

Determination of Viscosity, Ionic Conductivity, and Diffusion Coefficients in Some Binary Systems: Ionic Liquids + Molecular Solvents

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Experimental data for viscosities, diffusion coefficients of ferrocene, and conductivities were obtained for three ionic liquid mixtures: 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF₄), *N*-methyl-*N*-butylpyrrolidinium bis(trifluoromethylsulfonyl)imide (bmpyNTf₂), and *N*-methyl-*N*-hexylpyrrolidinium bis(trifluoromethylsulfonyl)imide (hmpyNTf₂) + dimethylformamide (DMF) or + 3-picoline as cosolvents, in the range of temperature $T = (295.2 \text{ to } 325.2) \text{ K}$. At a given temperature, the viscosity decreases exponentially with the mole fraction of the added cosolvent, and the variation of the diffusion coefficient agrees with the Stokes–Einstein law. Concerning the conductivity, addition of the polar solvent dimethylformamide produces an increase much greater than the addition of 3-picoline. The viscosity, diffusion coefficient, and conductivity follow the Arrhenius model in the explored temperature range. Consequently, moderate heating and addition of a cosolvent are two good means for obtaining conditions well adapted to electrosynthetic applications in ionic liquids.

Introduction

Modern organic chemistry seeks efficient and cheap synthetic procedures as well as environmentally benign experimental conditions. That is the reason the interest in the properties of room temperature ionic liquids (ILs) has been rapidly expanding in recent years. Indeed, it has been already demonstrated that a wide range of organic syntheses, including catalyzed reactions, can be carried out in these alternative nonflammable solvents, which are attractive for their easy access, thermal stability, and low vapor pressure. Besides, they often allow simple product recovery and solvent recycling.^{1–3}

In this context of eco-friendly procedures, electrosynthesis remains an attractive method since the use of electrons as a reagent does not involve the formation of any side product. So, regarding electrochemical processes, ILs appear at first sight to be convenient solvents since their ionic structure should afford a good conductivity without addition of a supporting electrolyte.

This explains why ILs have recently received increasing attention for their use in organic electrochemistry.^{4,5} As for us, we reported that various electroreductive couplings involving organic halides can be efficiently achieved in ILs either directly or by nickel-complex-mediated electrosyntheses.⁶ Electrolyses were conducted in a diaphragm-less cell by setting a constant current intensity. During this work, we noticed that pure ILs were not perfectly adapted to preparative scale electrosyntheses since a current density exceeding a few mA·cm⁻² resulted in a very high cell voltage (> 40 V). This drawback was overcome either by heating the solution to $T = (313 \text{ to } 323) \text{ K}$ or by adding a small amount of a molecular cosolvent (cs) such as volume fraction of dimethylformamide (DMF) (5 to 10) % or, even better, by combining these two means.

The important ohmic drop inducing the high cell voltage in pure IL may arise from a slow diffusion of electroactive species and/or a low ionic conductivity. These two features can be due

to a high viscosity for the medium. For the conductivity, poor ionic dissociation of the IL can also be involved. Many papers have already been devoted to the determination of physical properties of binary IL/molecular solvent systems (water, alcohols, and various organic solvents). They show that addition of a cosolvent produces a decrease in viscosity and an increase in conductivity.^{7–18}

Therefore, we have thought it advisable to acquire physico-chemical data in mixtures involving an IL and a molecular organic solvent. Actually, the knowledge of such properties seemed to us that it would provide a valuable means to find aprotic media well-adapted for organic electrosynthesis. This explains the choice of the binary systems used in the present work. Imidazolium or pyrrolidinium salts are ILs that present a large electrochemical window.^{14,19} In organic electrochemistry, dimethylformamide (DMF) is a polar aprotic solvent used in electroreductive processes and 3-picoline can act simultaneously as aprotic cosolvent and ligand for transition metal.

Experimental Section

Synthesis of Ionic Liquids. All chemicals were used as received, and ILs were prepared according to reported procedures.²⁰ *N*-Methylpyrrolidine or methylimidazole yield the corresponding ammonium salt by reaction with an alkyl bromide (1-butylbromide or 1-hexylbromide). Anions bromide (Br⁻) were replaced by tetrafluoroborate (BF₄⁻) or bis(trifluoromethylsulfonyl)imide (NTf₂⁻) by vigorous stirring of the alkylammonium bromide with aqueous solutions of sodium tetrafluoroborate (NaBF₄) or lithium bis(trifluoromethylsulfonyl)imide (LiNTf₂), respectively. ILs were washed with distilled water until no bromide traces were detected by addition of silver nitrate (AgNO₃) and then dried overnight at $T = 353 \text{ K}$ under vacuum. ¹H and ¹³C NMR spectra of ILs were recorded with a Bruker Avance 300 MHz and found to be in agreement with literature.^{21,22} Water content in each IL was determined by Karl Fischer titration. It did not exceed 10⁻² mole fraction.

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Chart 1. Ionic Liquids Studied in This Work

cation	anion	acronym
	BF_4^-	bmimBF ₄
	$\text{N}(\text{CF}_3\text{SO}_2)_2$	bmppyNTf ₂
$\text{R} = \text{n-C}_4\text{H}_9$ $\text{n-C}_6\text{H}_{13}$		hmpyNTf ₂

Table 1. Viscosity (η) of bmimBF₄ (1), bmppyNTf₂ (2), and hmpyNTf₂ (3) + DMF (4) Mixtures at $T = 295.2$ K with Standard Deviation ($s(\eta)$)

(1) + (4)		(2) + (4)		(3) + (4)	
x_4	$\eta/\text{mPa}\cdot\text{s}$	x_4	$\eta/\text{mPa}\cdot\text{s}$	x_4	$\eta/\text{mPa}\cdot\text{s}$
0.00	122.9	0.00	80.0	0.00	119.8
0.14	65.6	0.13	40.3	0.10	83.0
0.23	45.4	0.24	29.6	0.21	56.7
0.33	26.3	0.33	21.7	0.30	42.9
0.44	16.1	0.45	14.4	0.40	28.1
0.53	11.2	0.54	9.9	0.50	19.6
0.61	9.8	0.64	6.6	0.60	12.0
0.73	4.7	0.74	3.7	0.70	5.5
		$s(\eta)/\text{mPa}\cdot\text{s}$			
	0.68	1.03			2.31

Electrochemical and Physical Methods. Diffusion coefficients were obtained by classical electrochemical methods using a ParStat 2253 (Princeton Applied Research) with PowerSuite software, in a 20 cm³ homemade three electrode cell. The reference, working, and counter electrodes consisted respectively of a silver wire (pseudo-reference), a gold disk (≈ 0.5 mm diameter), and a gold wire. The effective working electrode area was determined from the reversible one-electron oxidation of ferrocene 1 mmol·L⁻¹ in DMF + NBu₄BF₄ 0.1 mol·L⁻¹ at $T = 298.2$ K and using the Cottrell law (eq 1):

$$I = nFAD^{1/2}C/(\pi t)^{1/2} \quad (1)$$

where I is the current intensity, n is the amount of electrons, A is the electrode area, D is the diffusion coefficient (taken as 1.07×10^{-5} cm²·s⁻¹ at 298.2 K),²³ C is the bulk concentration of the diffusing species, and t is the time. Since characteristics of the electrode are known to be independent of temperature for the temperature range of the measurements, calibration of the electrode area was done at only one temperature. The diffusion coefficient of ferrocene (D_{Fc}) was then measured in ILs, pure or mixed with DMF for $[\text{Fc}] = 3 \times 10^{-2}$ mol·L⁻¹, either by chronoamperometry using eq 1 or by cyclic voltametry and use of the Randle-Sevcik equation (eq 2):

$$I_p = 0.4463nF(nF/RT)^{1/2}AD^{1/2}C\nu^{1/2} \quad (2)$$

where I_p is the peak intensity and ν is the scan rate. Plotting I_p versus $\nu^{1/2}$ gives a linear function with a slope proportional to $D^{1/2}$ and with standard deviation $s(I_p) \leq 0.035 \mu\text{A}$ (typical peak current was in the range $I_p = (2 \text{ to } 35) \mu\text{A}$). In a first series of experiments, results obtained by potentiostatic or potentiodynamic method were well-concordant. Therefore, diffusion coefficients were determined only by cyclic voltametry.

Values of the viscosity were obtained using an AR 1000 (TA Instruments) rheometer equipped with a Peltier plate temperature controller (temperature uncertainty ± 0.1 K) and a 60 mm diameter aluminum cone. The 992, 97.5, and 9.4 mPa·s oils (from Brookfield Engineering Laboratories) were used as standards at $T = 298.2$ K since characteristics of the rheometer are known to be independent of temperature.

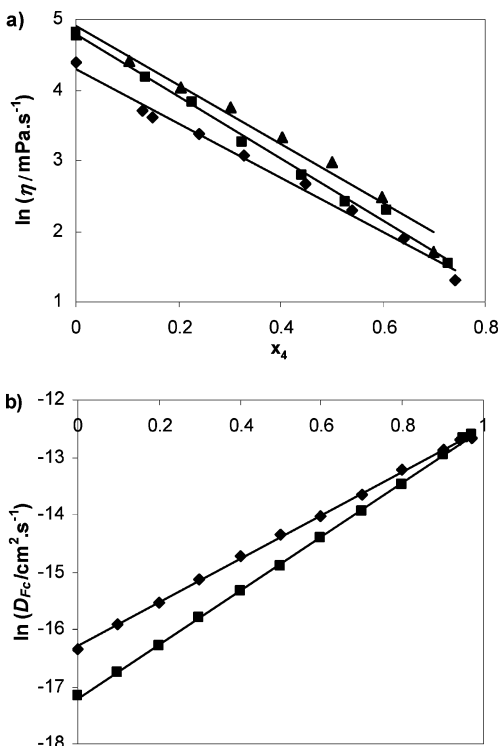


Figure 1. Logarithm of viscosity (η) (a) and logarithm of ferrocene diffusion coefficient (D_{Fc}) (b) in \blacksquare , bmimBF₄ (1); \blacklozenge , bmppyNTf₂ (2); \blacktriangle , hmpyNTf₂ (3) as a function of DMF (4) mole fraction. $T = 295.2$ K.

Conductimetry measurements were carried out with a Radiometer CDM 210 Meterlab conductimeter with a CDC 745-9 cell calibrated with a 0.1 mol·L⁻¹ aqueous KCl solution (12.88 mS·cm⁻¹ at $T = 293.2$ K). We have not considered the possibility of variation of the calibration with temperature.

Relative uncertainties were calculated to be $\pm 5\%$ for diffusion coefficients; $\pm 1\%$ for viscosities, and $\pm 0.2\%$ for conductivities. For all experiments, temperature was controlled at ± 0.1 K. Uncertainties presented for activation energies were calculated from the slope given by the linear regression with a confidence interval of 95%. Standard deviations were calculated according to classical methods.

Results and Discussion

The three imidazolium or pyrrolidinium salts presented in Chart 1 were chosen as model ILs for this study since they are convenient media for both cathodic and anodic electrochemical applications. We first measured the viscosity η for various amount of DMF (4) in each IL (Table 1). Figure 1a shows that the viscosity of IL + DMF mixtures decreases exponentially when the mole fraction (x) of (4) increases ($0 \leq x \leq 0.7$), according to the empirical equation (eq 3):

$$\ln \eta = \ln \eta_{\text{IL}} + Ax_4 \quad (3)$$

where η_{IL} is the viscosity of the pure IL and A is a constant. This behavior agrees with previous studies of various IL or inorganic salt/molecular solvent binary systems, which mention similar empirical results.^{8,9,13,24,25} Our results and literature data for η_{IL} and constant A are presented in Table 2. In most cases our results are in agreement with previous reported values. However, some literature data present large differences. The purity of IL (traces either of water or starting materials ...) is perhaps partly responsible for these differences.

Diffusion coefficient of ferrocene (D_{Fc}), which is usually chosen as a model of electroactive species in numerous solvents including ILs,²⁷⁻²⁸ was determined in bmimBF₄ (1) and bmppy-

Table 2. Comparison of the Experimental Viscosity of Pure IL (η_{IL}) and Constant A (see eq 3) with Literature for bmimBF₄ (1), bmpyNTf₂ (2), and hmpyNTf₂ (3) + DMF (4) Binary Systems

system	T/K	$\eta_{\text{IL}}/\text{mPa}\cdot\text{s}$		A	
		lit	exptl	lit	exptl
(1) + (4)	293	112, ^a 154 ^b		4.35 ^b	
	295.2		122.9		4.38 ± 0.32
	298	110.3, ^c 180 ^d		4.63 ^c	
(2) + (4)	295.2		80.0		3.86 ± 0.33
	298	76, ^d 70, ^e 85 ^f			
(3) + (4)	295.2		119.8		4.18 ± 0.60

^a Ref 31. ^b Ref 8. ^c Ref 9. ^d Ref 14. ^e Ref 26. ^f Ref 19.

Table 3. Ferrocene Diffusion Coefficient (D_{Fc}) in bmimBF₄ (1) or bmpyNTf₂ (2) + DMF (4) Mixtures at $T = 295.2$ K with Standard Deviation $s(D_{\text{Fc}})$

(1) + (4)		(2) + (4)	
x_4	$10^6 D_{\text{Fc}}/\text{cm}^2\cdot\text{s}^{-1}$	x_4	$10^6 D_{\text{Fc}}/\text{cm}^2\cdot\text{s}^{-1}$
0.00	0.04	0.00	0.08
0.10	0.05	0.10	0.12
0.20	0.08	0.20	0.18
0.30	0.14	0.30	0.27
0.40	0.22	0.40	0.40
0.50	0.34	0.50	0.59
0.60	0.56	0.60	0.81
0.70	0.88	0.70	1.20
0.80	1.40	0.80	1.80
0.90	2.40	0.90	2.60
0.95	3.20	0.94	3.00
0.97	3.40	0.97	3.10

$$s(D_{\text{Fc}})/\text{cm}^2\cdot\text{s}^{-1} \quad 5.8 \times 10^{-8} \quad 5.0 \times 10^{-8}$$

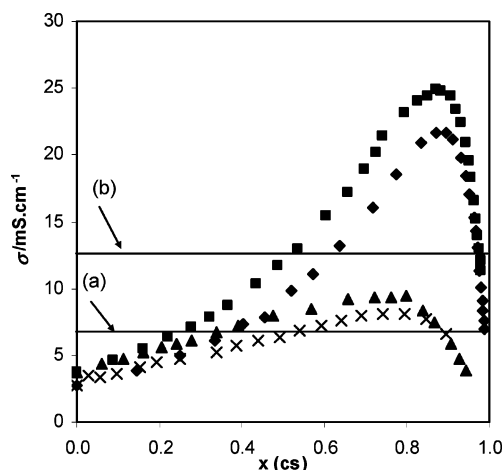
NTf₂ (2) + DMF (4) mixtures (Table 3). Figure 1b shows that the diffusion coefficient of ferrocene (D_{Fc}) increases exponentially when the mole fraction of DMF was increased in the IL + DMF mixture. Values of the diffusion coefficient in pure ILs agrees with literature.²⁸ The exponential increase of viscosity along with the exponential decrease of the diffusion coefficient versus the DMF mole fraction indicates that the diffusion of ferrocene follows the classical Stokes–Einstein equation (eq 4):

$$D = \frac{kT}{c\pi\eta r} \quad (4)$$

where k is Boltzmann's constant, r is the effective radius of the diffusing species, and c is a constant. It can be noted that, in pure ILs at room temperature, D_{Fc} is about 2 to 3 orders of magnitude lower than in common molecular solvents. This may explain why only low current densities can be obtained for electrolyses in pure ILs.

These results allow us to suggest the following conclusions. First, provided that respective viscosities of the IL and cosolvent are known (at the same temperature), the viscosity of any mixture of the two compounds can be estimated from eq 3. Second, when the diffusion coefficient of a species has been measured, either in one or the other pure liquid or in a mixture of them, approximate values in other IL + cosolvent mixtures can be easily calculated by using eq 4.

The ionic conductivity (σ) is another parameter that has a large influence on the ohmic drop observed during electrolyses. Therefore, we have investigated the variation in the conductivity of cosolvent + ILs mixtures. Table 4 and Figure 2 present results obtained with either DMF (4) or 3-picoline (5), which are both fully miscible with the three ILs employed. For low to moderate mole fraction of cosolvent (0 to 0.4), the behavior is almost the

**Figure 2.** Conductivity (σ) of IL vs mole fraction of cosolvent (cs), $T = 295.2$ K. ■, bmimBF₄ (1) + DMF (4); ▲, bmimBF₄ (1) + 3-picoline (5); ◆, bmpyNTf₂ (2) + DMF (4); ×, bmpyNTf₂ (2) + 3-picoline (5). (a) Bu₄-NBr 0.2 mol·L⁻¹ in DMF (4); (b) KCl 0.1 mol·L⁻¹ in water.**Table 4. Conductivities (σ) of bmimBF₄ (1) or bmpyNTf₂ (2) Mixtures with DMF (4) or 3-Picoline (5) at $T = 295.2$ K**

(1) + (4)		(1) + (5)		(2) + (4)		(2) + (5)	
x_4	σ mS·cm ⁻¹	x_5	σ mS·cm ⁻¹	x_4	σ mS·cm ⁻¹	x_5	σ mS·cm ⁻¹
0.000	3.75	0.000	3.78	0.000	2.80	0.000	2.80
0.088	4.64	0.061	4.40	0.144	3.87	0.029	3.53
0.161	5.51	0.114	4.76	0.252	4.95	0.057	3.35
0.224	6.29	0.162	5.20	0.336	6.12	0.095	3.67
0.324	7.90	0.205	5.55	0.403	7.40	0.153	4.16
0.366	8.71	0.244	5.88	0.457	7.80	0.194	4.45
0.434	10.33	0.279	6.16	0.519	9.81	0.249	4.67
0.490	11.69	0.340	6.74	0.574	11.05	0.338	5.22
0.535	12.96	0.392	7.20	0.637	13.17	0.387	5.78
0.606	15.49	0.474	8.02	0.716	16.01	0.439	6.06
0.658	17.24	0.568	8.45	0.773	18.49	0.490	6.35
0.728	20.11	0.659	9.15	0.835	20.95	0.540	6.86
0.793	23.15	0.721	9.28	0.871	21.65	0.591	7.26
0.828	24.03	0.763	9.36	0.894	21.70	0.640	7.61
0.852	24.37	0.798	9.40	0.910	21.20	0.691	7.93
0.906	24.36	0.838	8.38	0.931	19.83	0.743	8.14
0.957	18.27	0.866	7.47	0.953	17.04	0.794	8.08
0.973	13.92	0.906	5.90	0.971	13.12	0.845	7.71
0.981	11.28	0.928	4.74	0.981	10.10	0.896	6.65

same with one or the other cosolvent; the conductivity seems to be mainly dependent on the viscosity of the medium. A difference appeared between DMF and 3-picoline for supplementary additions. With the polar solvent DMF, very high values of conductivity were obtained when the mole fraction of DMF reached values between 0.75 and 0.9 (mass fraction = (55 to 70) %). We can remark that these mixtures have valuable properties for electrochemical applications since their conductivity reaches values higher than those obtained in DMF with concentrated electrolytes.²⁹ On the other hand, the increase in conductivity was more moderate with a less polar solvent like 3-picoline. Since variations of viscosity are not very dependent on the choice of added cosolvent,^{8,9} this cannot explain these different behaviors. Then, as already reported for ILs or other highly concentrated electrolytes,^{14,29,30} we assume that in a pure IL or in mixtures of an IL with a solvent of low dielectric constant, ionic associations play a significant role so leading to low or only moderate values of ionic conductivity. In exchange, the dissociation of ions pairs will be considerably enhanced in the presence of a polar solvent. In this way, the addition of DMF to an IL produces simultaneously a decrease of viscosity and an increase in the amount of charge carriers so yielding high levels of conductivity.

Table 5. Viscosities (η) of hmpyNTf₂ (3) Mixtures with DMF (4) from $T = 295.2$ K to 325.2 K and Calculated Activation Energy (E_a) with Standard Deviation ($s(\eta)$) for Viscosity

x_4	$\eta/\text{mPa}\cdot\text{s}$							Arrhenius plot	
	$T = 295.2$ K	$T = 300.2$ K	$T = 305.2$ K	$T = 310.2$ K	$T = 315.2$ K	$T = 320.2$ K	$T = 325.2$ K	$E_a/\text{kJ}\cdot\text{mol}^{-1}$	$s(\eta)/\text{mPa}\cdot\text{s}$
0.000	119.8	96.8	79.6	64.8	54.2	45.9	38.9	30.0 ± 0.8	0.25
0.104	83.0	67.5	55.8	45.9	38.0	32.4	27.6	29.4 ± 0.7	0.14
0.205	56.7	47.2	39.8	33.6	28.8	24.8	21.8	25.6 ± 0.7	0.12
0.301	42.9	36.4	30.8	26.3	22.6	19.5	16.9	24.8 ± 0.1	0.02
0.402	28.1	24.0	20.9	17.9	15.7	13.9	12.0	22.4 ± 0.6	0.04
0.500	19.6	17.0	14.7	13.0	11.4	10.0	9.1	20.6 ± 0.7	0.04
0.599	12.0	10.5	9.3	8.4	7.5	6.8	6.2	17.5 ± 0.7	0.03
0.700	5.5	5.1	4.7	4.3	3.9	3.6	3.4	13.3 ± 0.8	0.02

Table 6. Temperature Dependence of Conductivities (σ) of HmpyNTf₂ (3) Mixtures with DMF (4) and Calculated Activation Energy (E_a) with Standard Deviation for Conductivity ($s(\sigma)$)

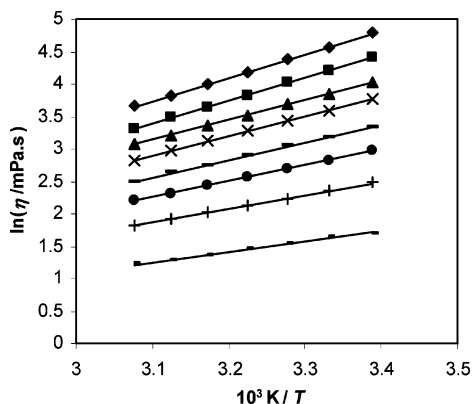
T/K	$\sigma/\text{mS}\cdot\text{cm}^{-1}$		
	$x_4 = 0.1$	$x_4 = 0.5$	$x_4 = 0.9$
293.2	1.55	3.82	16.82
295.2	1.70	4.18	17.40
298.2	1.91	4.70	18.23
301.2	2.11	5.22	19.04
303.2	2.24	5.57	19.58
305.2	2.39	5.92	20.15
308.2	2.60	6.45	21.01
311.2	2.80	6.97	21.87
313.2	2.95	7.32	22.43
315.2	3.10	7.67	23.05
318.2	3.30	8.19	23.93
321.2	3.51	8.71	24.80
323.2	3.65	9.10	25.44
$E_a/\text{kJ}\cdot\text{mol}^{-1}$	22.1 ± 1.3	22.4 ± 1.4	10.8 ± 0.1
$s(\sigma)/\text{mS}\cdot\text{cm}^{-1}$	0.02	0.05	0.01

The various parameters (η , D_{Fc} , σ) investigated in this work are obviously also dependent on temperature. For this purpose, the viscosity and the ionic conductivity of several ILs + cosolvent mixtures were measured in the range of temperature (295.2 to 328.2) K. Results obtained for the binary system hmpyNTf₂ + DMF are presented in Table 5 and Figure 3. They show that, for all mixtures, the viscosity depends on temperature according to the classical Andrade equation analogous to the Arrhenius law (eq 5):

$$\eta = \eta^\circ \exp\left[\frac{E_a}{RT}\right] \quad (5)$$

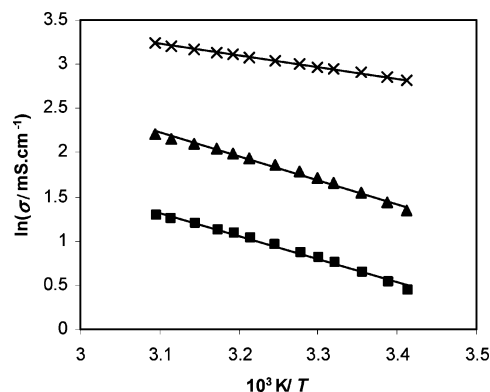
where η° is a constant and E_a is the activation energy.

From these Arrhenius plots, values of activation energy corresponding to various mixtures hmpyNTf₂ + DMF were calculated and given in Table 5. The E_a value found for pure

**Figure 3.** Arrhenius plots for viscosity (η) in hmpyNTf₂ (3) pure or added with DMF (4). \blacklozenge , $x_4 = 0$; \blacksquare , $x_4 = 0.1$; \blacktriangle , $x_4 = 0.2$; \times , $x_4 = 0.3$; $-$, $x_4 = 0.4$; \bullet , $x_4 = 0.5$; $+$, $x_4 = 0.6$; $-$, $x_4 = 0.7$.**Table 7. Temperature Dependence of Ferrocene Diffusion Coefficient (D_{Fc}) in hmpyNTf₂ (3) + DMF (4) ($x_4 = 0.1$) and Calculated Activation Energy (E_a) with Standard Deviation for Ferrocene Diffusion Coefficient ($s(D_{\text{Fc}})$)**

T/K	$10^6 D_{\text{Fc}}/\text{cm}^2\cdot\text{s}^{-1}$
295.15	0.073
300.15	0.098
304.15	0.12
309.15	0.13
316.15	0.18
321.15	0.20
326.15	0.24
$E_a/\text{kJ}\cdot\text{mol}^{-1}$	29.4 ± 4.2
$s(D_{\text{Fc}})/\text{cm}^2\cdot\text{s}^{-1}$	2.7×10^{-9}

hmpyNTf₂ agrees well with previous data collected for pure ILs such as pyrrolidinium or imidazolium salts.³¹ As expected, heating of the IL or its mixture with a cosolvent results in an increase in conductivity. Some examples presented in Table 6 and Figure 4 show that Arrhenius dependence applies also to the conductivity. Finally, the diffusion coefficient of ferrocene was measured in the range (295.2 to 325.2) K in hmpyNTf₂ containing a mole fraction of 10 % DMF. Plotting D_{Fc} as a function of T^{-1} (Table 7, Figure 5) indicates once more a quite good fit with the Arrhenius model. The experimental results obtained for the variation of D_{Fc} with temperature agree well with variations calculated from the Stokes–Einstein equation (eq 4) using our experimental values of viscosity. Activation energies for different mole fraction of DMF are given in Tables 5, 6, and 7 for viscosity, conductivity, and ferrocene diffusion coefficient. Therefore, when starting from a pure IL, either addition of a cosolvent or increase of temperature produces significant modifications of viscosity and, consequently, of conductivity and diffusion coefficient of a solute. We thought interesting to attempt to have a general view on what will be obtained by combining both effects. This can be illustrated by a three-dimensional graph, and one example is presented in Figure 6. The gray surface represents the envelope of the two series of curves (full lines), which were obtained from data given in this paper by plotting the viscosity either as a function of

**Figure 4.** Arrhenius plots for conductivity (σ) in hmpyNTf₂ (3) + DMF (4). \blacksquare , $x_4 = 0.1$; \blacktriangle , $x_4 = 0.5$; \times , $x_4 = 0.9$.

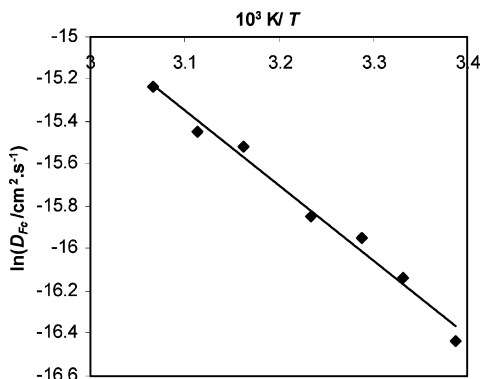


Figure 5. Arrhenius plot for ferrocene diffusion coefficient (D_{Fc}) in hmpyNTf₂ (3) + DMF (4). $x_4 = 0.1$.

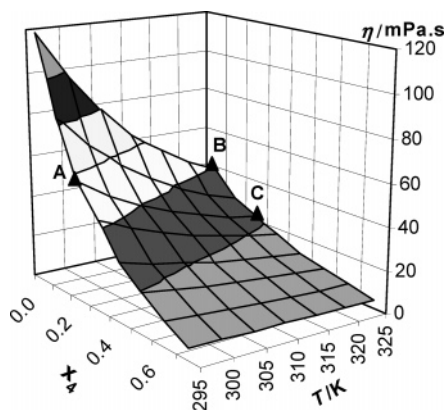


Figure 6. Composition (x_4) and temperature (T) dependence of viscosity (η) in hmpyNTf₂ (3) + DMF (4) mixtures from $x_4 = (0 \text{ to } 0.7)$ and $T = (295 \text{ to } 325)$ K.

mole fraction of DMF at various temperatures or as a function of temperature for various mixtures IL + DMF. For instance, the viscosity of pure hmpyNTf₂ at room temperature (≈ 120 mPa·s) can be approximately divided by two when adding a mole fraction of 20 % DMF (Figure 6, mark A) or by three when heating the IL up to 325.2 K (Figure 6, mark B) or even divided almost by six when combining both actions (Figure 6, mark C).

Conclusion

In conclusion, the pure ILs employed at room temperature are not quite suitable solvents for electrochemical purposes. Their high viscosity and moderate conductivity are strong limitations preventing an easy mass transfer of charge carriers and of electroactive species that produce high ohmic drop even for moderate current densities. The heating of solutions affords significant improvements by decreasing the viscosity. However, this mean may be unsuitable when chemicals or devices are poorly heat-resistant, for instance when using a cell divided by an ion exchanger diaphragm. Another means to obtain well-adapted electrolytic media is then the addition of a cosolvent. In considering the access to less viscous media, only the viscosity and the ratio of the cosolvent are determinant factors. For this purpose, the selection is very large, provided that the cosolvent is miscible in the IL, chemically compatible with the aimed electrochemistry, and also well-suited for economical and environmental aspects. Concerning an increase in the ionic conductivity, better results will be obtained when the cosolvent is chosen among the polar ones. Moreover, combining both effects of temperature and cosolvent provides a large range of possibilities in order to obtain experimental conditions which

are very appropriate to perform within organic electrochemistry and which would not present processing problems.

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