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TRANSPORT PROPERTIES OF BINARY MIXTURES OF 1-BUTYL-3-METHYLIMIDAZOLIUM TETRAFLUOROBORATE WITH SOME ORGANIC SOLVENTS AT 298.15 K

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În această lucrare se raportează proprietăţi de transport pentru sistemele binare de lichid ionic, 1-butil-3-metilimidazoliu, în solvenţii organici: dimetilsulfoxid, acetonitril, etilenglicol şi 1,4-dioxan. S-au determinat viscozitatea dinamică şi conductivitatea electrică pentru cele patru sisteme binare la 298.15 K pe întreaga gamă de compoziţii şi presiune atmosferică. Din datele experimentale s-au calculat cu ecuaţii specifice deviaţia în viscozitate şi conductivitatea molară. Proprietăţile de transport s-au discutat apoi în termenii regulii lui Walden.

In this paper we report the transport properties for the binary mixtures of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate, in organic solvents: dimethylsulfoxide, acetonitrile, ethylene glycol *and* 1,4-dioxane. *The dynamic viscosity and specific electrical conductivity for their binary mixtures have been determined over the whole composition range at 298.15 K and atmospheric pressure. Viscosity deviations and molar conductivity were derived from experimental data and fitted to suitable equations. The transport properties were discussed in terms of Walden's rule.*

Keywords: 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid, DMSO, acetonitrile, ethylene glycol, 1,4-dioxane, viscosity, conductivity

1. Introduction

Room temperature ionic liquids (ILs) are a class of organic salts that are liquids at or near room temperature in their pure state. They exhibit interesting properties, such as negligible vapor pressure, low melting point, a wide liquid range, suitable viscosity, unique permittivity, high thermal stability high electrical conductivity and wide electrochemical window, being good solvents for both polar and nonpolar organic and inorganic substances, which suggest many

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applications as green and benign replacements o the traditional volatile organic solvents.

Despite their importance and interest, the properties data on the mixtures of ionic liquids with organic molecular solutes are very limited. They are necessary for the design of many technological processes. Many of the proposed nonreactive applications of ILs are related with the unique character of molten salts at room temperature, which are conductive liquids. In particular, ILs based on the 1-butyl-3-methylimidazolium cation ($[bmim]^+$) have received much attention in the recent years [1].

In this paper we report the transport properties for the binary mixtures of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF4], with dimethylsulfoxide (DMSO), acetonitrile, ethylene glycol (EG), and 1,4-dioxane; with the exception of [bmim][BF4] + acetonitrile system [2], no such data are available in literature for the other three systems.

2. Experimental

Chemicals. 1-butyl-3-methylimidazolium tetrafluoroborate (> 99.9 mass %), DMSO (> 99.9 mass %), acetonitrile (> 99.5 mass %), ethylene glycol (> 99.5 mass %), and 1,4-dioxane (> 99.0 mass %), were purchased from Merck. The organic solvents were dried and stored over 3A molecular sieves and were used without further purification. Due to the hygroscopic character of the ionic liquids, was treated for 11 h at 333 K under vacuum. It was then conditioned under a nitrogen atmosphere. To avoid any contact of the sample with atmosphere, a Schlenk tube and a syringe equipped with a Luer Lock valve were used to prepare the samples and to load it into the instruments.

Apparatus and procedures. The binary mixtures were prepared by mass on a HR-120 (A&D Japan) electronic balance with a precision of $\pm 10^{-4}$ g. The experimental uncertainty in mole fractions was estimated to be less than ± 0.0002. Dynamic viscosity, η, was obtained using an Anton-Paar AMVn falling ball viscometer. Temperature was controlled by means of a built-in Peltier thermostat within ±0.01 K. Various combinations of ball/capillary of different diameters *d* were selected allowing to measure viscosities from 1 to 105 mPa·s. Measurements were made with different angles using three capillaries with diameters of 1.6 mm, 1.8 mm and 3 mm. Samples were loaded into tubes in N_2 atmosphere, and sealed with glass stoppers and glass caps. The repeatability of the viscosity measurements is less than 0.1 %, and the reproducibility < 0.35%. The conductivity measurements were carried out with a Cobra 3 Chem-Unit (PHYWE) conductivity meter, using a specially designed cell (electrode LTG 1/24) suitable for low conductivity measurement. Before the measurement the conductivity cell was calibrated with a certified solution ($\lambda = 1.4\ mS \cdot cm^{-1}$). The temperature was kept constant within ±0.05 K with an external oil bath. The uncertainty of the conductivity measurements was estimated to be ± 0.5 %.

The experimental densities and viscosities of the pure components are in agreement with the literature values, as can be seen in Table 1. The experimental apparatus for density measurements have been described in our previous work [3].

The dynamic viscosity and specific electrical conductivity have been determined over the whole composition range at 298.15 K and atmospheric pressure for all four binary systems. Note that 1,4-dioxane is only partially miscible in [bmim][BF4] at the studied temperature and atmospheric pressure. Viscosity deviations and molar conductivity were derived from experimental data and fitted to suitable equations. Transport properties were discussed in terms of Walden's rule.

Table 1

Comparison of measured density, ρ, and viscosity, η, with literature values at 298.15 K

	ρ, g·cm^{-3}		η, mPa·s	
	lit.	exp.	lit.	exp.
[bmim][BF4]	1.20100 [4] 1.2011 [5]	1.20089	103.8 [6]	104.7
DMSO	1.0957 [7] 1.09562 [8]	1.09574	1.9946 [9]	2.012
ethylene glycol	1.109957 [10] 1.1100 [11]	1.10996	16.1 [12]	17.41
acetonitrile	0.77667 [2]	0.77655	0.341 [2]	0.370
1,4-dioxane	1.02760 [3] 1.02772 [13]	1.02792	1.1925 [3] 1.196 [14]	1.180

3. Results and discussions

The obtained experimental data of dynamic viscosity, η, and electrical conductivity, λ, measured for the binary systems of [bmim][BF4] with DMSO, acetonitrile, EG and 1,4-dioxane at 298.15 K as a function of mole fraction of ionic liquid are given in Table 2.

The $\ln\eta$ vs X_s data for the ionic liquid + organic solvent systems are plotted in Fig. 1. As shown, data for each system form straight lines, following an exponential equation, as previously observed in similar systems [2, 15-16]

$$ln\eta = ln\eta_0 - X_s / a \tag{1}$$

where η_0 is the viscosity of the pure ionic liquid, X_s is the mole fraction of the organic solvent and a is the equation coefficient, which can be obtained by fitting the experimental data. The best fitting parameters a^{-1} for the four systems are given in Table 3, where the standard deviation, σ, and the linear correlation coefficient, r^2, are also included.

Table 2

Dynamic viscosities, η, and electrical conductivities, λ, of the binary mixtures of [bmim][BF4] with different organic solvents at 298.15 K

X_1	η, mPa s	λ, mS/cm	X_1	η, mPa s	λ, mS/cm
[bmim][BF4](1)+DMSO(2)			[bmim][BF4](1)+ acetonitrile(2)		
0.0000	2.0123	0.42	0.0000	0.3700	0.002
0.0722	3.1441	9.74	0.1059	0.8794	12.50
0.1764	5.4886	10.32	0.2213	2.0270	11.64
0.2145	6.8359	10.16	0.3008	3.3723	10.80
0.3225	11.3800	8.31	0.3894	5.5482	7.82
0.4189	17.1973	6.72	0.4432	7.7086	7.33
0.6070	34.0005	4.36	0.6178	18.7436	5.09
0.6557	38.8705	3.52	0.7111	26.0855	3.74
0.8283	64.7310	2.84	0.8146	41.6900	3.38
0.9155	82.7136	-	0.9113	68.5059	2.52
1.0000	104.6533	2.43	1.0000	104.6533	2.43
[bmim][BF4](1)+EG(2)			[bmim][BF4](1)+ 1,4-dioxane(2)		
0.0000	17.4098	0.01	0.0000	1.1800	0.00
0.0895	15.4984	-	0.2559	6.0112	4.03
0.1758	15.5208	6.30	0.3956	12.1670	3.95
0.3578	18.8665	7.27	0.4988	19.8778	3.40
0.4397	21.3037	7.66	0.6000	29.4767	3.06
0.6482	31.9656	5.77	0.7021	42.9676	-
0.8121	51.8037	-	0.8993	79.5376	2.52
1.0000	104.6533	2.43	1.0000	104.6533	2.43

Table 3

Values of parameters (a^{-1}) for the best fit of natural logarithm of viscosity vs. the mole fraction of organic solute at 298.15 K following equation (1)

system	a^{-1},	σ	r^2
[bmim][BF4] + DMSO	3.569	0.214	0.983
[bmim][BF4] + acetonitrile	3.929	0.303	0.988
[bmim][BF4] + EG	2.284	0.330	0.878
[bmim][BF4] + 1,4-dioxane	5.171	0.221	0.972

The dependence of conductivity on IL concentration follows the typical pattern of concentrated electrolyte solutions: after a rapid initial rise at low X_{IL} due to the increasing number of charge carriers, λ, passes through a pronounced maximum at around $X_{IL} \approx 0.1$ to 0.25 (depending on the mixture) due to the counterbalancing effect of the rapidly rising viscosity on ion mobility, as other authors has observed [17].

The empirical Casteel-Amis equation is widely used to reproduce such concentration dependence [18]. Generally, data fitting is done on the molality scale, and obtained parameters are the maximum conductivity, λ_{max}, the corresponding concentration, and shape parameters, *a* and *b*. For the present systems, the Casteel-Amis equation can be reasonably applied in the mole fraction scale, that is

$$\lambda = \lambda_{max}\left(\frac{X_{IL}}{X_{max}}\right)^{a} exp\left(b\left(X_{IL} - X_{max}\right)^{2} - a\frac{X_{IL} - X_{max}}{X_{max}}\right) \tag{2}$$

where X_{max} is the IL mole fraction at λ_{max}.

The obtained fitting parameters are summarized in Table 4 together with the corresponding standard deviations of the fits, σ. Generally, the four-parameter description of conductivity as a function of IL mole fraction with eq. 2 is good, $\sigma < 0.35$ mS·cm^{-1} for most mixtures, except the system with EG, where the number of experimental data are insufficient.

The viscosity deviations $\Delta\eta$ have been calculated using the following equation:

$$\Delta\eta = \eta - \left(X_{IL}\eta_{IL} + X_{S}\eta_{S}\right) \tag{3}$$

This property was mathematically represented by the Redlich-Kister polynomials

$$\Delta\eta = X_{Il}X_{S}\sum_{k=0}^{M} A_{k}\left(2X_{IL} - 1\right)^{k} \tag{4}$$

where A_k are adjustable parameters which can be obtained by least-squares analysis. Values of the fitted parameters are presented in Table 5 along with the standard deviations of the fit.

The very large negative values obtained for viscosity deviations, as is shown in Fig. 4, are due to the big differences between the ionic liquid’s and the organic solvent’s viscosity in the studied ranges of composition for all three investigated binary mixtures, as is indicated in literature for similar systems [19]. The less negative values for the binary systems of [bmim][BF4] + DMSO and 1,4-dioxane indicate stronger interactions in these systems.

Walden’s rule was used to correlate molar conductivity and viscosity, for which the product must be constant [20].

$$\Lambda \cdot \eta = K \tag{5}$$

where *K* is constant at a fixed temperature in the original formulation of this rule. The molar conductivity, Λ, was calculated as the ratio between specific conductivity and molar concentration.

The resulting product is approximate constant for a broad range of concentrations and increases its value for the binary systems of [bmim][BF4] + DMSO and 1,4-dioxane, and decreases for the [bmim][BF4] + acetonitrile (Fig. 3).

Table 4

The best fitting parameters and standard deviation for the equation Casteel-Amis used to correlate conductivity data at 298.15 K

	a	b	λ_{max}	X_{max}	σ
[bmim][BF4] + DMSO	0.688	1.884	10.783	0.137	0.276
[bmim][BF4] + acetonitrile	0.724	1.756	12.793	0.141	0.347
[bmim][BF4] +1,4-dioxane	1.948	3.504	4.104	0.298	0.072

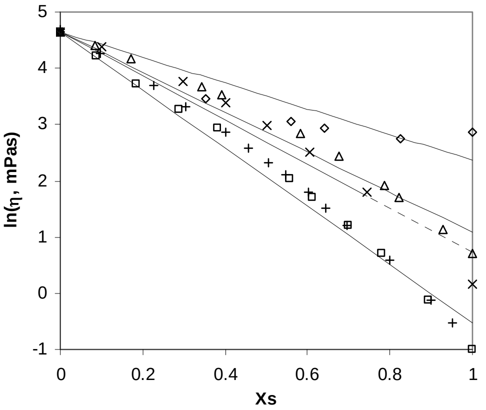

Fig. 1. Natural logarithm of dynamic viscosity vs mole fraction of organic solvents for the binary mixtures of [bmim][BF4] with: Δ, DMSO; □, acetonitrile; ◊, EG; ×, 1,4-dioxane; +, ref. 2; The solid line represents the fit of these data to eq. 1

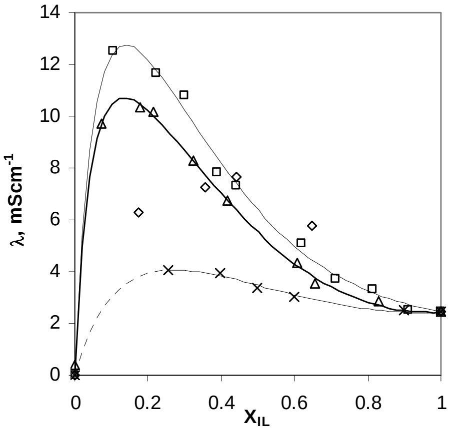

Fig. 2. Electrical conductivities vs mole fraction of [bmim][BF4] for the binary mixtures with: Δ, DMSO; □, acetonitrile; ◊, EG; ×, 1,4-dioxane; The solid line represents the fit of these data to eq. 2

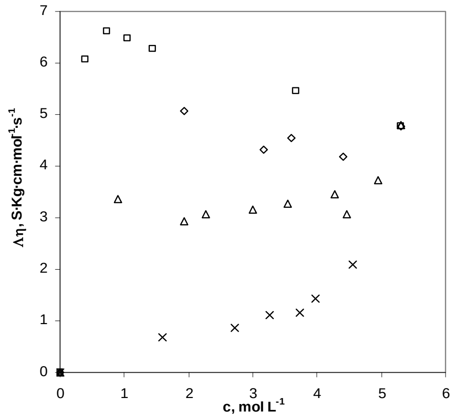

Fig. 3. Product of molar conductivity by viscosity vs molarity for the binary mixtures of [bmim][BF4] with:
Δ, DMSO; □, acetonitrile; ◊, EG; ×, 1,4-dioxane

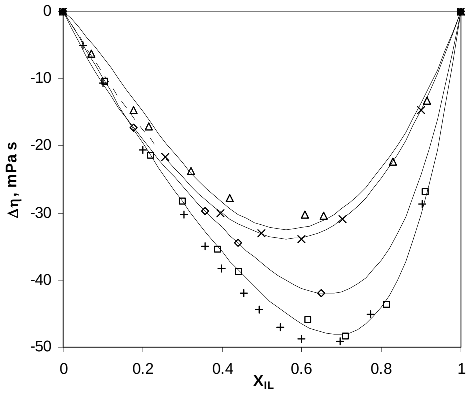

Fig. 4. Viscosity deviation vs mole fraction of [bmim][BF4] for the binary mixtures with: Δ, DMSO; □, acetonitrile; ◊, EG; ×, 1,4-dioxane; +, ref. 2; The solid line represent the fit with eq. (4)

Table 5

Parameters A_k and standard deviation of $\Delta\eta$ for [bmim][BF4] + organic solvent systems at 298.15 K

	A_0	A_1	A_2	A_3	σ
[bmim][BF4] + DMSO	-119.569	-36.944	-20.383	-14.103	0.185
[bmim][BF4] + acetonitrile	-168.188	-109.653	-85.836	-48.808	0.649
[bmim][BF4] + EG	-150.303	-93.497	-69.665	-	0.030
[bmim][BF4] +1,4-dioxane	-132.829	-37.646	-0.751	-	0.134

4. Conclusions

The dynamic viscosities and electrical conductivities of selected binary mixtures of the ionic liquid, [bmim][BF4], with polar solvents, DMSO, acetonitrile, ethylene glycol, and nonpolar 1,4-dioxane, at 298.15 K were reported. All investigated systems are completely miscible over the whole composition range at 298.15 K except for [bmim][BF4] + 1,4-dioxane.

The viscosities of the mixtures decrease rapidly when organic compounds are added to the ionic liquid. This decrease is particularly strong in dilute solutions of organic compounds in the ionic liquid. The strong coulomb interactions between the $[BF4]^-$ anion and $[bmim]^+$ cation are weakened upon mixing with the polar/neutral organic compounds, which leads to a higher mobility of the ions and a lower viscosity of the mixtures.

Transport properties were discussed in terms of Walden's rule, which is partially correct.

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