

New integrated measurement protocol using capillary electrophoresis instrumentation for the determination of viscosity, conductivity and absorbance of ionic liquid–molecular solvent mixtures

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Abstract

The low vapor pressure and the versatility of the physico-chemical properties of ionic liquids make them really attractive as an alternative for conventional molecular solvents. The knowledge of their physico-chemical properties (viscosity, conductivity, miscibility with organic solvents and anion–cation interactions) has appeared mandatory for better targeting their applications, although it is generally still lacking or incomplete.

This work promotes capillary electrophoresis instrumentation as an integrated apparatus for measurement of viscosity, conductivity and absorbance of pure ionic liquids and ionic liquid–molecular solvent mixtures. Compared to current conventional techniques, the assets of this instrumentation for this purpose are the combined availability of a pressure delivery system, power supply, diode array absorbance detector and thermoregulation device, allowing unattended, automatic and easy operation, involving minimum sample handling. Most importantly, the required sample volume can be reduced to about 50 μL , making this protocol very cost-effective. A protocol was optimized with respect to time, sample consumption and data reliability for the determination of these physico-chemical parameters. Ionic liquids selected for method development and validation differed in the nature of their cation (butyl- and ethyl-methylimidazolium) and anion (trifluoromethanesulfonate and bis(trifluoromethanesulfonyl)imide). Various molecular solvents were mixed with these ionic liquids (acetonitrile, methanol, dimethylformamide and trifluoroethanol) and the same physico-chemical properties were determined by optimized methods. The knowledge of these data should be of great support in various application areas, including the development of new separation media for capillary electrophoresis and chromatographic techniques.

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1. Introduction

A great interest is being drawn towards ionic liquids (IL) as alternatives for conventional molecular solvents used in organic synthesis and catalytic reactions [1]. They supplement the family of “green solvents” including water and supercritical fluids. Among these, room temperature ionic liquids are defined as materials containing only ionic species and having a melting point lower than 298 K. They exhibit many interesting properties such as negligible vapor pressure, low melting point, large liquid range, unique solvation ability and overall, the versatility of their

physico-chemical properties makes them really attractive. Most of the ILs studied are based on *N,N'*-dialkylimidazolium. They have been recently proposed as solvents in chemical reactions [2–4], multiphase bioprocess operations [5] and liquid–liquid separations [6,7], electrolytes for batteries and fuel cells [8], stationary phases in gas chromatography [9–12], mobile phase additives in liquid chromatography [13–15] and electrolyte additives in capillary electrophoresis (CE) [16–23]. Nevertheless, the knowledge of their physico-chemical properties, which has been shown to be closely related to their purity level (for instance, dependence of density, viscosity, conductivity and ¹H NMR chemical shifts on water, halide or alkali ion contents) is very limited [24,25], although it should be of prime importance for a proper design of any technological process. This lack of physico-chemical data is even more pronounced for their mixtures with molecular solvents.

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For now, viscosity, conductivity and spectroscopic properties of ILs were determined separately by classical methods, using current conventional instrumentation (viscosimeter, conductimeter, impedance measurement, absorbance spectrometer) [26–29]. All these measurements commonly required at least several milliliters of sample to be performed, which turns out to be a constraint considering the current cost of most ILs. Aside from the different techniques available for determining such properties, CE instrumentation may offer powerful attributes, namely combined pressure delivery system, power supply, diode array absorbance detector and thermoregulation device, making it very attractive for unattended, automatic, fast and miniaturized determinations. Especially since CE instrumentation has formally been used for viscosity determination in zonal [30] or frontal [31] modes.

This work promotes CE instrumentation for combined and high-throughput measurement of viscosity, conductivity and absorbance of pure ILs and mixtures of ILs and organic solvents. The availability of such an approach should be of interest for various applications, especially in liquid chromatography and CE. Four pure ILs were selected for method development and evaluation of the results, differing in the nature of their cation (1-butyl-3-methylimidazolium (BMIM) and 1-ethyl-3-methylimidazolium (EMIM)) and anion (trifluoromethanesulfonate (Tf), and bis(trifluoromethanesulfonyl)imide (NTf₂)). The mixtures of these ILs with various molecular solvents (acetonitrile (ACN), methanol (MeOH), dimethylformamide (DMF), trifluoroethanol (TFE)) were next investigated and the same physico-chemical properties were determined by the optimized methods.

2. Experimental

2.1. Chemicals and reagents

1-Butyl-3-methylimidazolium trifluoromethanesulfonate (BMIM Tf) ($\geq 99\%$), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BMIM NTf₂) ($\geq 99\%$) were a gift from Institut Français du Pétrole (Solaize, France). 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMIM Tf) ($\geq 98\%$) was provided from Fluka (Buchs, Switzerland) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMIM NTf₂) ($\geq 99\%$) was kindly donated by Solvionic (Varilhes, France). Methanol (GC grade, 99.9% purity) and *N,N'*-dimethylformamide were purchased from Fluka (Buchs, Switzerland). Acetonitrile (Chromasolv grade) and 2,2,2-trifluoroethanol (99.5% purity) were obtained from Riedel de Haën (Seelze, Germany) and Aldrich (St. Louis, MI, USA), respectively.

2.2. Sample preparation

Before each experiment, all ILs were lyophilized for 12 h with a Modulyo lyophilisator (Edwards, Faremoutiers, France) and kept in a dessicator. The water content was measured before and after each lyophilization by a Karl Fischer KF 684 Metrohm apparatus (Herisau, Switzerland). The IL–molecular solvent

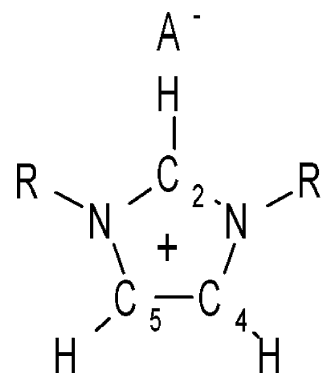


Fig. 1. Ionic liquids studied in this work:

- 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (R = Et, R' = Me, A[−] = Tf) $d = 1.387 \text{ g cm}^{-3}$, MW = 260.25 g mol^{−1},
- 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (R = Et, R' = Me, A[−] = NTf₂) $d = 1.518 \text{ g cm}^{-3}$, MW = 391.34 g mol^{−1},
- 1-*n*-butyl-3-methylimidazolium trifluoromethanesulfonate (R = Bu, R' = Me, A[−] = Tf) $d = 1.29 \text{ g cm}^{-3}$, MW = 288.30 g mol^{−1},
- 1-*n*-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (R = Bu, R' = Me, A[−] = NTf₂) $d = 1.429 \text{ g cm}^{-3}$, MW = 419.39 g mol^{−1}.

mixtures were prepared by weighing and the volume to volume ratios and molar fractions were calculated from their respective densities and molar masses (Fig. 1; Table 1). Contents of each vial were 50 μL .

2.3. Capillary electrophoresis instrumentation

Viscosity, conductivity and UV-absorbance measurements were performed with a HP^{3D}CE (Agilent Technologies, Waldbronn, Germany) or a P/ACE 5510 (Beckman Coulter, Fullerton, CA, USA) capillary electrophoresis systems. This apparatus automatically realized all the steps of the measurement protocols, including capillary conditioning, sample introduction, voltage application and diode array detection, and allows running unattended measurement sequences. Throughout the study, 33 cm total length capillaries of internally uncoated fused silica from Polymicro Technologies (Phoenix, AZ, USA) were used. Taking into account the differences in sample viscosity, these capillaries were of 100 μm i.d. for pure ILs and 95:5, 90:10 and 75:25 (v/v) IL–molecular solvent mixtures, and 50 μm i.d. for 50:50, 25:75, 10:90 and 5:95 (v/v) IL–molecular solvent mixtures. The length from the UV detection window to capillary outlet was fixed at 8.5 cm for CE instrumentation compliance. New capillaries were conditioned by successive flushes with 1 and 0.1 M NaOH and then with water under a pressure of 100 kPa, for 10 min each. The temperature in the capillary cartridge was set at 25 °C. The acquisition rate was 10 points s^{−1}. Capillaries were rinsed with water and dried by air when not in use.

2.4. UV–vis absorbance, viscosity and conductivity measurements

Just before each series of measurements, capillaries were cleaned by successive flushes with water, methanol and dried by

Table 1
Main physico-chemical properties of the organic solvents used in mixtures with ILs

Solvent	d^*	T_m (°C)	T_{eb} (°C)	V_{mol}^* (cm ³ mol ⁻¹)	μ^* (D)	α^* (10 ⁻³⁰ m ³)	ϵ_r^*	η^* (mPa s)	ϵ/η^* (mPa ⁻¹ s ⁻¹)	ϵ^2/η^* (mPa ⁻¹ s ⁻¹)	pK_{HS}^*	λ_{lim}^* (nm)
ACN	0.77	-45	82	53	3.44	4.41	35.9	0.34	105	3791	19.6	190
MeOH	0.79	-98	65	41	2.87	3.26	32.7	0.54	61	1980	16.6	205
TFE	1.37		78	72	2.52		26	1.74	15	388		190
DMF	0.94	-61	153	77	3.86	7.90	36.7	0.80	46	1693	29.4	268

d : Density; T_m : melting point; T_{eb} : ebullition point; V_{mol} : molar volume; μ : dipole moment; α : polarisability; ϵ : dielectric constant; η : viscosity; pK_{HS} : auto protolysis solvent pK ; λ_{lim} : cutoff wavelength.

* At 25 °C.

air under a pressure of 100 kPa for 120, 180 and 120 s, respectively.

For UV–vis measurements, capillaries were first filled with water. Continuous hydrodynamic introduction of the IL samples was then performed under a pressure of 50 mbar (5 kPa), for a time modulated according to the expected viscosity. UV–vis spectra (190–600 nm) were recorded with the CE instrument after the front of the IL sample had passed the detector.

For viscosity measurements, a short plug (ca. 4 nL) of a flow marker, benzyl alcohol, 0.03% (v/v) (3×10^{-5} mol L⁻¹) in the IL sample, was injected under a pressure of 50 mbar for a few seconds, according to the estimated viscosity. The marker zone was displaced by introducing the IL sample (free of the marker) under 50 mbar until the marker was detected. The measurement of the detection time of the marker, t_d , was used to calculate viscosity according to Hagen–Poiseuille law:

$$\eta = \frac{d_c^2 \Delta P t_d}{32lL} \quad (1)$$

with d_c the inner diameter of the capillary, ΔP the pressure applied, and L and l are the total capillary length and length to detection window, respectively. The calibration of both the pressure delivery system and inner diameter of the capillary ($d_c^2 \Delta P$ term) was realized with solutions of ethyleneglycol ($\eta = 16.1 \times 10^{-3}$ Pa s at 25 °C) and diethyleneglycol ($\eta = 29.0 \times 10^{-3}$ Pa s at 25 °C).

Finally, for conductivity determinations, a voltage was applied to the capillary after the flow marker had been pushed out of the capillary. For pure ILs and 95:5, 90:10 and 75:25 (v/v) IL–molecular solvent mixtures, the voltages successively applied were 0.5, 0.8, 1.0, 1.2 and 1.5 kV. For 50:50, 25:75, 10:90 and 5:95 (v/v) IL–molecular solvent mixtures, the voltages were 0.5, 0.6, 0.7, 0.8 and 1.0 kV. The voltages applied were chosen so that the linearity of Ohm's law was perfectly verified. Conductivity was obtained from the measured current intensity according to Ohm's law after rearrangement:

$$\kappa = \frac{4LI}{\pi d_c^2 V} \quad (2)$$

where V is the applied voltage and I is the measured current intensity. Calibration of both the CE power supply and microammeter (I/V term) was realized with standard solutions of 0.1 and 0.01 M KCl ($\kappa = 1.288$ and 0.1413 S m⁻¹ at 25 °C, respectively).

For precision evaluation, the whole protocol of measurements was repeated five times with the same IL sample in different

vials. Numerical data were processed using Originpro 7.0 software (OriginLab Corporation, Northampton, USA).

3. Results and discussion

3.1. Setup and evaluation of the experimental protocol

Considering both the need for knowing physico-chemical properties of ILs and their current price, efforts aiming at developing miniaturized and automated methods enabling easy access to some of these properties appeared valuable. Capillary electrophoresis instrumentation was therefore evaluated for integrated measurement of absorbance, viscosity and conductivity of pure ionic liquids and their mixtures with some molecular solvents. An integrated protocol allowing determination of absorbance, viscosity and conductivity, in this order, was developed and optimized, as described in Section 2. To exemplify this prospect, four ILs belonging to the classical family of the 1-alkyl-3-methylimidazolium salts were selected for this work (Fig. 1), the alkyl chain consisting of either the ethyl or butyl group. Both cations were associated with either trifluoromethanesulfonate (Tf), or bis(trifluoromethanesulfonyl)imide (NTf₂) anions. To mix with these ILs, four molecular solvents (MeOH, ACN, DMF and TFE) were selected according to their physico-chemical properties (Table 1) and their special interest for use in nonaqueous CE separations [32–34].

As already emphasized, water content has a great impact on viscosity and conductivity of ILs. “Pure” IL samples were therefore lyophilized, kept in a dessicator to prevent water uptake, and the residual water content was determined just before each measurement. The water contents of the studied IL samples before and after lyophilization are given in Table 2. A preliminary study of the measurement protocol was carried out with either an Agilent HP^{3D}CE or a Beckman P/ACE 5510. The pressure device of the CE instruments only allowed to obtain repeatable results for two consecutive measurements from the same vial. On both instruments, a drift in viscosity and conductivity values, likely due to the hygroscopic properties of IL, was noted from the third measurement on the same vial. For a higher number of replicates, the sample had to be replaced on the carousel every two injections. Subsequently, all experiments were carried out with the HP^{3D}CE instrument for convenience.

The protocol (choice of capillary i.d. and applied voltages) was optimized with respect to time, sample consumption and accuracy. A total IL volume of 5 mL was necessary to carry out the determinations for a given IL–molecular solvent mix-

Table 2
Viscosity and conductivity for pure ionic liquids from this work and literature [1]

Cation	Anion	Water content (ppm)		Viscosity, η (10^{-3} Pa s)		Conductivity, κ ($S m^{-1}$)		Molar conductivity, Λ ($S cm^2 mol^{-1}$)		Walden product, $\Lambda\eta$ ($10^{-3} S Pa s cm^2 mol^{-1}$)	
		NL	L	This work	Lit.	This work	Lit.	This work	Lit.	This work	Lit.
EMIM	Tf: $[CF_3SO_3]^-$	850	170	44.7	43	1.05	0.92	1.96	1.73	87.6	74.4
EMIM	NTf ₂ : $[(CF_3SO_2)_2N]^-$	3740	410	32.7	34	0.85	0.92	2.20	2.38	72.0	80.9
BMIM	Tf: $[CF_3SO_3]^-$	1100	340	88.1	90*	0.30	0.37*	0.66	0.83*	58.5	74.7*
BMIM	NTf ₂ : $[(CF_3SO_2)_2N]^-$	1000	235	51.9	52*	0.41	0.39*	1.21	1.14*	62.6	59.3*

Temperature: 25 °C, unless otherwise specified. Experimental conditions: see Section 2. NL: non-lyophilized. L: lyophilized.

* $T = 20$ °C.

ture (eight proportions: 100:0, 95:5, 90:10, 75:25, 50:50, 25:75, 10:90 and 5:95%, v/v). The precisions obtained were 1–3% R.S.D. for viscosity and less than 1% R.S.D. for conductivity.

3.2. Physico-chemical properties of pure ILs

The absorbance spectra of ILs are of concern in any process followed by UV monitoring, especially for chromatographic and electrophoretic applications using ILs as mobile phase or electrolyte additives. The UV–vis spectra of the pure ILs were acquired in the 190–600 nm range (Fig. 2). The four ILs studied present an intense band at 213 nm whatever the nature of IL cation and anion. This band is due to the presence of the imidazole ring in the IL cation [29,35]. These ILs also showed transparency above $\lambda_{lim} = 240$ nm. For this reason, benzyl alcohol was selected as a flow marker for viscosity measurement and was detected at 254 nm.

Viscosity and conductivity values determined in this work are presented in Table 2 and compared to literature values. The differences between these values did not exceed 4% for viscosity and 14% for conductivity. They nevertheless can be considered as in reasonable agreement, taking into account possible differences in temperature and impurity levels (water, chloride and

sodium ions). Indeed, trace amounts of impurities in ILs have been recognized to have a dramatic effect on density and viscosity values. An increase in halide content was reported to lead to an increase in viscosity [1,24] and a decrease in conductivity. A 200 ppm (w/w) water content in [BMIM][BF₄] results in a twofold decrease in viscosity [1] and in an increase in conductivity.

The four ILs tested have viscosity values ranging from 30 to 90 mPa s (R.S.D. < 3%, $n = 5$) at 25 °C, confirming that the ILs belonging to the alkylimidazolium family present moderate viscosity values (28–373 mPa s) [1], as compared to other classes, for which viscosity may reach up to 500 mPa s. The differences in viscosities observed among the ILs tested can be explained in part by the hydrogen bonding ability between the IL anion and the hydrogen at the C₂ position of the imidazolium cation (Fig. 1), and in part by the Van der Waals interactions mainly exerted between the anions. The lower viscosity observed with NTf₂-based ILs as compared with Tf-based ones, can be explained by H-bonding suppression which overcompensated the increase in Van der Waals interaction [29,36]. Conversely, the increase of the alkyl chain length of the cation results in an increase in viscosity for BMIM-based ILs as compared with EMIM-based ones, due to stronger Van der Waals

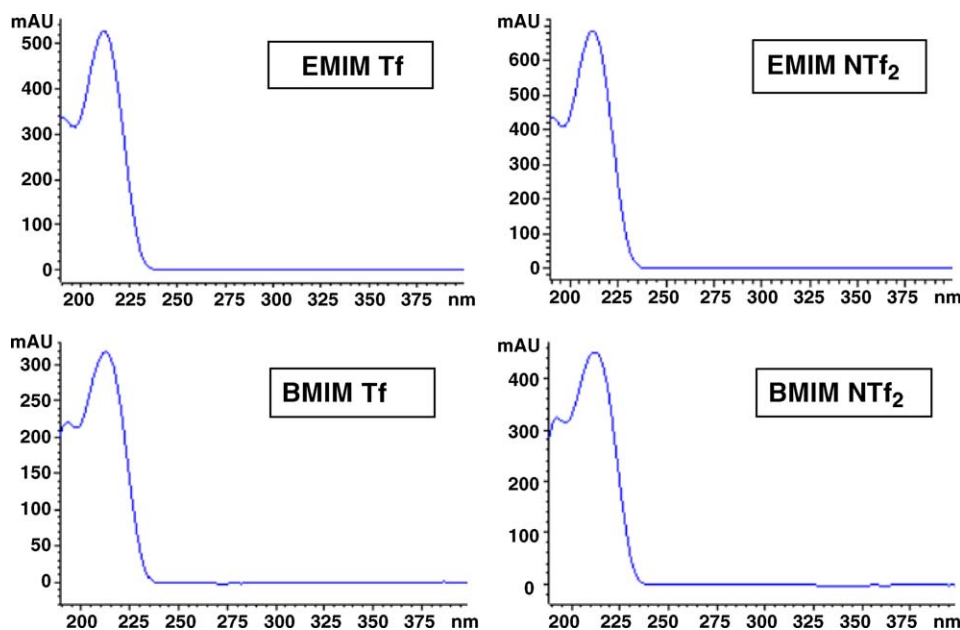


Fig. 2. UV–vis spectra of studied pure ILs acquired using an Agilent HP^{3D}CE. Operating conditions: see Section 2.

interaction which overcompensated H-bonding suppression [6,29,37].

The conductivity values of the ILs of interest in this study ranged from 0.3 to 0.9 S m⁻¹ (R.S.D. < 1%, $n = 5$), as given in Table 2. ILs generally present high conductivity values (from ca. 0.05 to 2.0 S m⁻¹) [1] for the alkylmethylimidazolium family, which can be explained by the totally ionic character of these liquids. As for viscosity, both the anion and cation natures may influence conductivity, but from this work, the influence of the cation appears to be prevailing. A clearer understanding of the phenomena involved can be derived from the molar conductivity values, calculated using the densities and molar masses reported in the caption of Fig. 1. Higher molar conductivities are noticed for EMIM-based ILs, as compared with BMIM-based ones, which should be due to the smaller size and hence the higher ionic conductivity of the former cation. Higher molar conductivities are also observed for NTf₂-based ILs as compared with Tf-based ones, which better corroborates with the strength of the ionic interaction rather than directly with the size or the ionic conductivity of the anion.

For the four ILs studied, molar conductivities varied in the reversed order of viscosities. It is worth noting that the extreme values of their product (referred to as Walden product), however, varied by about 25% (Table 2). According to the application aimed, this product can be a better descriptor of the global interest for a pure IL than the viscosity and conductivity values taken individually. For instance, for tentative applications as electrolyte in CE, Walden product should be as low as possible. Nevertheless, independently of Walden product considerations, direct inspection of viscosity remains important as well. At present, the too high value of this product precludes the use of pure ILs for this application.

3.3. Viscosity and conductivity of ionic liquid–molecular solvent mixtures

ILs are non-miscible with solvent of low dielectric constant ($\epsilon_r < 7$) and generally miscible with those of medium to high dielectric constant [29]. The four organic solvents selected for this study (ACN, MeOH, TFE and DMF) have dielectric constant values ranging from 26 to 37 and are miscible with the four preceding ILs in all proportions. They cover a range of viscosity of from 0.34 to 1.74 mPa s (Table 1). Especially, their interest for CE separations is related to possible analyte ion-pair formation and shift in acid base properties, as well as alteration of electroosmotic flows. The high-throughput measurement protocol developed in this work allowed us to complete the viscosity and conductivity determinations in a cost effective and timely fashion for seven different compositions covering the whole range (95:5, 90:10, 75:25, 50:50, 25:75, 10:90, 5:95 IL–molecular solvent, v/v), and all four IL–molecular solvent binary mixtures.

The viscosity of ILs dramatically decreases upon addition of molecular solvents. Quite remarkably, for each IL, the viscosity variations according to the molar fraction of molecular solvent are practically independent of the solvent nature (Fig. 3). In agreement with results previously reported for other mixtures [24,38], the experimental data obtained with different organic solvents can be fitted to a single exponential equation:

$$\eta = \eta_i e^{-x_s/a} \quad (3)$$

where η and η_i are the viscosity of the mixture and pure ionic liquid i , respectively, x_s the organic solvent molar fraction and a is the constant depending on ionic liquid nature. For each IL studied, Table 3 indicates the a -values obtained from non-linear regressions, taking into account the experi-

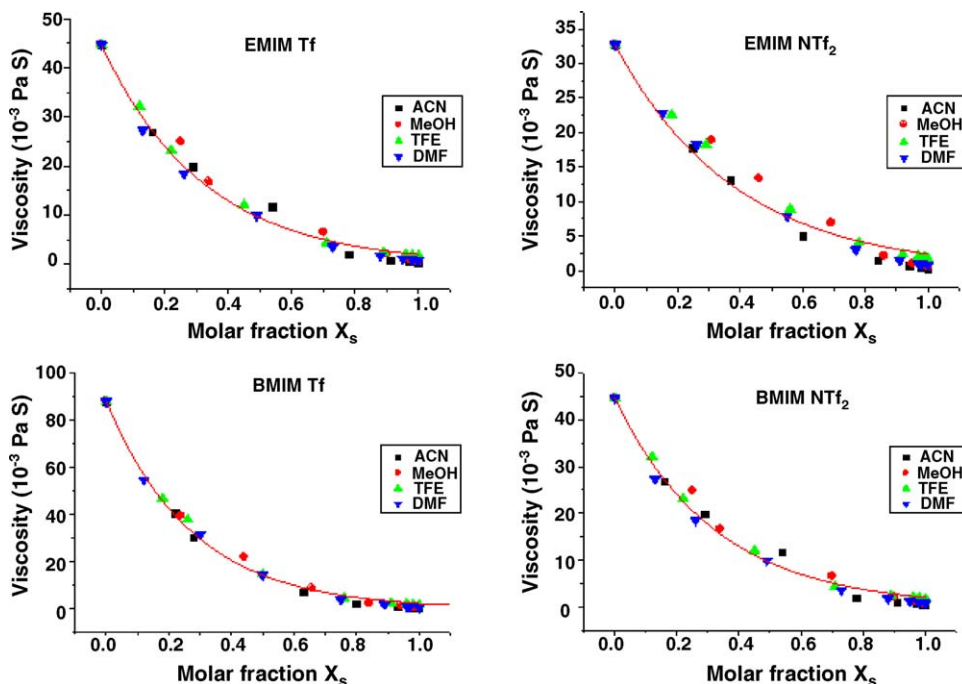


Fig. 3. Variation of the viscosity of IL–molecular solvent mixtures as a function of the molar fraction of the molecular solvent. For each IL, the solid line represents the common fit of the data to Eq. (3) from the four molecular solvents. Temperature: 25 °C. Operation conditions: see Section 2.

Table 3

a -Value for the exponential variation law of IL–molecular solvent mixture viscosity in terms of molecular solvent molar fraction (Eq. (3)) were obtained using OriginPro 7.0[®] software

Solvent	Ionic liquid			
	EMIM Tf, a	EMIM NTf ₂ , a	BMIM Tf, a	BMIM NTf ₂ , a
ACN	0.323 ± 0.020 ($R^2 = 0.985$)	0.342 ± 0.022 ($R^2 = 0.982$)	0.261 ± 0.008 ($R^2 = 0.997$)	0.314 ± 0.018 ($R^2 = 0.989$)
MeOH	0.344 ± 0.020 ($R^2 = 0.987$)	0.411 ± 0.038 ($R^2 = 0.956$)	0.287 ± 0.011 ($R^2 = 0.995$)	0.385 ± 0.036 ($R^2 = 0.961$)
TFE	0.331 ± 0.007 ($R^2 = 0.999$)	0.413 ± 0.020 ($R^2 = 0.988$)	0.285 ± 0.006 ($R^2 = 0.998$)	0.363 ± 0.016 ($R^2 = 0.992$)
DMF	0.290 ± 0.008 ($R^2 = 0.997$)	0.367 ± 0.021 ($R^2 = 0.988$)	0.268 ± 0.008 ($R^2 = 0.997$)	0.342 ± 0.018 ($R^2 = 0.988$)
All solvents	0.323 ± 0.008 ($R^2 = 0.990$)	0.383 ± 0.014 ($R^2 = 0.975$)	0.275 ± 0.004 ($R^2 = 0.996$)	0.351 ± 0.012 ($R^2 = 0.979$)

Results are given as the a -value ± standard regressions deviation ($n = 8$ for a given solvent, $n = 32$ for all solvents).

mental points for the four organic solvents separately ($n = 8$) or simultaneously ($n = 32$). In all cases, good regression coefficients were obtained. The lower a -value is the stronger the decrease in viscosity in terms of solvent molar fraction. This decrease is therefore less and less pronounced in the order: BMIMTf > EMIMTf > BMIMNTf₂ > EMIMNTf₂. This order emphasized the prominent role of the IL anion in the viscosity variation. The structure of Tf-based ILs therefore appears to be more perturbed by the molecular solvent than that of NTf₂-based ones. Although viscosity and conductivity properties of pure ILs have revealed that Tf anion interacts with IL cations more strongly than NTf₂, it can be inferred that Tf anion is more easily solvated by the molecular solvents because of its smaller size. As for the influence of the IL cation, the viscosity variations of IL–molecular solvent mixtures might be controlled by the strength of the anion–cation interaction, BMIM interacting less than EMIM and hence showing the stronger decrease in viscosity. Although a -values for a given IL are quite similar for the four solvents, a general tendency can nevertheless be observed for the influence of the solvent nature. In effect, ACN provides the lowest a -values (except for EMIMTf), followed in increasing order by DMF, TFE and last MeOH (inversion of the last two

ones for EMIMNTf₂). This tendency should be due to combined effects, as it is not correlated to either the viscosity or the anion or cation solvating ability of these solvents.

For anyone of the IL–molecular solvent mixtures studied, conductivity exhibits a non-monotonous variation in terms of the solvent molar fraction (Fig. 4). The initial increase in conductivity upon addition of a molecular solvent suggests a decrease in ion-pairing between imidazolium cation and ionic liquid anion. The maximum in conductivity is reached for a solvent molar fraction of ca. 0.9 (corresponding to ca. of 65%, v/v). Conductivity eventually decreases due to a dilution effect with the molecular solvent. For all four ILs, the increase in conductivity is less and less pronounced in the order ACN > MeOH > DMF > TFE. Except for DMF, this order also corresponds to the decreasing order of the dielectric constants, which supports the assumption of the influence of ion-pairing loosening on the increase in conductivity. The decreases in conductivity in ACN, MeOH and DMF are also sorted in the order of increasing viscosity in agreement with classical expectations. Finally, on comparing the conductivities of the IL–molecular solvent mixtures for the different ILs with a given solvent, no systematic behaviour can be drawn, but a tendency appears with decreasing conductivities

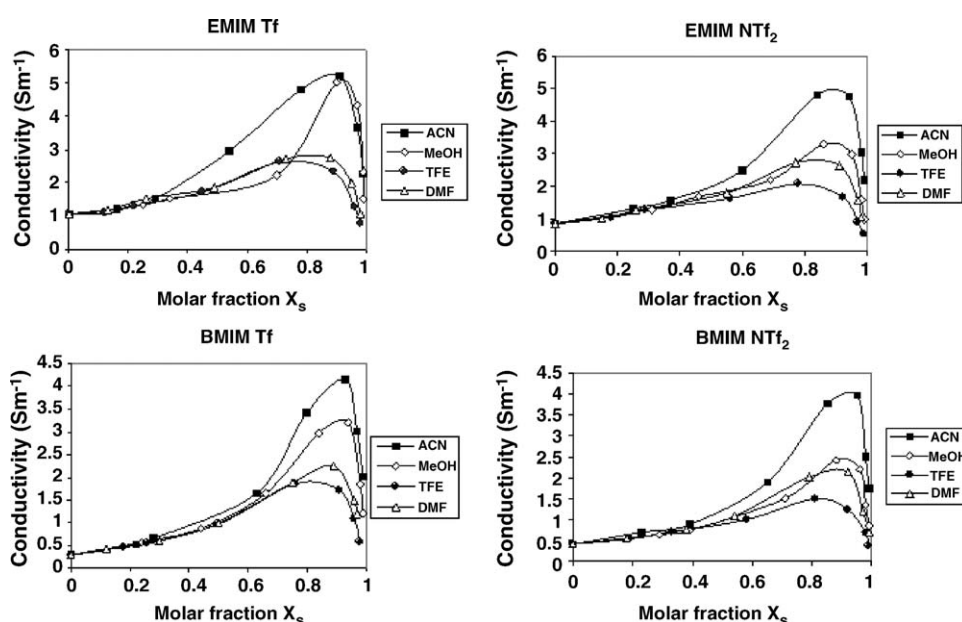


Fig. 4. Variation of the conductivity of IL–molecular solvent mixtures as a function of the molar fraction of the molecular solvent. Temperature: 25 °C. Operation conditions: see Section 2. The solid lines for each binary mixture were just drawn as an eye guide.

in the order $\text{BMIMTf} > \text{EMIMNTf}_2 > \text{BMIMTf} > \text{EMIMNTf}_2$. This tendency confirms the prevailing influence of the conductivity of the IL cation, as for the conductivity of pure ILs, over the anion–cation interaction. The slightly higher conductivities observed for ILs containing Tf anion, as compared with those containing NTf_2 seem to corroborate the major role of ion conductivity, but no definitive conclusion can be drawn from these results concerning the anion nature.

4. Conclusion

A new protocol using CE instrumentation has been established for unattended, automatic, miniaturized, reliable and therefore time- and cost-effective determinations of IL viscosity, conductivity and absorbance spectrum. The possibility of modeling viscosity of the mixtures of a given ionic liquid with various molecular solvents by a unique exponential function was confirmed and extended. For any IL, viscosity variations are practically independent of the organic solvent nature, and a tendency was observed according to the solvation ability of the IL anion by the solvent and according to the strength of the anion–cation interaction for the IL cation. The conductivity of IL–molecular solvent mixtures exhibits a non-monotonous variation whatever the couple tested, due to an overlay of ion-pairing loosening and dilution effects. Additional modeling of conductivity accounting for ion-pairing phenomena is clearly needed. The availability of these data should be a great support in various application areas, including the screening of new separation media for CE.

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