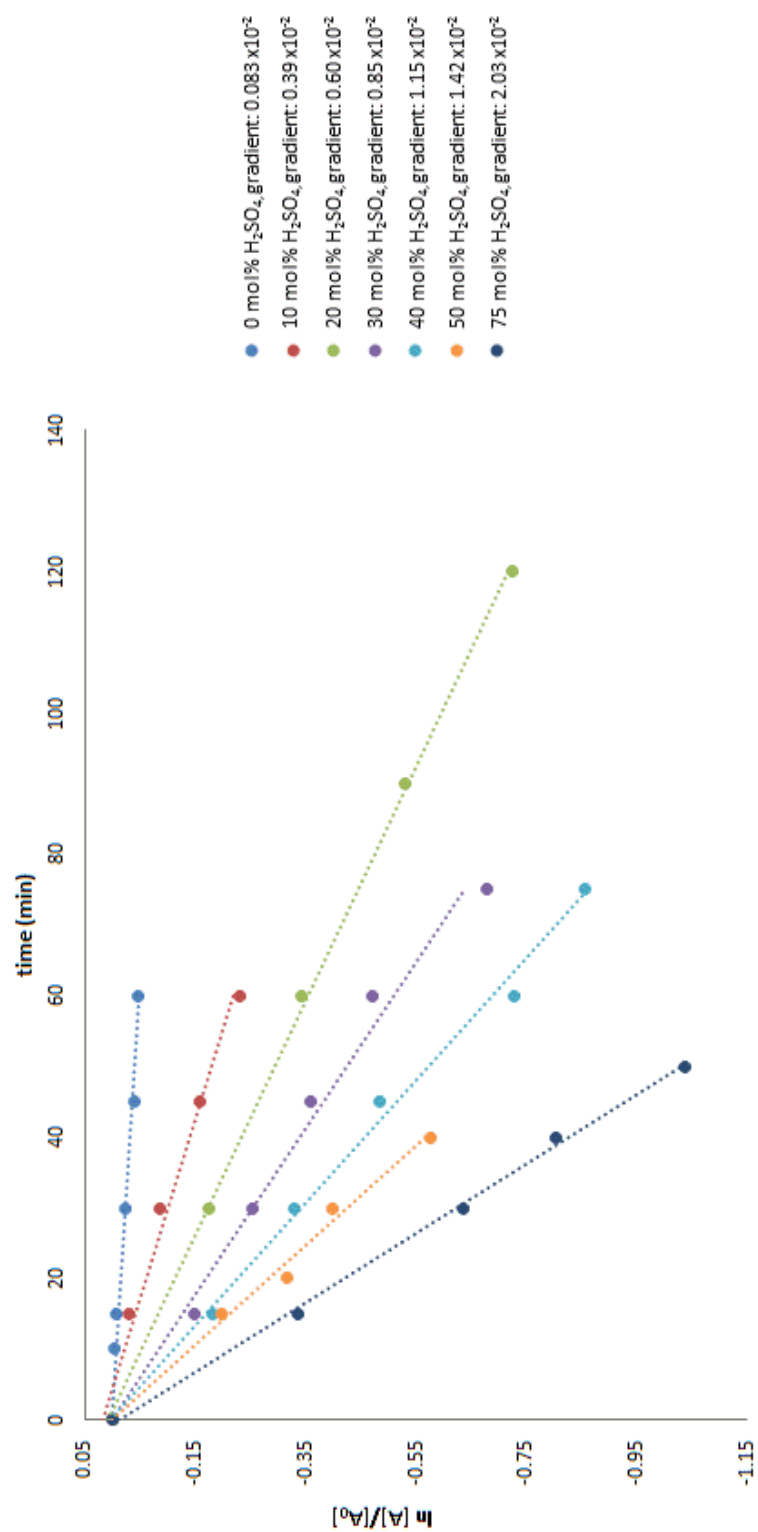


Figure A.2.30 Hydrolysis of THFF in [HC₄im][HSO₄] with 20% water and varying acid content at 80 °C.

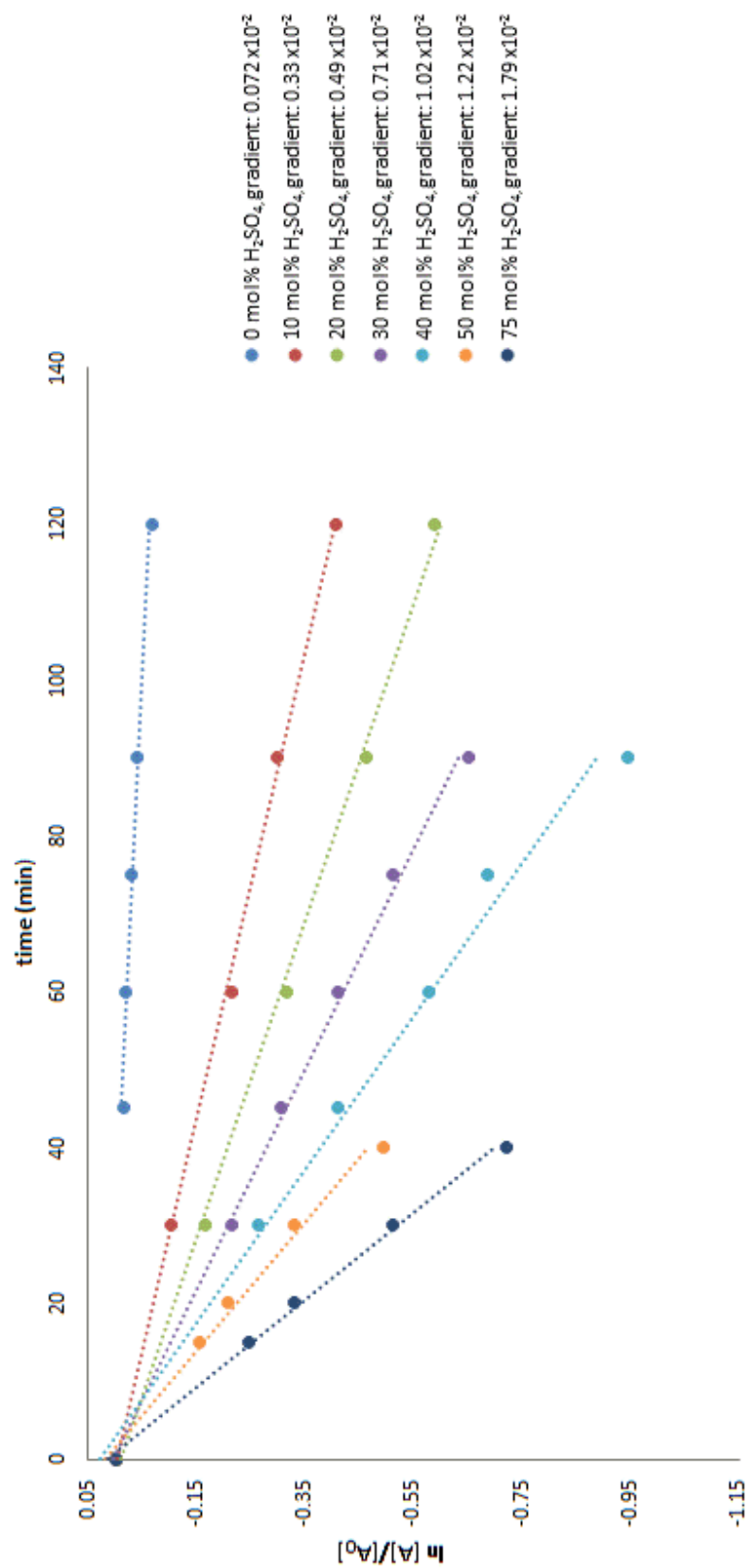


Figure A.2.31 Hydrolysis of THFF in $[\text{HC}_4\text{im}][\text{HSO}_4]$ with 30% water and varying acid content at 80 °C.

A.3 Hammett Acidity Measurement

Table A.3.1 Hammett Dyes and pKa used in this study

Dye/Hammett Indicator	pKa
4-nitroaniline	1.00
2-nitroaniline	-0.26

Table A.3.2 Calculation of H_0 of $[HC_4im][HSO_4]$ with 10% water and varying acid content

H_2SO_4 (mol%)	Dye	A_0	A	$(A_0-A)/A$	$\log (A_0-A)/A$	H_0
0	4-nitroaniline	1.612	1.561	1.561	-1.493	2.493
9.09	4-nitroaniline	1.612	1.360	1.360	-0.732	1.732
16.67	2-nitroaniline	1.884	1.438	1.438	-0.508	0.248
23.1	2-nitroaniline	1.884	0.823	0.823	0.110	-0.370
28.58	2-nitroaniline	1.884	0.494	0.494	0.449	-0.709
33.33	2-nitroaniline	1.884	0.177	0.177	0.985	-1.245
42.86	2-nitroaniline	1.884	0.384	0.384	0.592	-0.852

Table A.3.3 Calculation of H_0 of $[HC_{4im}][HSO_4]$ with 20% water and varying acid content

H_2SO_4 (mol%)	Dye	A_0	A	$(A_0-A)/A$	$\log (A_0-A)/A$	H_0
0	4-nitroaniline	1.612	1.442	0.118	-0.929	1.930
9.09	4-nitroaniline	1.612	0.844	0.909	-0.041	1.042
16.67	4-nitroaniline	1.612	0.405	2.978	0.474	0.526
23.1	4-nitroaniline	1.612	0.310	4.208	0.624	0.376
28.58	4-nitroaniline	1.612	0.166	8.715	0.940	0.060
33.33	2-nitroaniline	1.884	0.739	1.548	0.190	-0.891
42.86	2-nitroaniline	1.884	0.245	6.677	0.825	-0.624

Table A.3.4 Calculation of H_0 of $[HC_{4im}][HSO_4]$ with 30% water and varying acid content

H_2SO_4 (mol%)	Dye	A_0	A	$(A_0-A)/A$	$\log (A_0-A)/A$	H_0
0	4-nitroaniline	1.612	1.384	0.164	-0.784	1.784
9.09	4-nitroaniline	1.612	0.806	1.001	0.000	1.000
16.67	4-nitroaniline	1.612	0.470	2.431	0.386	0.614
23.1	4-nitroaniline	1.612	0.457	2.531	0.403	0.597
28.58	4-nitroaniline	1.612	0.125	11.930	1.077	-0.077
33.33	4-nitroaniline	1.612	0.200	7.060	0.849	0.151
42.86	4-nitroaniline	1.612	0.116	12.869	1.110	-0.110

