Temperature Effects on the Kinetics of Ferrocene and Cobaltocenium in Methyltriphenylphosphonium Bromide Based Deep Eutectic Solvents

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The oxidation of ferrocene (Fc/Fc⁺) and reduction of cobaltocenium (Cc⁺/Cc) under different temperatures has been studied by cyclic voltammetry and double potential step chronoamperometry in deep eutectic solvents (DESSs) consisting of methyltriphenylphosphonium bromide salt with tri-ethylene glycol, glycerol or ethylene glycol as hydrogen bond donors. The temperature dependence of the measured physical properties of DESSs (such as viscosity and conductivity) is discussed in detail. The kinetics of the redox couples are studied using cyclic voltammetry, and the standard heterogeneous electron transfer rate constant, k^0 is found to be of the order of 10^{-5} to 10^{-4} cm s⁻¹ at different temperatures. The diffusion coefficient, D , of Fc and Cc⁺ is determined to lie between 8.28×10^{-10} to 6.65×10^{-9} cm² s⁻¹. These results show that both k^0 and D increase with temperature in the studied DESSs. In addition, better kinetic parameters for the DES with ethylene glycol as hydrogen bond donor means that this could be evaluated favorably as both solvents and electrolytes for redox flow cells.

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In recent years, to overcome the toxicity and high price of ionic liquids (ILs), deep eutectic solvents (DESSs) have been investigated as potential alternatives.¹⁻³ DESSs share many characteristics of conventional ILs (e.g., they have intrinsic ionic conductivity, low-volatility, biodegradability, high thermal and chemical stability, good electrochemical stability as well as non-flammability). In addition, they are simple to synthesize on a large scale.⁴⁻⁶ These properties have been explored for applications such as solvents for electrodeposition and electropolishing,⁷⁻⁹ electrochemistry,¹⁰ separation processes,¹¹ chemical and enzymatic reactions,¹² biochemistry¹³ as well as organic and inorganic syntheses.^{14,15} In its most common form, a DES is a eutectic mixture of an organic salt (ammonium or phosphonium) and a hydrogen bond donor (HBD), that is made up of different components such as amides, metal salts, alcohols, carboxylic acids and amines that may be used as complexing agents (typically an H-bond donor).^{16,17} A DES has a melting point that is far below that of its individual constituents. This is because the complexing agent interacts with the anion and increases its effective size. This, in turn, decreases the anionic interaction with the cation thereby reducing the melting point of the mixture.¹⁸

Organometallic redox couples such as ferrocene/ferrocenium (Fc/Fc⁺) or cobaltocenium/cobaltocene (Cc⁺/Cc) are frequently used as a standard reference for non-aqueous solvents in conjunction with a quasi-reference electrode (QRE) to control and evaluate electrode potentials.¹⁹⁻²² Fc is often used as an ideal internal reference system for comparison of redox processes in different ILs, although Torriero et al.²³ indicate that the standard redox potential of Fc is dependent on the solvation effects of the solvent and supporting electrolyte used. Fc is often poorly soluble in some ILs, mostly in those with high viscosity. In contrast, Cc is generally soluble in ILs, where the reduction of the Cc⁺/Cc appears to be an ideal reversible process.^{21,22} There are some unexpected complexities in the literature as to the behavior of Fc/Fc⁺ in a range of commonly-used ILs. For example, the diffusion coefficient of Fc is a function of concentration, nonlinear peak current versus Fc concentration relationships²⁴ as well as nonlinear correlations between the enthalpy of vaporization and molar surface energy

of the [C_nC₁Im][BF₄] ILs.^{25,26} With the exception of some electrochemical studies in organic solvents at different temperatures,²⁷⁻²⁹ the investigation has been performed at room temperature. In the case of ILs, the voltammetry of both Fc and Cc was evaluated over a range of temperatures²¹ and the kinetics of the Fc/Fc⁺ electrochemical system was investigated in the temperature range of 298–373 K.³⁰

Despite such progress, no fundamental study on the effect of temperature on Fc/Fc⁺ oxidation and Cc⁺/Cc reduction processes in DESSs is available. DESSs, just as ILs, perform the dual function of electrolyte and solvent and hence represent a different kind of medium for electrochemical applications. In the present work the electrochemical data and kinetics of the Fc/Fc⁺ and Cc⁺/Cc redox couples obtained with cyclic voltammetry and chronoamperometry in Type III DESSs (there are four different types of DESSs as described in the literature)^{1,31} based on a quaternary phosphonium salt and three different alcohol-based hydrogen bond donors are reported over a range of temperatures. In addition, the effect of temperature on the physicochemical properties of the studied DESSs is investigated.

Experimental

Materials.— In this work methyltriphenylphosphonium bromide (C₁₉H₁₈PBr) was used as a quaternary phosphonium salt while tri-ethylene glycol (C₆H₁₄O₄), glycerol (C₃H₈O₃) or ethylene glycol (C₂H₆O₂) were employed as hydrogen bond donors. All chemicals were supplied by Merck (Germany) with high purity (≥98%). These chemicals were stored in an inert glove box (Innovative Technology, Pure Lab^{HE}, USA) purged with argon (oxygen-free) with no additional purification being required. The water mass fraction of the chemicals (as per the manufacturer's guide) was <10⁻³.

Preparation of DESSs.— The eutectic mixtures were prepared by following the method prescribed earlier in several publications.^{3,8,32} Briefly, each DES solution was prepared by stirring the quaternary phosphonium salt and HBD mixture vigorously with a magnetic stirrer, in the stated proportions (Table I), at 373 K and atmospheric pressure, while observing the formation of a homogeneous colorless liquid. The synthesized DESSs were stored in the argon-filled glove box with a moisture content of less than 1 ppm during the entire study.

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Table I. Physicochemical properties of phosphonium-based DESs.

DESs	Formulae		Molar ratio	M_w (g mol ⁻¹)	Melting Point (K)	ρ (g cm ⁻³)	η (mPa s)	σ (mS cm ⁻¹)	pH
	Salt	HBD ^a							
C ₁₉ H ₁₈ BrP/TEG	C ₁₉ H ₁₈ BrP Methyltriphenylphosphonium bromide	C ₆ H ₁₄ O ₄ Triethylene glycol	1:4	191.58	254	1.20	270	0.62	5.53
C ₁₉ H ₁₈ BrP/Glycerol	C ₁₉ H ₁₈ BrP Methyltriphenylphosphonium bromide	C ₃ H ₈ O ₃ Glycerol	1:3	158.38	267 ^b	1.29	3040 ^b	0.08 ^b	5.60
C ₁₉ H ₁₈ BrP/EG	C ₁₉ H ₁₈ BrP Methyltriphenylphosphonium bromide	C ₂ H ₆ O ₂ Ethylene glycol	1:2	160.46	230 ^b	1.25	213 ^b	1.43 ^b	6.12

^aHBD = Hydrogen Bond Donor^bData from Ref. 30

The preparation process was complete within 3–5 h. Table I shows the DESs studied in the present work.

Physicochemical properties test.— Conductivity measurement of synthesized DESs was carried out with DZS-708 Multi-parameter analyzer, which was calibrated using a 0.001 M standard solution of KCl (Merck) at different temperatures. The viscosities of the DESs were obtained by averaging each measurement at least three to five times, using a Brookfield DV-II +Pro EXTRA instrument. The standard uncertainty in viscosity measurements did not exceed $\pm 1\%$ in this study. The densities were measured at various temperatures using a DMA 4100 Density Meter (Anton Paar, Austria) with three replicates for each reading with an uncertainty of ± 0.00008 g · cm⁻³. The adjustment of the density meter was checked using water (degassed and distilled) at 298 K and compared with the corresponding value in density tables. The results exhibited a difference of ± 0.00005 g cm⁻³ which showed good accuracy. The pH was determined by means of a Metrohm pH meter, which was calibrated using a standard pH buffer solution. The temperature control of DESs during the measurement of all properties, from 298 to 368 K, was ensured by means of a Wisecircu thermostatic water bath.

Electrochemical measurements.— All electrochemical experiments were performed with a computer-controlled *i*-Autolab potentiostat (Metrohm PGSTAT302N) using a typical three-electrode cell that was assembled within a Faraday cage inside the dry argon-filled glove box to minimize electrochemical noise. A platinum microelectrode (20 μ m diameter) and a Glassy Carbon macro-electrode (GC, 3 mm diameter) were used as working electrodes. Silver wire (immersed in 65% HNO₃ prior to experiments, then rinsed thoroughly with water and ethanol) was used as the quasi-reference electrode (AgQRE) while Pt. wire was employed as the counter electrode. The working electrodes were polished prior to each experiment with 0.25 μ m alumina slurry (Wirth Buehler) and ultrasonically rinsed in acetone. The limiting potentials for the electrochemical window of each DES were arbitrarily determined as the potential corresponding to the current density beyond 0.2 mA cm⁻², which was selected as the cutoff current density for comparison purposes.

Results and Discussion

Preparation and characterization of DESs.— The structures of DESs from the association between the phosphonium salt and three alcohol-based HBDs are summarized in Table I. The same is applicable for the fundamental physicochemical properties of conductivity, viscosity, density, melting point and pH of all synthesized DESs (for a better understanding of the interactions in these compounds). All of these alcohol-based DESs in the present study are liquid at room temperature.

Figure 1. Dependence of densities (ρ) on temperature for the DESs employed in this investigation.

The densities of the DESs were determined in the temperature range of 298–363 K at atmospheric pressure. As expected, it was observed (Figure 1) that the densities of the DESs decreased linearly with increasing temperature because of thermal expansion. The difference in the values of density for the studied DESs could be ascribed to a different molecular association or packing of the DES and the difference in the density of the HBDs. In general, there was good agreement between the values obtained in this work and those reported in the literature.³³ The following equation fitted the experimental data for the densities (ρ) of the DESs well over the entire temperature range:

$$\rho = AT + B \quad [1]$$

Where T is the absolute temperature (K) while A and B are empirical constants that depend on the type of DES. The adjustable parameters of Equation 1 for the density of the phosphonium based DESs are displayed in Table II. As shown in Table I, C₁₉H₁₈BrP/Glycerol has a higher density due to a higher intermolecular packing.

Table II. The adjustable parameters for density and pH of phosphonium-based DESs.

DESs	A		B	
	Density	pH	Density	pH
C ₁₉ H ₁₈ BrP/TEG	-0.0005	0.0231	1.3582	-1.3567
C ₁₉ H ₁₈ BrP/Glycerol	-0.0007	-0.0075	1.5077	7.8614
C ₁₉ H ₁₈ BrP/EG	-0.0007	-0.0055	1.4578	7.7286

Figure 2. Arrhenius plot of viscosity (η) for the DESs used.

It is important to establish a reliable viscosity database for electrochemical studies, due to its strong effect on the rate of mass transport within the solution that significantly affects diffusion of species in media such as ionic liquids.³⁴ The viscosity is usually influenced by the interaction of the salt to HBD and their ability to coordinate. The relative capacity to form hydrogen bonds, anionic species, size, higher alkalinity, van der Waals forces and the size of the cation can affect the viscosity values. Figure 2 indicates that with an increase in temperature from 298 to 363 K, the viscosity of the DESs decreased due to the higher mobility of ions. DESs with the glycerol HBD exhibit higher viscosities than other alcohol based DESs, which may be ascribed to the presence of a comprehensive hydrogen bond network between each component because of the presence of three hydroxyl groups in each molecule of glycerol; this results in a lower mobility of free species within the DES. As shown in Figure 2, the temperature dependence of the viscosity values is fitted using the Arrhenius equation, which describes the temperature dependence for non-associating electrolytes.³⁵

$$\ln \eta = \ln \eta_0 + \frac{E_\eta}{RT} \quad [2]$$

Where T is the temperature, E_η is the activation energy, η is the viscosity, η_0 is a constant and R is the gas constant. The regression correlation coefficients are of values higher than 0.97 showing a reasonably good fit. The E_η , η_0 and sums of square errors in measurements are depicted in Table III.

Ionic conductivity is a function of both the mobility and number of carrier ions. Conductivity evolution can be attributed to various factors, such as the geometrical and electronic structure of the salts and hydrogen bond donors, the diffusion coefficient of protons and hydrogen-bond interactions. It needs to be noted that the conductivity of C₁₉H₁₈BrP/EG is much higher than that for C₁₉H₁₈BrP/TEG and C₁₉H₁₈BrP/Glycerol. This may be attributed to the high viscosity of glycerol. As the temperature rises, conductivity of DESs generally increases significantly as a consequence of faster movement of ions at higher temperatures as well as lower viscosity of the neat DES. The

Figure 3. Arrhenius plot of specific conductivity (σ) for the DESs used.

temperature dependence of conductivity for the DESs is depicted in Figure 3. The conductivity of DESs (σ) varies over the entire temperature range according to Equation 3:³⁶

$$\ln \sigma = \ln \sigma_0 + \frac{E_\sigma}{RT} \quad [3]$$

Where T is the temperature, σ_0 is a constant and E_σ is the activation energy for conduction. Consequently, from Equation 3³⁶ E_σ , σ_0 and sums of square errors are shown in Table IV. The regression correlation coefficients are of values higher than 0.96. Molar conductivity Λ (m² S mol⁻¹) of the DESs as electrolytes was calculated using the expression $\Lambda = V_e \sigma$. The equivalent weight (V_e) of the DESs is measured from the experimental density using the equation $V_e = M/\rho$, where ρ is the density and M is the molar mass.³⁴

In order to discuss the ionic behavior, the plot of the equivalent conductivity against the inverse of viscosity (Walden plot) for the phosphonium based DESs over a temperature range of 298–363 K is shown in Figure 4. When the conductivity is strongly correlated with the viscosity, the Walden rule can be written as follows:

$$\Lambda \eta^\alpha = C \quad [4]$$

Where α is the slope of the line in the Walden plot, which reflects the decoupling of the ions and C (Walden product) is a temperature-dependent constant. This scheme provides a useful basis for classifying and arranging the ILs^{34,37} due to the practical measure for examining the ion pairing problem in electrolytes. It also helps in understanding the relationship between conductivity and low vapor pressure that is, otherwise, not so apparent. The dotted ideal line in Figure 4 represents the data for aqueous KCl solutions at high dilution, which corresponds to a system composed of equally mobile and fully dissociated ions.³⁸ The curve for C₁₉H₁₈BrP/TEG and C₁₉H₁₈BrP/EG lie below the ideal Walden line. C₁₉H₁₈BrP/Glycerol examined from Walden plots lie on the ideal line which indicates that it is good IL.³⁹ The deviations of the Walden plot of these DESs from the ideal line show an increased electrostatic interaction between the phosphonium salts and the hydrogen bond donors. In this study, we also

Table III. Regression parameters for viscosity and conductivity of phosphonium-based DESs.

DESs	η_0 / mPa s	E_η / kJ mol ⁻¹	SSE $_\eta$	σ_0 /mS cm ⁻¹	E_σ /kJ mol ⁻¹	SSE $_\sigma$
C ₁₉ H ₁₈ BrP/TEG	3.70	22.97	0.031	12.30	25.32	0.032
C ₁₉ H ₁₈ BrP/Glycerol	6.55	36.36	0.089	14.30	39.85	0.103
C ₁₉ H ₁₈ BrP/EG	4.37	23.93	0.042	11.93	30.74	0.058

SS = Sum of Square

Table IV. The experimental voltammetric data for Fc/Fc^+ and Cc^+/Cc in DESs with different operating temperatures.

DESs	T/K	Fc/Fc^+						Cc^+/Cc					
		$j_{pa}/\text{mA cm}^{-2}$	$j_{pc}/\text{mA cm}^{-2}$	E_{pa}/V	E_{pc}/V	$\Delta E_p/\text{V}$	$E_{1/2}/\text{V}$	$j_{pa}/\text{mA cm}^{-2}$	$j_{pc}/\text{mA cm}^{-2}$	E_{pa}/V	E_{pc}/V	$\Delta E_p/\text{V}$	$E_{1/2}/\text{V}$
$\text{C}_{19}\text{H}_{18}\text{BrP}/\text{TEG}$	298	0.016	-0.011	0.435	0.336	0.099	0.385	0.096	-0.165	-0.661	-0.731	0.070	-0.696
	308	0.021	-0.013	0.421	0.325	0.096	0.373	0.146	-0.203	-0.655	-0.724	0.069	-0.689
	318	0.027	-0.017	0.411	0.319	0.092	0.365	0.192	-0.247	-0.648	-0.715	0.067	-0.681
	328	0.030	-0.020	0.401	0.312	0.089	0.356	0.223	-0.291	-0.641	-0.706	0.065	-0.673
	338	0.035	-0.024	0.392	0.306	0.086	0.349	0.258	-0.342	-0.637	-0.700	0.063	-0.668
$\text{C}_{19}\text{H}_{18}\text{BrP}/\text{Glycerol}$	298	0.019	-0.022	0.417	0.340	0.073	0.380	0.186	-0.218	-0.645	-0.741	0.096	-0.693
	308	0.028	-0.023	0.409	0.338	0.071	0.373	0.203	-0.246	-0.641	-0.736	0.095	-0.688
	318	0.035	-0.025	0.398	0.330	0.068	0.364	0.235	-0.302	-0.635	-0.727	0.092	-0.681
	328	0.046	-0.028	0.389	0.323	0.066	0.356	0.258	-0.333	-0.629	-0.718	0.089	-0.673
	338	0.052	-0.031	0.381	0.319	0.062	0.350	0.297	-0.389	-0.621	-0.709	0.088	-0.665
$\text{C}_{19}\text{H}_{18}\text{BrP}/\text{EG}$	298	0.098	-0.089	0.433	0.342	0.091	0.387	0.297	-0.325	-0.658	-0.752	0.094	-0.705
	308	0.110	-0.092	0.425	0.334	0.091	0.379	0.339	-0.362	-0.652	-0.744	0.092	-0.698
	318	0.131	-0.125	0.419	0.331	0.088	0.375	0.351	-0.403	-0.649	-0.738	0.089	-0.693
	328	0.159	-0.142	0.411	0.325	0.086	0.368	0.379	-0.456	-0.638	-0.725	0.087	-0.681
	338	0.171	-0.161	0.405	0.320	0.085	0.362	0.402	-0.509	-0.634	-0.717	0.083	-0.675

measured the pH of the synthesized DESs as a function of temperature as indicated in Figure 5. The temperature dependence of pH was fitted linearly and the parameters for fitting are depicted in Table II. These results indicate that the pH increases with rising temperature for $\text{C}_{19}\text{H}_{18}\text{BrP}/\text{TEG}$. On the other hand, the pH of $\text{C}_{19}\text{H}_{18}\text{BrP}/\text{Glycerol}$ and $\text{C}_{19}\text{H}_{18}\text{BrP}/\text{EG}$ tends to decrease with temperature.

Electrochemical stability.— The electrochemical stability of the electrolyte is an important design criterion for proper reactor operation. Electrochemical stability depends on the type of electrodes, the measurement conditions, the references employed, and the arbitrary current cutoff used to define the onset of redox processes (typically between 0.1 and 1.0 mA cm^{-2}).⁴⁰ The cathodic stability potential of DESs is mainly ascribed to the reduction of the cation (salt), while the anodic stability of DESs is affected by the oxidation potential of the anionic (HBDs) part. However, Figure 6 indicated that the cathodic limiting potentials do vary even when the salt present is common. The variation of these potentials infers that the interaction between the salt and HBDs plays a significant role in the electrochemical stability.

Figure 4. Walden plots for the phosphonium based DESs, where Λ is the molar conductivity and η^{-1} is the fluidity. The dotted line indicates the data for a dilute aqueous KCl solution to fix the position of the ideal Walden line (for good ILs).

For particular applications (e.g., supercapacitors), it is the overall potential window that matters, while in other applications, the actual anodic and cathodic limits with respect to an arbitrary reference electrode (normal hydrogen or saturated calomel electrodes are typical examples) or the standard potential of a reversible redox couple in the solvent of interest (e.g., ferrocene) is the limiting factor. Typical cyclic voltammograms (at room temperature and a scan rate of 100 mV s^{-1}) recorded at GC and Pt microelectrodes to determine the limiting reduction and oxidation potentials of the neat DESs are given in Figures 6a and 6b (where the current cutoff value was 0.2 mA cm^{-2}). It is very clear from Figure 6 that the type of HBD plays a significant role in determining the electrochemical window of the DES. As expected, the electrochemical window of $\text{TEG} > \text{Glycerol} > \text{EG}$. The reduction hump at around 0.5 V for EG DES could be due to capacitance current or perhaps due to an irreversible process of adsorbed species.

The voltammetric parameter for Fc/Fc^+ and Cc^+/Cc in DESs as function of temperature.— The quantitative relationship (determined from voltammetric data) of two IUPAC recommended standard potential references in different phosphonium-based DESs is evaluated here as a function of temperature. The Fc/Fc^+ couple is commonly used to provide a reference potential scale in voltammetric studies. In addition, Bond and co-workers have also presented the Cc^+/Cc redox couple as a functional reference scale in organic solvents as well

Figure 5. Temperature-dependency of pH of selected DESs.

Figure 6. (a) Electrochemical stability obtained using Pt. Microelectrode; (b) Electrochemical stability of phosphonium based DESs using GC working electrode.

as in ILs.^{20,22,41} In the investigated DESs, Fc and Cc⁺ demonstrate reversible one-electron redox processes that can be described by the following reactions:

The temperature dependence of representative cyclic voltammograms of Fc and Cc⁺ in C₁₉H₁₈BrP/EG are shown in Figures 7 and 8, respectively. Voltammetric data obtained from individually prepared 10 mM solutions of Fc and Cc⁺ by using a GC working electrode at different scan rates over a temperature range of 298–348 K are summarized in Table IV. The difference between the corresponding anodic and cathodic peaks (ΔE_p) observed in Table IV varies between 62–99 mV for Fc/Fc⁺ and 63–96 mV for Cc⁺/Cc. As expected, ΔE_p decreases with the increase in temperature due to faster heterogeneous electron transfer kinetics. The differences between the experimental and theoretical values, 0.059 V, of ΔE_p for a reversible process are attributed to uncompensated solution resistance (R_u).^{42,43} The half wave potential ($E_{1/2}$) of the redox couples mentioned above against the Ag wire quasi reference electrode is calculated from the difference in the anodic peaks (E_{pa}) and ΔE_p .

$$E_{1/2} = E_{pa} - \frac{\Delta E_p}{2} \quad [7]$$

Considerable drifts in potential were discerned for the Ag wire QRE dipped directly in DESs including electroactive compounds. However, segregating the Ag wire immersed in DESs from the bulk solution through a glass frit eliminated this drift in potential. The

Figure 7. (a) Cyclic voltammetry for the reduction of Cc⁺ in the used DESs at varying temperatures of (i) 298 K, (ii) 308 K, (iii) 318 K, (iv) 328 K, (v) 338 K and (vi) 348 K, at 100 mV s⁻¹; (b) Double potential step chronoamperometry measured on the same system across the Cc⁺/Cc at temperatures of 298, 308, 318, 338 and 348 K.

$E_{1/2}$ was demonstrated to be inversely proportional to temperature. Table IV indicated that $E_{1/2}$ shifted to more negative potentials for the oxidation of Fc and more positive potentials for the reduction of Cc⁺, which could be attributed to donor-acceptor Lewis-type interactions.⁴⁴ Additionally, the peak current ratio of the reverse and the forward scans (i_{pa}/i_{pc}) was greater than unity and was dependent on the temperature in all the studied DESs over the entire scan range (as well as for all scan rates studied). Figures 7a and 8b showed that the peak currents increased with rising temperature for the cathodic side in case of Cc⁺ and the anodic side in case of Fc.

Determination of diffusion coefficient activation energy for Fc/Fc⁺ and Cc⁺/Cc.— Double potential step chronoamperometry at a Pt. microelectrode was carried out to evaluate the diffusion coefficients, D , of both Fc and Cc⁺ in DESs at various temperatures. The technique was performed using a sample time of 0.01 s. The pre-treatment step comprised holding the potential at a point corresponding to the passage of zero faradaic current (with 20 s pre equilibration time), after which the potential was stepped from +0.10 to +0.60 V (oxidation of Fc to Fc⁺ with respect to the AgQRE) and -0.50 to -0.90 V (reduction of Cc⁺ to Cc), and the current was measured for 5 s. The potential was then stepped back to +0.10 V (reduction of Fc⁺ to Fc) and -0.50 V (oxidation of Cc to Cc⁺), and the current response was measured for a further 5 s. The software package Origin 7.0 (Microcal Software Inc.) was used to fit the first potential step experimental data. The

Figure 8. Cyclic voltammetry for the oxidation of Fc in the DESs at varying temperatures of (i) 298 K, (ii) 308 K, (iii) 318 K, (iv) 328 K and (v) 338 K, at 100 mV s^{-1} ; (b) Double potential step chronoamperometry measured on the same system across the Fc/Fc⁺ at temperatures of 298, 308, 318 and 338 K.

equations empirically derived by Shoup and Szabo⁴⁵ were regressed to the potential-current data using a least squares minimization algorithm. The correlation below (shown in Equations 8–10) describes the

Table VI. Activation energies of the diffusion coefficients and rate constants for Fc/Fc⁺ and Cc⁺/Cc in studied DESs.

DESs	$E_D(\text{Fc})/\text{kJ mol}^{-1}$	$E_D(\text{Cc}^+)/\text{kJ mol}^{-1}$	$E_k^0(\text{Fc})/\text{kJ mol}^{-1}$	$E_k^0(\text{Cc}^+)/\text{kJ mol}^{-1}$
C ₁₉ H ₁₈ BrP/TEG	28.36	29.45	26.30	31.48
C ₁₉ H ₁₈ BrP/Glycerol	49.35	52.32	38.23	58.41
C ₁₉ H ₁₈ BrP/EG	24.05	22.93	22.07	27.63

current response to within an accuracy of 0.6%.

$$I = -4nFDcr_d f(\tau) \quad [8]$$

$$f(\tau) = 0.7854 + 0.8863\tau^{-1/2} + 0.2146 \exp(-0.7823\tau^{-1/2}) \quad [9]$$

$$\tau = \frac{4Dt}{r_d^2} \quad [10]$$

Here, r_d represents the radius of the microdisk electrode, D is the diffusion coefficient, F is Faraday's constant, c is the bulk concentration of the electro-active species, t is the time, and n is the number of electrons transferred. An example of an experimental and best-fit theoretical chronoamperometric transients for the Fc/Fc⁺ and Cc⁺/Cc redox couples in C₁₉H₁₈BrP/EG are shown in Figures 7b and 8b. As the temperature increases the limiting currents of the first step decrease systematically and the trend of the second step becomes less steep for both Fc and Cc⁺.

As expected, the diffusion coefficient of the electroactive species increased systematically with temperature (Table V). To calculate the activation energy for diffusion, E_D , the D_{Fc} and D_{Cc^+} were analyzed in terms of the Arrhenius equation:

$$D = D_0 \exp\left(\frac{-E_D}{RT}\right) \quad [11]$$

Where D_0 is a constant corresponding to the hypothetical diffusion coefficient at infinite temperature, and D is the diffusion coefficient of the electroactive species.

Figures 9a and 9b show plots of $\ln D$ vs. T^{-1} for the oxidized and reduced forms of Fc and Cc⁺, which display good linearity over the range of temperatures studied. Table VI shows E_D , which was calculated from the gradient of the best-fit line ($R^2 > 0.97$ for Fc and $R^2 > 0.98$ for Cc⁺). These values are similar with E_η for DESs, which was estimated from viscosity dependence temperature measurements and summarized in Table III. It is also observed that the less viscous DESs have correspondingly smaller activation energies.

Table V. Kinetic parameters and diffusion coefficients for Fc/Fc⁺ and Cc⁺/Cc in DESs at various temperatures.

DESs	T/K	$D_{Fc}/\text{cm}^2 \text{ s}^{-1}$	$D_{Cc^+}/\text{cm}^2 \text{ s}^{-1}$	$k_{Fc}^0/\text{cm s}^{-1}$	$k_{Cc^+}^0/\text{cm s}^{-1}$
C ₁₉ H ₁₈ BrP/TEG	298	$3.76 \times 10^{-9} (\pm 0.07)$	$2.85 \times 10^{-9} (\pm 0.05)$	$1.38 \times 10^{-4} (\pm 0.08)$	$1.14 \times 10^{-4} (\pm 0.05)$
	308	$4.23 \times 10^{-9} (\pm 0.04)$	$3.69 \times 10^{-9} (\pm 0.08)$	$2.58 \times 10^{-4} (\pm 0.06)$	$3.21 \times 10^{-4} (\pm 0.08)$
	318	$4.54 \times 10^{-9} (\pm 0.08)$	$4.21 \times 10^{-9} (\pm 0.07)$	$3.14 \times 10^{-4} (\pm 0.05)$	$3.96 \times 10^{-4} (\pm 0.07)$
	328	$5.20 \times 10^{-9} (\pm 0.06)$	$4.76 \times 10^{-9} (\pm 0.05)$	$5.27 \times 10^{-4} (\pm 0.08)$	$4.08 \times 10^{-4} (\pm 0.09)$
	338	$5.63 \times 10^{-9} (\pm 0.09)$	$5.24 \times 10^{-9} (\pm 0.04)$	$6.56 \times 10^{-4} (\pm 0.09)$	$4.97 \times 10^{-4} (\pm 0.06)$
C ₁₉ H ₁₈ BrP/Glycerol	298	$9.08 \times 10^{-10} (\pm 0.05)$	$8.28 \times 10^{-10} (\pm 0.09)$	$2.11 \times 10^{-5} (\pm 0.09)$	$1.91 \times 10^{-5} (\pm 0.06)$
	308	$9.92 \times 10^{-10} (\pm 0.06)$	$9.22 \times 10^{-10} (\pm 0.08)$	$4.38 \times 10^{-5} (\pm 0.05)$	$2.42 \times 10^{-5} (\pm 0.08)$
	318	$1.38 \times 10^{-9} (\pm 0.09)$	$1.98 \times 10^{-9} (\pm 0.05)$	$5.16 \times 10^{-5} (\pm 0.04)$	$4.53 \times 10^{-5} (\pm 0.05)$
	328	$2.12 \times 10^{-9} (\pm 0.07)$	$2.12 \times 10^{-9} (\pm 0.06)$	$5.56 \times 10^{-5} (\pm 0.09)$	$5.32 \times 10^{-5} (\pm 0.08)$
	338	$2.86 \times 10^{-9} (\pm 0.05)$	$2.66 \times 10^{-9} (\pm 0.05)$	$5.96 \times 10^{-5} (\pm 0.07)$	$6.12 \times 10^{-5} (\pm 0.09)$
C ₁₉ H ₁₈ BrP/EG	298	$4.23 \times 10^{-9} (\pm 0.08)$	$3.74 \times 10^{-9} (\pm 0.05)$	$1.71 \times 10^{-4} (\pm 0.07)$	$1.02 \times 10^{-4} (\pm 0.06)$
	308	$4.92 \times 10^{-9} (\pm 0.07)$	$4.56 \times 10^{-9} (\pm 0.06)$	$3.88 \times 10^{-4} (\pm 0.06)$	$2.56 \times 10^{-4} (\pm 0.06)$
	318	$5.53 \times 10^{-9} (\pm 0.05)$	$5.02 \times 10^{-9} (\pm 0.09)$	$5.68 \times 10^{-4} (\pm 0.08)$	$4.56 \times 10^{-4} (\pm 0.08)$
	328	$6.12 \times 10^{-9} (\pm 0.04)$	$5.51 \times 10^{-9} (\pm 0.06)$	$7.43 \times 10^{-4} (\pm 0.05)$	$6.31 \times 10^{-4} (\pm 0.05)$
	338	$6.65 \times 10^{-9} (\pm 0.08)$	$6.28 \times 10^{-9} (\pm 0.07)$	$8.96 \times 10^{-4} (\pm 0.05)$	$7.84 \times 10^{-4} (\pm 0.05)$

Error bars calculated from the standard deviation from four experimental repetitions.

Figure 9. Dependence of diffusion and rate constant on temperature using Arrhenius rule for (a) Fc and (b) Cc^+ redox couples in $C_{19}H_{18}BrP/TEG$.

Evaluation of the heterogeneous rate constant for Fc/Fc^+ and Cc^+/Cc : verification of the Arrhenius law.— Heterogeneous rate constants (k^0) at stationary macro-electrodes are typically evaluated by applying the well-known Nicholson method, which is based on the degree of peak potential separation between cathodic and anodic reactions in a cyclic voltammogram for a simple one electron transfer process.^{46–49} The methodology, however, is susceptible to errors resulting from residual R_u and charging currents, which can result in overstated rate constants. When the temperature of solutions of Fc and Cc^+ in DESs was varied and rate constants were estimated, it was possible to construct Arrhenius plots for the two redox couples. The temperature dependences of the rate constant of Fc and Cc^+ in $C_{19}H_{18}BrP/TEG$ are presented in Figures 9a and 9b and nearly identical slopes were found in the D and k^0 Arrhenius plots. In general, it was found that the rate constant rose with increasing temperature for both Fc and Cc^+ . The activation energy corresponding to the rate constant (E_k) was then calculated from the slope and listed in Table VI.

Conclusions

Various physicochemical and electrochemical properties, such as viscosity, density, conductivity, molar conductivity, rate constant, and diffusion coefficients of Fc and Cc^+ in DESs, were evaluated over the temperature range from 298 to 363 K. These results indicated that the k^0 and D improved with increasing temperature in DESs. The validity of the Arrhenius law was confirmed by exploring the temperature dependences of k^0 and D . The activation energies (E_η , E_{σ} , E_D , and E_k) for each DES were calculated from the slopes of the Arrhenius plots. The correlation of viscosity to conductivity was evaluated by using the Walden plot which serves as a practical means of evaluating the

relative fluidity and degree of decoupling of ions of the tested DESs. A slight decrease in ΔE_p was observed with the increase of temperature while $E_{1/2}$ values changed to more negative potentials for oxidation of Fc and more positive potentials for the reduction of Cc^+ in DESs. Finally, kinetic parameters showed that DES with ethylene glycol as the hydrogen bond donor had consistently higher rate constants and lower activation energies than its tested counterparts. This meant that this DES could be a reasonable choice for further tests as both solvent and electrolyte for redox flow cells.

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