

KINETIC STUDY OF THE FERROCENE COMPLEX IN BINARY IONIC LIQUID MEDIA

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ABSTRACT

A binary ionic liquid (ILs)-based electrolyte with advanced physicochemical properties has been successfully prepared. The ionic conductivity (σ) values of ILs [C₄mim][PF₆] and [C₄mim][Tf₂N] were measured using electrochemical impedance spectroscopy are 2.12 and 4.75 mS/cm at 30 °C, respectively. The results of electrode kinetics measurement using cyclic voltammetry revealed a value of the diffusion coefficient (D) of ferrocene in [C₄mim][PF₆] of 3.3×10^{-7} cm²/s and [C₄mim][Tf₂N] 1.60×10^{-6} cm²/s. The ferrocene complex obtained has an electron transfer rate constant (k_s) of 7.9×10^{-4} cm/s in [C₄mim][PF₆] and 1.82×10^{-3} cm/s in [C₄mim][Tf₂N]. The addition of [C₄mim][Tf₂N] to [C₄mim][PF₆] increased ionic conductivity, diffusion coefficient, and electron transfer rate constant overall, but only to the range of pure ILs. Furthermore, changes in conductivity, diffusion coefficient, and electron transfer rate constant value are proportional to temperature changes, according to the Arrhenius equation. Based on the diffusion activation energy (E_{ad}) and the slight decrease in conductivity with temperature, [C₄mim][PF₆]_{0.50}-[C₄mim][Tf₂N]_{0.50} is a superior electrolyte candidate at low-temperature operation.

Keywords: Binary Ionic Liquids, Ferrocene, Conductivity, Diffusion Coefficient, Electron Transfer Rate Constant.

RASAYAN J. Chem., Vol. 16, No. 3, 2023

INTRODUCTION

A large amount of energy demand directly impacts the increase in the use of batteries as energy storage devices. The Global Battery Alliance projects that world battery demand will grow by at least 25% annually to reach 2,600 GWh by 2030.¹ However, this progress still leaves some critical issues unresolved in recent years. For example, South Korea, one of the countries with the most significant number of energy storage installations, had 23 cases of battery fires reported between 2017 and 2018.² Furthermore, that was recorded from 2006 to April 2022; the Federal Aviation Administration reported at least 357 air/airport incidents which involve burning lithium batteries as baggage or cargo.³ This case has received special attention from various circles, especially the demands of developing an efficient and safe battery. In general, the causes of battery explosions and fires were described by Kolbasov *et al.*⁴ This incidence is primarily caused by an internal short circuit, the battery overheating, surpassing the allowed maximum voltage, and intensive charging/ discharging process. All of these factors lead to the formation of thermal runaway, which decomposes the electrolyte upon interaction with the electrodes. So far, the electrolyte often used in conventional lithium batteries is a lithium salt dissolved in an organic carbonate solvent, especially an ethylene/dimethyl carbonate mixture (EC/DMC).⁵ The solvent composition has a high vapor pressure (4.8 kPa at 25 °C) and a low flash point (25 °C);⁶ thus, it decomposes quickly as the battery temperature rises. Meanwhile, replacement with an aqueous solvent with a higher flash point,⁷ has limitations due to a restricted electrochemical window (1.23 V), where an excess potential causes water electrolysis.⁸ Recent studies have shown that one of the leading candidates for electrolytes that are thermally, electrochemically, and environmentally safe are ionic liquids (ILs).⁹⁻¹³

As electrolytes, ILs can act as solvents without additional salts and can be combined with electroactive species in electrochemical systems.¹⁴ However, the wide variety of design possibilities for ILs affords several competitive options. According to Kazemiabnavi *et al.*,¹⁵ 1-butyl-3-methylimidazolium hexafluorophosphate [C₄mim][PF₆] has the broadest electrochemical window, making it an excellent

candidate for use as an electrolyte. Despite satisfying the basic parameters for an ideal electrolyte ($> 10^{-3}$ mS/cm),¹⁶ the conductivity of [C₄mim][PF₆] 1.46 mS/cm is lower than that of EC/DMC 11.4 mS/cm, limiting its battery performance.^{17,5} Thawarkar *et al.*¹⁸ outline several treatments for increasing the conductivity of ILs, including adding molecular solvents or mixing ILs with higher conductivity. According to Fox *et al.*,¹⁹ adding an organic solvent to an ILs enhanced conductivity greatly, but the mixture was volatile since it did not interact strongly with each other. On the other hand, mixing two ILs produced better outcomes by increasing conductivity and electrochemical stability.²⁰⁻²² Many researchers attempt to create the ideal mixture of ILs because of the potential obtained from this mixing. In this study, the conductivity of [C₄mim][PF₆] was increased by adding 1-butyl-3-methylimidazolium bis(trifluoro-methylsulfonyl)imide [C₄mim][Tf₂N] with a conductivity 4.02 mS/cm and an electrochemical window of 4.2 V.^{23,15} The two ILs are expected to be able to substitute for each other through mixing at various mole fractions, resulting in a superior electrolyte in electrochemistry. In electrochemistry, kinetic aspects must be studied in addition to conductivity, which gives an idea of ion conduction because electrolyte performance is affected by mass and charge transfer when interacting with electroactive species at the electrode/electrolyte interface.²⁴ Besides, Patah *et al.* reported that the type of species affected the kinetics.¹⁴ As the kinetics of species in binary ILs have yet to be extensively studied, a widely-accepted standard complex is required for this measurement. Ferrocene (Fc) is frequently used as a standard in electrochemical measurements due to its sandwich structure with cyclopentadienyl ligand. It produces molecular stability and fast Fc/Fc⁺ redox changes, reversible and kinetically uncomplicated.²⁵ As a result, in this study, ferrocene was used as an electroactive species to investigate the kinetics of binary ILs to develop a fundamental instrument for designing energy storage systems.

EXPERIMENTAL

Material and Methods

The equipment used in this study consisted of glassware, VWR ultra high-performance single channel pipettors, glove boxes, and electrochemical cells with ± 1 mm glassy carbon (GC) as the working electrode, tungsten wire (W/WO₃) as the pseudo-reference electrode, and a platinum sheet (Pt) as the counter electrode. The instruments include electrochemical impedance spectroscopy (EIS) Gamry Ref. 3000 potential/galvanostat, cyclic voltammetry (CV) Palmsens Emstat³⁺ potential/galvanostat, Haake Type G thermostat with ± 1 K accuracy, Mettler Toledo analytical balance, and Branson 2510 sonicator were used. Meanwhile, the chemicals used include ferrocene [Fe(Cp)₂], 1-butyl-3-methylimidazolium hexafluorophosphate [C₄mim][PF₆], 1-butyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide [C₄mim][Tf₂N], distilled water, and potassium chloride (KCl) that Merck Sigma Aldrich supplied. All of these materials are used directly without any further purification.

General Procedure

The preparation of the binary ILs refers to the procedure reported by Li *et al.*²⁶ and Vorotyntsev *et al.*²⁷ In a glove box, five variations of [C₄mim][PF₆]_(x)-[C₄mim][Tf₂N]_(1-x) were prepared gravimetrically with mole fraction (x) 0; 0.25; 0.5; 0.75; and 1.0. Afterward, ferrocene in binary ILs at a concentration of 5 mM was generated by dissolving ferrocene solution aliquots. The solution is then sonicated until it is homogeneous.

Conductivity Measurement

The conductivity of binary ILs was measured using EIS with a three-electrode system cell. The cell constant was determined in the frequency range of 1 MHz to 1 Hz using a standard solution of 0.01 molal (m) KCl with known conductivity.²⁸ The conductivity measurements were taken at 30–50 °C for each mole fraction of binary ILs and determined using the following equation:

$$\sigma = \frac{1}{R_s} \cdot \frac{l}{A} \quad (1)$$

Where σ is the conductivity (S/cm), R_s is the ILs resistance (Ω), and l/A is the cell constant (1/cm).

The Arrhenius equation examined the correlation between conductivity and temperature.

$$\sigma_T = \sigma_o \exp \left(-\frac{Ea_\sigma}{RT} \right) \quad (2)$$

by plotting $\ln \sigma_T$ vs. $1000/T$, where σ_T is conductivity at a given temperature (mS/cm), σ_0 is the pre-exponential factor, $E_{a\sigma}$ is the activation energy or the energy needed to activate the conduction process (kJ/mol), and T is the temperature ($^{\circ}\text{C}$).²⁹

Kinetics Determination

Determination of diffusion and electron transfer kinetics of ferrocene complex in binary ILs was conducted using CV. The redox reaction was observed at temperatures ranging from 30 to 50 $^{\circ}\text{C}$ with 20–300 mV/s scanning rates.

The Nicholson method was used to perform the calculations.³⁰ The peak current data (I_p) obtained through the voltammogram in the first cycle was corrected by the Nicholson equation:

$$\frac{I_{pc}}{I_{pa}} = \frac{I_{(pc)0}}{I_{pa}} + 0.48 \left(\frac{I_{\lambda}}{I_{pa}} \right) + 0.086 \quad (3)$$

the magnitude (I_{pc})₀ is the peak reduction current calculated from the baseline, and I_{λ} is the current measured at the time of potential change.

The corrected peak current is then used in the Randles-Sevcik equation to calculate the diffusion coefficient.

$$I_p = (0.4463)nFAC \left(\frac{nFvD}{RT} \right)^{1/2} \quad (4)$$

with:

I_p	= peak current (A)	F	= Faraday's constant (96485 C/mol)
D	= diffusion coefficient (cm^2/s)	v	= scan rate (mV/s)
A	= the surface area of the working electrode (cm^2)	R	= gas constant (8.314 J/mol.K)
n	= number of electron transfer	T	= absolute temperature (K)
		c	= the concentration of electroactive species (mol/cm^3)

Plotting the I_p data against the scan rate root ($v^{1/2}$) produces a linear regression gradient, which is then multiplied by the constants and variables of eq. (4) to obtain the diffusion coefficient value (D). This value is calculated for the oxidation (D_o) and reduction (D_r) processes.

Using the Arrhenius equation, the temperature dependency of the diffusion coefficient is quantitatively stated, allowing the activation energy for the diffusion process (E_{aD}) to be determined.

$$D_T = D_o \exp \left(-\frac{E_{aD}}{RT} \right) \quad (5)$$

Where D_T denotes the diffusion coefficient of electroactive species at a given temperature (cm^2/s). The gradient plot of $1000/T$ to $\ln D$ can be utilized to compute E_{aD} .

The electron transfer rate constant (k_s) is the following kinetic parameter examined and calculated using the Nicholson method (eq. 6). In Roussel's equation (eq. 7), α is the transfer coefficient, and Ψ is the dimensionless kinetic parameter derived from peak separation data (ΔE_p).

$$k_s = \frac{\Psi}{\left(\frac{D_r}{D_o} \right)^{\alpha}} \sqrt{\left[D_o \pi v \left(\frac{nF}{RT} \right) \right]} \quad (6)$$

$$\Delta E_p (\text{mV}) = 81.34 - 3.06 \Psi^{-1} + 149 \Psi^{-\frac{1}{2}} - 145.5 \Psi^{-\frac{1}{3}} \quad (7)$$

Finally, applying the Arrhenius equation, the activation energy for the electron transfer (E_{ks}) is calculated.

$$k_s = k_0 \exp \left(-\frac{E_{ks}}{RT} \right) \quad (8)$$

RESULTS AND DISCUSSION

The Conductivity of Binary ILs

As shown in Fig.-1(a), the obtained Nyquist plot has a similar shape for each variation of the binary ILs fraction. A small semi-circle appears at high frequencies, followed by a large semi-circle at low frequencies. Because of the many inconsistencies in the literature, as Mei *et al.* mentioned,³¹ the interpretation of the Nyquist plot in several studies cannot be accurately ascertained. However, Nazet *et al.*³² and Jiuyong Li *et al.*³³ calculated total resistance (R_s) as the sum of bulk and interface transfer resistances for ionic conductivity analysis. This resistance is estimated at the point where the second semi-circle plot intersects the x-axis (Z_{real}).

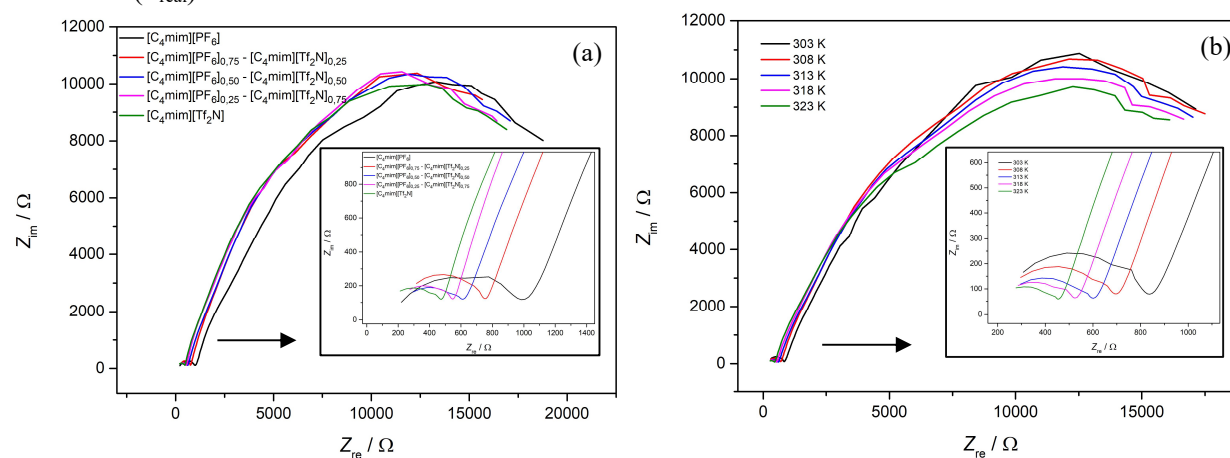


Fig.-1: The Nyquist Plot of (a) Binary ILs at 40 °C and (b) $[C_4mim][PF_6]_{0.50}-[C_4mim][Tf_2N]_{0.50}$ at Various Temperatures

Based on the measurements, the conductivities of $[C_4mim][PF_6]$ and $[C_4mim][Tf_2N]$ are 2.12 and 4.75 mS/cm at 30 °C, respectively. At the same temperature, these results are not significantly different from the conductivity values reported in other studies, which are 1.90 mS/cm for $[C_4mim][PF_6]$ ³⁴ and 4.88 mS/cm for $[C_4mim][Tf_2N]$.²³ Meanwhile, as set out in Table-1, the conductivity of $[C_4mim][PF_6]$ increased after the addition of many $[C_4mim][Tf_2N]$ in the following order: $[C_4mim][PF_6] < [C_4mim][PF_6]_{0.75}-[C_4mim][Tf_2N]_{0.25} < [C_4mim][PF_6]_{0.50}-[C_4mim][Tf_2N]_{0.50} < [C_4mim][PF_6]_{0.25}-[C_4mim][Tf_2N]_{0.75} < [C_4mim][Tf_2N]$. A binary ILs with a conductivity intermediate between the two pure ILs is formed when mixing occurs.

In general, the conductivity tendency can be explained by the solvent's conductivity, which is affected by the number of charge carrier species and the ion mobility according to the equation:

$$\sigma = \sum n_i q_i u_i \quad (9)$$

Where n_i denotes the number of charge carriers, q_i is the charge, and u_i is the mobility of each ion.¹⁸ The round $[PF_6]^-$ anion would be easier to associate with $[C_4mim]^+$ than the bulk and steric $[Tf_2N]^-$ structure.³⁵ This strengthens the interaction between the ions formed in $[C_4mim][PF_6]$, reducing its mobility. Moreover, intermolecular interaction has a significant impact on conductivity. Lovelock found that $[C_4mim][PF_6]$ has stronger electrostatic or Coulombic interactions (116 kJ/mol) and van der Waals (induction, dispersion, and hydrogen bonding) interactions (68 kJ/mol) than $[C_4mim][Tf_2N]$ (elec. = 78 kJ/mol; vdW = 50 kJ/mol).³⁶ Because of this intense interaction, the mobility of $[C_4mim][PF_6]$ is lower than that of $[C_4mim][Tf_2N]$, resulting in lower conductivity. Meantime, the addition of $[C_4mim][Tf_2N]$ into $[C_4mim][PF_6]$ increases the number of charge carriers while decreasing ion mobility. Despite the opposite effect, the rising conductivity trend of the binary ILs shown above indicates that the number of charge carriers is the dominant variable affecting conductivity rather than ion mobility. Furthermore, as shown in the Nyquist plot of $[C_4mim][PF_6]_{0.50}-[C_4mim][Tf_2N]_{0.50}$ at various temperatures (Fig.-1b) and Table-1, increasing temperature causes the resistance of the binary ILs to decrease, resulting in increased conductivity. It is expected behavior because increasing the temperature increases the kinetic energy of the molecules, which further

reduces cation-anion interactions of ILs. Weakening the interaction will reduce viscosity while increasing conductivity.³⁷

The plotting results ($\ln \sigma$) vs. ($1000/T$) obtained by the Arrhenius equation in Fig.-2 show that the change in conductivity is linear with temperature changes. This linearity is analogous to the findings of Jarosik *et al.* who investigated the temperature-dependent conductivity of ILs mixtures.³⁸ However, the curve gradient obtained at $[\text{C}_4\text{mim}][\text{PF}_6]_{0.50}-[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{0.50}$ is smaller than in the other compositions. These results indicate that the binary ILs with a mixing mole fraction of 0.5:0.5 perform better as an electrolyte when operated at low temperatures.

Table-1: The Conductivities (σ) of $[\text{C}_4\text{mim}][\text{PF}_6]_{(x)}-[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{(1-x)}$ at Various Temperatures

Mole fractions (x)	σ (mS/cm)				
	30 °C	35 °C	40 °C	45 °C	50 °C
1.00	2.12 ± 0.01	2.61 ± 0.02	3.21 ± 0.03	3.95 ± 0.04	4.79 ± 0.06
0.75	2.88 ± 0.01	3.51 ± 0.01	4.21 ± 0.01	5.05 ± 0.02	5.98 ± 0.03
0.50	3.88 ± 0.09	4.52 ± 0.05	5.22 ± 0.06	6.07 ± 0.12	6.94 ± 0.08
0.25	4.11 ± 0.02	4.93 ± 0.02	5.81 ± 0.02	6.79 ± 0.06	7.92 ± 0.06
0.00	4.75 ± 0.01	5.60 ± 0.03	6.60 ± 0.03	7.76 ± 0.03	8.91 ± 0.04

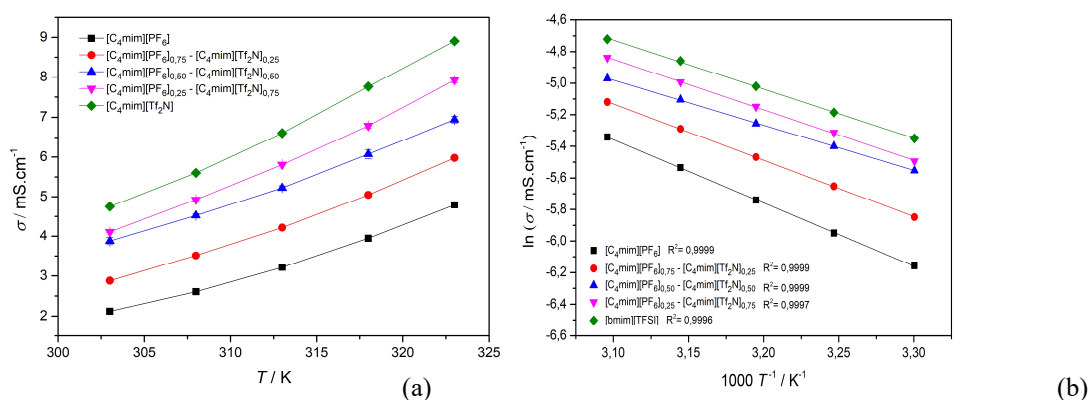


Fig.-2: The Conductivity Plots for (a) σ vs. T and (b) $\ln \sigma$ vs. T^{-1} of binary ILs by the Arrhenius Equation

This condition is also evident when each composition's conductivity activation energy ($E_{a\sigma}$) is compared. According to Table-2, the binary ILs $[\text{C}_4\text{mim}][\text{PF}_6]_{0.50}-[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{0.50}$ has the lowest $E_{a\sigma}$ compared to others, indicating that this composition requires the least energy in the ion conduction process. The cause and rationalization of this condition cannot be determined clearly because many other factors, such as ion size, charge delocalization, density, and specific aggregation, affect conductivity due to structural rearrangements.³⁹

Table-2: The Conductivity Coefficient (σ) and Conductivity Activation Energy ($E_{a\sigma}$) plots of $[\text{C}_4\text{mim}][\text{PF}_6]_{(x)}-[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{(1-x)}$ using the Arrhenius Equation

Mole fractions (x)	σ_0 (mS/cm)	Gradient	$E_{a\sigma}$ (kJ/mol)	R^2
1.00	7.06	4.00	33.30	0.9999
0.75	5.93	3.57	29.66	0.9999
0.50	3.88	2.86	23.76	0.9999
0.25	5.06	3.20	26.59	0.9997
0.00	4.89	3.10	25.80	0.9996

Diffusion and Electron Transfer Kinetics of Ferrocene in Binary ILs

The kinetics of diffusion and electron transfer were analyzed using the voltammogram obtained during the potential scanning process, as shown in Fig.-3(a-e). The overall voltammogram shows that increasing the scan rate (ν) results in a higher peak current (I_p). This result is because the diffusion layer becomes thinner as the scanning rate increases resulting in a larger current.²⁴

The diffusion coefficient (D) of ferrocene in binary ILs was calculated using the current response to variations in the applied scan rate. As shown in Fig.-3(f), plotting the peak current (I_p) against the root of the scan rate ($\nu^{1/2}$) yields a high linearity (R^2) of 0.9999 for I_{pa} and 0.9974 for I_{pc} . These results suggest mass

transfer from the binary ILs' bulk phase to the electrode surface via planar diffusion.⁴⁰ In this diffusion, molecules move perpendicular to all points normal to the surface of the electrode.⁴¹ The resulting diffusion pattern is influenced by the electrode size, typically at the macro electrode (mm).⁴² The gradient of the obtained curve is then applied to the Randles-Sevcik equation to calculate the D value. Based on the calculations, D of ferrocene in $[\text{C}_4\text{mim}][\text{PF}_6]$ and $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ are 0.33×10^{-6} and $1.6 \times 10^{-6} \text{ cm}^2/\text{s}$, respectively, at 30°C . This value is quite different from the results reported by other researchers, where D of ferrocene in $[\text{C}_4\text{mim}][\text{PF}_6]$ ⁴³ is $2.8 \times 10^{-8} \text{ cm}^2/\text{s}$ and in $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ ²⁷ is $1.7 \times 10^{-6} \text{ cm}^2/\text{s}$. This difference is possible because many factors affect the diffusion coefficient, such as concentration, impurities in solution, and especially the type and morphology of the electrodes used.^{42,44}

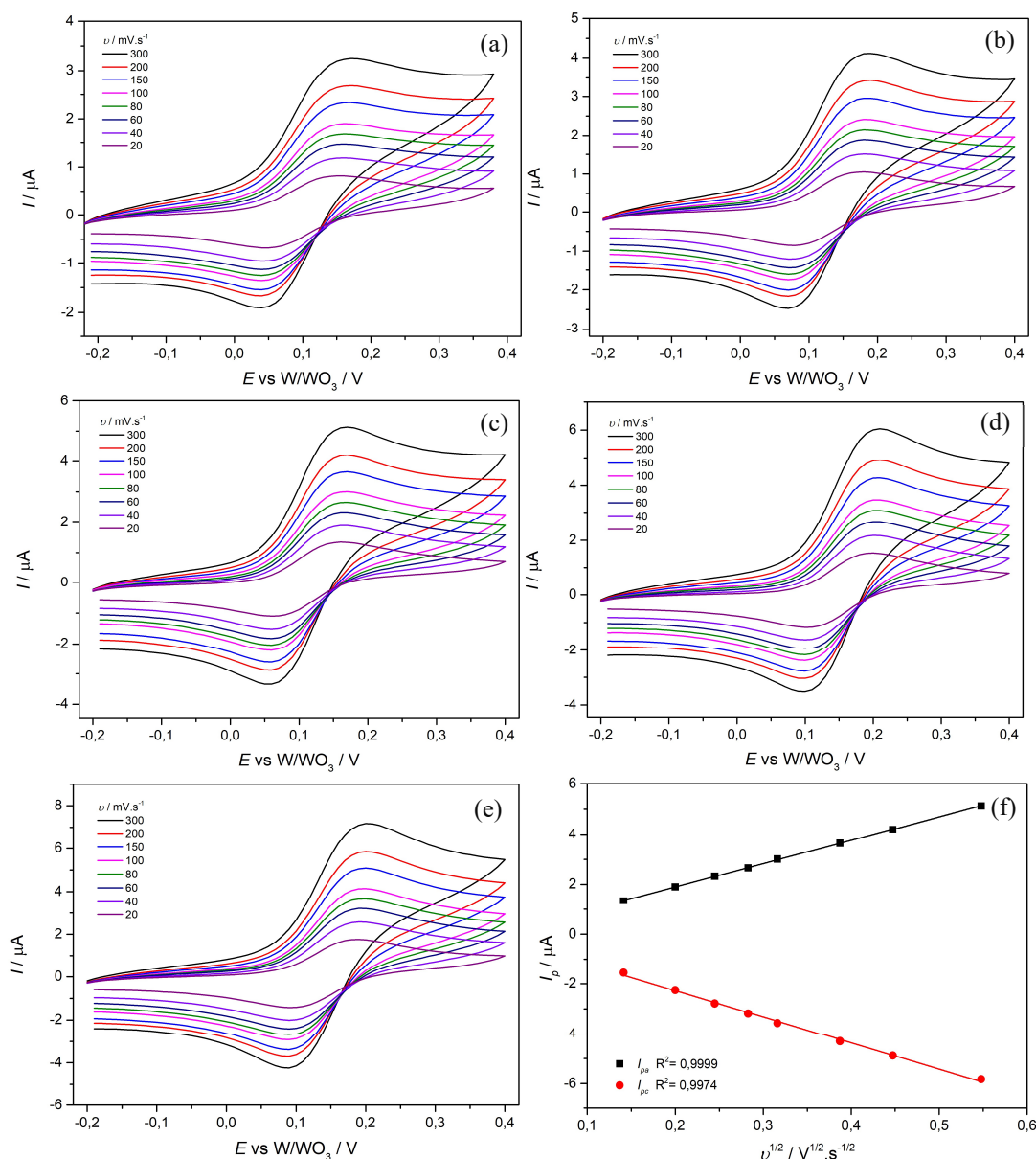


Fig.-3: Cyclic Voltammograms of Ferrocene in $[\text{C}_4\text{mim}][\text{PF}_6]_{(x)}-[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{(1-x)}$ with Various Mole Fractions (x): (a) 1.00 (b) 0.75 (c) 0.50 (d) 0.25 (e) 0.00 and (f) the Plots of Corresponding I_{pa} and I_{pc} of $[\text{C}_4\text{mim}][\text{PF}_6]_{0.50}-[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{0.50}$

According to these results, ferrocene diffuses more easily in $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ than $[\text{C}_4\text{mim}][\text{PF}_6]$. The addition of $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ to $[\text{C}_4\text{mim}][\text{PF}_6]$ increased diffusion in proportion to the mole fraction added. The values of D of ferrocene in order $[\text{C}_4\text{mim}][\text{PF}_6] < [\text{C}_4\text{mim}][\text{PF}_6]_{0.75}-[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{0.25} <$

$[\text{C}_4\text{mim}][\text{PF}_6]_{0.50}-[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{0.50} < [\text{C}_4\text{mim}][\text{PF}_6]_{0.25}-[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{0.75} < [\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ as fully presented in Table-3.

In general, this condition can be explained by the Stokes-Einstein equation:

$$D = \frac{RT}{N_A} \cdot \frac{1}{6\pi\eta a} \quad (10)$$

which describes the correlation between diffusion coefficient and viscosity.⁴⁵ The slower the molecular diffusion, the higher the solvent's viscosity. Based on the viscosity data obtained from the study of Almeida *et al.*⁴⁶ and the diffusion coefficient from this study (Table-3), it is evident that the two have a strong correlation, as plotted in Fig.-4(a). This reasonably good linearity ($R^2 = 0.99$) demonstrates that viscosity is the most crucial factor influencing ferrocene diffusion in binary ILs.

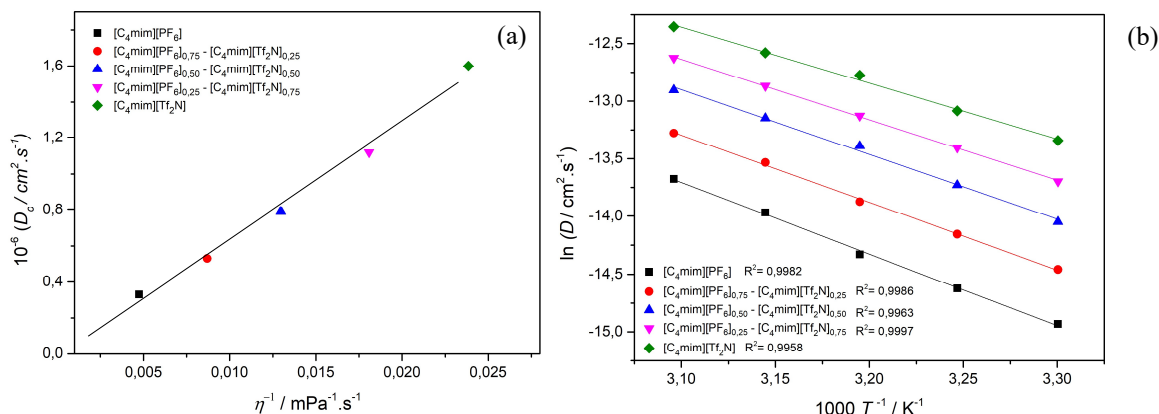


Fig.-4: The plots for (a) D vs. η^{-1} by the Stokes-Einstein Equation and (b) $\ln D$ vs. T^{-1} by the Arrhenius Equation of Ferrocene in a Binary ILs

Another factor that influences diffusion is the solute's molecular size.⁴⁷ When the ferrocene complex is oxidized from Fe^{2+} to Fe^{3+} , the size of the ionic radius of the iron central atom changes. Because Fe^{2+} has a larger ionic radius (83 pm) than Fe^{3+} (67 pm)⁴⁸, the diffusion of ferrocene during oxidation (D_o) is smaller than that during reduction (D_r). These observations are consistent with the data obtained, showing overall $D_o < D_r$ in Table-3.

Table-3: Diffusion coefficients (D) of ferrocene in $[\text{C}_4\text{mim}][\text{PF}_6]_{(x)}-[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{(1-x)}$ at 30 °C			
Mole fractions (x)	Viscosity (η) ⁴⁶ (mPa.s)	10 ⁻⁶ D (cm ² /s)	
		D_o	D_r
1.00	210.9	0.33	0.36
0.75	115.1	0.53	0.57
0.50	77.1	0.79	1.00
0.25	55.3	1.12	1.21
0.00	41.9	1.60	1.62

In addition, temperature variation has shown that the D of ferrocene increases with increasing temperature and follows the Arrhenius equation. The viscosity of ILs decreases as the temperature rises. Temperature increases kinetic energy while weakening intermolecular bonds. Weakening bonds facilitate and accelerate mass transfer or molecular movement, as shown by the increase in the diffusion coefficient in Fig.-4(b). Table-4 shows that ferrocene dissolved in $[\text{C}_4\text{mim}][\text{PF}_6]$ requires 51.37 and 50.82 kJ/mol energy to diffuse in the oxidation and reduction reactions, respectively. Because of the high viscosity of $[\text{C}_4\text{mim}][\text{PF}_6]$, ferrocene takes much energy to diffuse through it. In contrast, the lower viscosity of $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ allows ferrocene to diffuse more quickly, requiring only 40.42 and 42.15 kJ/mol for oxidation and reduction, respectively. The diffusion activation energy of the two ILs is in the range of the two, proportional to the number of mole fractions added in the order $[\text{C}_4\text{mim}][\text{PF}_6] < [\text{C}_4\text{mim}][\text{PF}_6]_{0.75}-[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{0.25} < [\text{C}_4\text{mim}][\text{PF}_6]_{0.50}-[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{0.50} < [\text{C}_4\text{mim}][\text{PF}_6]_{0.25}-[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{0.75} < [\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$.

Table-4: Diffusion Coefficients (D) and Activation Energies (E_{aD}) of Ferrocene in $[\text{C}_4\text{mim}][\text{PF}_6]_{(x)}-[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{(1-x)}$

			Mole fractions (x)				
			1.00	0.75	0.50	0.25	0.00
$10^{-6} D \text{ (cm}^2/\text{s)}$	30 °C	D_o	0.33	0.53	0.79	1.12	1.60
		D_r	0.36	0.57	1.00	1.21	1.62
	35 °C	D_o	0.45	0.71	1.09	1.51	2.08
		D_r	0.49	0.78	1.32	1.66	2.14
	40 °C	D_o	0.60	0.94	1.53	1.99	2.83
		D_r	0.65	1.02	1.83	2.13	2.95
	45 °C	D_o	0.86	1.32	1.95	2.58	3.44
		D_r	0.91	1.41	2.35	2.85	3.59
	50 °C	D_o	1.15	1.71	2.49	3.29	4.31
		D_r	1.27	1.78	3.06	3.62	4.57
$Ea_D \text{ (kJ/mol)}$		Ea_{D_o}	51.37	48.50	46.83	43.71	40.42
		Ea_{D_r}	50.82	46.59	45.88	44.61	42.15

Determined the Electron Transfer Rate Constants

The electron transfer rate constant (k_s) expresses how quickly electrons transfer in redox reactions. The k_s values of ferrocene in $[\text{C}_4\text{mim}][\text{PF}_6]$ and $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ are 0.79×10^{-3} and 1.82×10^{-3} cm/s, respectively, according to calculations performed using the Nicholson method (eq. 6 and 7). Meanwhile, mixing the two liquids obtains a k_s value in the range of the two, as shown in Table-5.

This result can be explained using the following equation:

$$\ln k_s = -\theta \ln \eta + c \quad (11)$$

Which relates the electron transfer rate constant to the solvent's viscosity (η).⁴⁹ According to the obtained linearity ($R^2 = 0.97$), viscosity is an essential factor influencing the k_s value. The high viscosity of $[\text{C}_4\text{mim}][\text{PF}_6]$ will slow the rate of ferrocene diffusion to the electrode, causing the ferrocene to lose/gain electrons longer. However, ferrocene dissolved in $[\text{C}_4\text{mim}][\text{PF}_6]_{0.50}-[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{0.50}$ showed a significant deviation. This result is made possible by rearranging the positions of the ILs when mixed, which affects the interactions that occur. According to Patah *et al.*,¹⁴ in addition to viscosity, the Coulombic interactions formed between the anions of the ILs and the electroactive species of the analyte affect the electron transfer rate constant. The greater the interaction strength, the greater the stability of electroactive species, making electron transfer in oxidation and reduction reactions more difficult and slower. The electron transfer rate constants and the viscosity of binary ILs are presented in Table-5, and their relationship is shown in Fig.-5(a).

Table-5: Electron Transfer Rate Constants (k_s) of Ferrocene in $[\text{C}_4\text{mim}][\text{PF}_6]_{(x)}-[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{(1-x)}$ at 30 °C

Mole fractions (x)	Viscosity (η) ⁴⁶ / mPa.s	$10^{-3} k_s$ / cm/s
1.00	210.9	0.79
0.75	115.1	1.01
0.50	77.1	1.14
0.25	55.3	1.48
0.00	41.9	1.82

Furthermore, temperature variations on measurements have revealed that the electron transfer rate constant depends on temperature changes. Table-6 shows that the k_s value of ferrocene in the binary ILs increases as the temperature rises. This result is due to the decrease in viscosity and the weakening of the interactions that occur as temperature increases. As a result, the electroactive species of ferrocene and ferrocenium lose or gain electrons more easily. The linearity obtained from the plot $\ln k_s$ vs. T^{-1} in Fig.-5(b) using the Arrhenius equation provides an overview of the activation energy value required in the electron transfer process ($E_{a_{ks}}$). The $E_{a_{ks}}$ of ferrocene in $[\text{C}_4\text{mim}][\text{PF}_6]$ and $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ are 24.77 and 18.08 kJ/mol, respectively, based on the calculation results. Meanwhile, $E_{a_{ks}}$ of ferrocene in binary ILs are in the range of $[\text{C}_4\text{mim}][\text{PF}_6] < [\text{C}_4\text{mim}][\text{PF}_6]_{0.75}-[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{0.25} < [\text{C}_4\text{mim}][\text{PF}_6]_{0.50}-[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{0.50} < [\text{C}_4\text{mim}][\text{PF}_6]_{0.25}-[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{0.75} < [\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$.

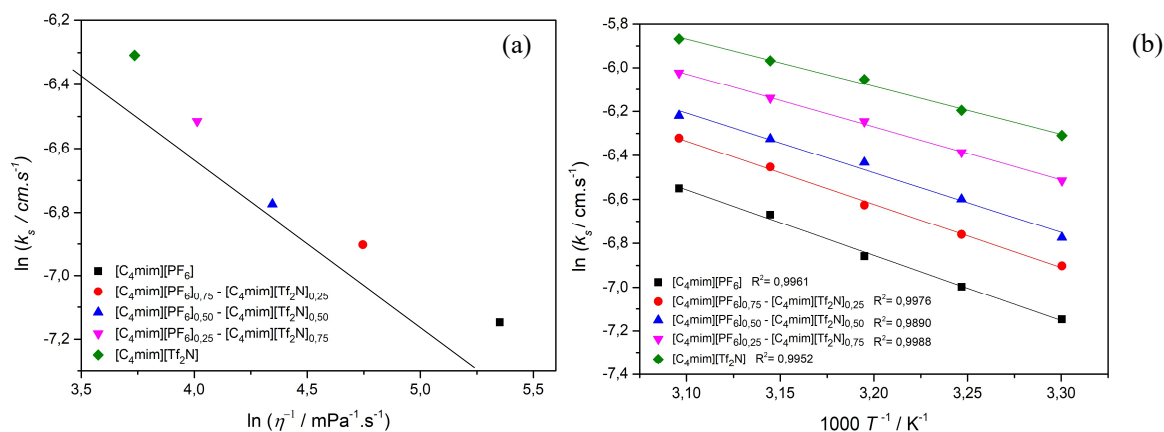


Fig.-5: The Plots for (a) $\ln k_s$ vs. $\ln \eta^{-1}$ and (b) $\ln k_s$ vs. T^{-1} by the Arrhenius Equation of Ferrocene in a Binary ILs

Table-6: Electron Transfer Rate Constants (k_s) and Activation Energies ($E_{a_{ks}}$) of Ferrocene in $[\text{C}_4\text{mim}][\text{PF}_6]_{(x)} - [\text{C}_4\text{mim}][\text{TF}_2\text{N}]_{(1-x)}$ at Various Temperatures

Mole fractions (x)	$10^{-3} k_s$ (cm/s)					$E_{a_{ks}}$ (kJ/mol)
	30 °C	35 °C	40 °C	45 °C	50 °C	
1.00	0.79	0.92	1.05	1.27	1.43	24.77
0.75	1.01	1.16	1.33	1.58	1.80	23.90
0.50	1.14	1.36	1.61	1.79	1.99	22.59
0.25	1.48	1.69	1.94	2.16	2.42	20.03
0.00	1.82	2.04	2.35	2.56	2.83	18.08

This result is consistent with the prediction that a solvent or ILs with a higher viscosity will require more energy to allow the dissolved species to transfer electrons. Conversely, the low viscosity of ILs will facilitate electron transfer, requiring less energy for the reaction. The energy needed to initiate the electron transfer process is presented in Table-6.

CONCLUSION

The presence of ILs mixing $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ on $[\text{C}_4\text{mim}][\text{PF}_6]$ was able to increase the ionic conductivity, diffusion coefficient, and electron transfer rate constant of ferrocene. However, it was in the range of pure ILs in the order $[\text{C}_4\text{mim}][\text{PF}_6] < [\text{C}_4\text{mim}][\text{PF}_6]_{0.75} - [\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{0.25} < [\text{C}_4\text{mim}][\text{PF}_6]_{0.50} - [\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{0.50} < [\text{C}_4\text{mim}][\text{PF}_6]_{0.25} - [\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{0.75} < [\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$. Furthermore, temperature variations showed that changes in conductivity values, diffusion coefficients, and electron transfer rate constants were proportional to temperature changes, according to the Arrhenius equation. Based on the diffusion activation energy (E_{a_D}) and the slight decrease in conductivity with temperature, the ILs $[\text{C}_4\text{mim}][\text{PF}_6]_{0.50} - [\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{0.50}$ is a superior electrolyte candidate for low-temperature operation.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge all participants in this study, the Department of Chemistry, Institut Teknologi Bandung, and the financial support of The Indonesia Endowment Funds for Education (LPDP), Ministry of Finance. AP and IM thanks to P2MI 2022 Program, FMIPA-ITB.

CONFLICT OF INTERESTS

The authors declare no conflict of interest in publishing this paper.

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