Effect of Relative Humidity of Air on Density, Apparent Molar Volume, Viscosity, Surface Tension, and Water Content of 1-Ethyl-3-methylimidazolium Ethylsulfate Ionic Liquid

José S. Torrecilla,*,† Tatiana Rafione,‡ Julián García,† and Francisco Rodríguez†

Department of Chemical Engineering, Faculty of Chemistry, Complutense University of Madrid, 28040-Madrid, Spain, and
Department of Environment, Faculté Des Sciences et Techniques, Paul Cézanne University, Aix-Marseille III,
13397 MARSEILLE CEDEX 20, France

The effect of relative humidity (RH) of air on the water content, density, apparent molar volume, dynamic viscosity, and surface tension of the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate has been studied. Physical property measurements were conducted at a temperature of 298.15 K, at atmospheric pressure, and in a RH range of (0 to 100) %. The experimental data were fit to first- and third-order polynomials that relate the physical properties with the relative humidity of air and the water content of [emim][$EtSO_4$] with correlation coefficients higher than 0.9. The apparent molar volume was fit by the Redlich−Mayer equation with a relative standard deviation (σ) less than 2 $cm^3 \cdot mol^{-1}$. Excess molar volumes, viscosity, and surface tension deviations of a mole fraction average were calculated, and a second- and third-order Redlich–Kister polynomial was applied (σ equal to 0.01 $cm^3 \cdot mol^{-1}$, 0.5 mPa·s, and 0.6 $mN \cdot m^{-1}$, respectively).

Introduction

Ionic liquids (ILs) are a class of low-temperature molten salts consisting of an organic cation and inorganic or organic anion. In recent years, ILs have attracted increasing attention as replacements for conventional organic solvents in catalysis, separation processes, electrochemistry, and many other fields.[1]

One of the most attractive features of ILs is their ability to be tailor-made for a specific purpose by careful selection of the cation, anion, or both.[2] However, given the enormous number of possible cation/anion combinations, IL design would be greatly assisted by theoretical models to estimate the thermophysical properties of intended combinations.[3] Ionic liquid design would further be assisted if it were possible to predict what effect common IL impurities such as water have on their physical properties. Most ILs absorb water to varying extents from wet surfaces or from the atmosphere,[4,5] and even low levels of water in ILs can dramatically alter their physical properties. Therefore, in this work, we studied the effect of relative humidity (vide infra) on the density, apparent molar volume, dynamic viscosity, surface tension, and water content on the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate, [emim][$EtSO_4$]. Relative humidity (RH) is a measure of the amount of moisture in the air relative to the amount the air is capable of holding at a given temperature.

Seddon et al.[4] and others[5–11] have previously studied the effect of water absorption on the physical properties of ionic liquids, but to the best of our knowledge, the effect of RH has not been conducted to date.

To test the quality of our experimental data as well as to probe the nature of real aqueous solutions of ionic liquids, we used Redlich–Kister and Redlich-Mayer equations to model the viscosity and surface tension deviations and excess molar volume.

Table 1. Equilibrium Relative Humidities of Saturated Salt Solutions at T = 298.15 K[13]

chemical	RH/%
lithium chloride	11.1
potassium acetate	22.5
magnesium chloride	32.5
potassium carbonate	43.7
sodium dichromate	53.3
sodium bromide	58.1
sodium nitrite	64.4
sodium chloride	75.4
potassium chloride	84.3
ammonium dihydrogen phosphate	92.5
Milli-Q water	100.0

Experimental Section

Chemicals. The ionic liquid [emim][$EtSO_4$] (≥ 95 % purity) was purchased from Sigma-Aldrich Chemie GmbH, chloride mass fraction < $0.3 \cdot 10^{-4}$ and water mass fraction < $4.7 \cdot 10^{-4}$. Lithium chloride (LiCl ≥ 99 % from Panreac Chimie S.A.R.L.), potassium acetate (CH_3COOK ≥ 99 % from Panreac Chimie S.A.R.L.), magnesium chloride 6-hydrate ($MgCl_2 \cdot 6H_2O$ ≥ 99 % from Panreac Chimie S.A.R.L.), potassium carbonate (K_2CO_3 ≥ 99 % from Panreac Chimie S.A.R.L.), sodium dichromate 2-hydrate ($Na_2Cr_2O_7 \cdot 2H_2O$ ≥ 99.5 % from Panreac Chimie S.A.R.L.), sodium nitrite ($NaNO_2$ ≥ 98 % from Panreac Chimie S.A.R.L.), sodium chloride (NaCl ≥ 99.95 % from Panreac Chimie S.A.R.L.), potassium chloride (KCl ≥ 99.5 % from Panreac Chimie S.A.R.L.), ammonium phosphate ($(NH_4)H_2PO_4$ ≥ 99.5 % from Panreac Chimie S.A.R.L.), methanol dry (CH_3OH, Riedel-de Haën, HYDRANAL−water mass fraction < 0.01 %), and the standard for volumetric Karl Fischer titration (Riedel-de Haën, HYDRANAL-standard (5.00 ± 0.02)

---

* Corresponding author. Tel.: +34 91 394 42 40. Fax: +34 91 394 42 43. E-mail address: jstorre@quim.ucm.es.
† Complutense University of Madrid.
‡ Paul Cézanne University.

10.1021/je700523b CCC: $40.75

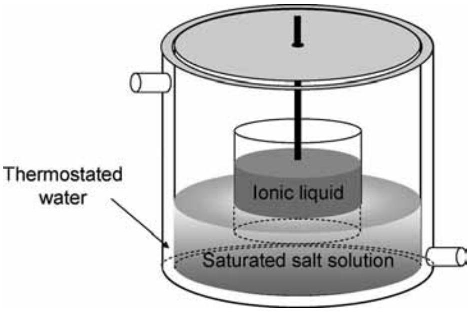

Figure 1. Scheme of hydration equipment. Device (0.175 m height, 0.042 m I.D.); small cubic container (0.045 m height, 0.03 m I.D.).

Table 2. Experimental Water Content, Density, Apparent Molar Volume, Dynamic Viscosity, and Surface Tension of [emim][EtSO$_4$] as a Function of its Water Content at T = 298.15 K

RH/%	$10^6\ w_{H_2O}$	ρ/g·cm^{-3}	V_φ/cm^3·mol^{-1}	η/mPa·s	γ/mN·m^{-1}
-	475	1.23626	190.8	91.85	47.00
11.1	7540	1.23451	190.6	83.60	47.23
22.5	14399	1.23393	190.5	70.21	48.01
32.5	25306	1.23135	190.2	65.61	48.08
43.7	30466	1.23000	190.1	55.78	48.09
53.3	41850	1.22801	189.9	33.30	48.14
58.1	38486	1.22715	189.8	41.85	47.93
64.4	56434	1.22630	189.7	30.63	47.95
75.4	69373	1.22245	189.6	24.80	48.25
84.3	75187	1.21951	189.6	23.63	48.97
92.5	92916	1.21544	189.4	17.41	49.35
100.0	94926	1.21498	189.4	14.73	50.11

mg·mL^{-1} as water) were used. The aqueous solutions were prepared using ultrapure water obtained from a Milli-Q water purification system (Millipore, Saint Quentis Yvelines, France).

All the ionic liquid samples were dried by heating at 333 K for 24 h under reduced pressure. All experiments were carried out in a vacuum atmosphere glovebox under dry nitrogen due to the sensitivity of the ILs to humidity. The mean of three replicate measurements was reported. The water content of the sample was measured before and after each volumetric property determination.[5,6]

Hydration Equipment. To determine the absorption equilibrium moisture of [emim][EtSO$_4$], an isopiestic method was used.[12,13] Several runs were carried out in air with different relative humidities that were generated by saturated solutions of different salts in water at 298 K and atmospheric pressure (Table 1). The experimental device (Figure 1) consists of a cylindrical glass vessel half-filled with a saturated salt solution at 298 K. The type of salt resulted in a known equilibrium air humidity inside the device. A small cubic container made of glass was filled with [emim][EtSO$_4$] and hung at the top of the vessel. The container was periodically weighed until the mass remained constant. The IL was hydrated until the relative change of the water content rate, WCR (described by eq 1), between two consecutive mass measurements of the container was ≤ 0.03 %.

$$\mathrm{WCR} = \frac{M_s(t+1) - M_s(t)}{t \cdot M_{so}} \tag{1}$$

where M_{so}, M_s, and t are the initial sample mass, sample mass, and the hydration time in hours, respectively. The operating procedure consisted of placing 15 cm^3 of [emim][EtSO$_4$] IL in a small closed vessel in which the relative humidity (RH) is controlled by the saturated salt solutions (25 cm^3). After 5 days, it was assumed that equilibrium between water vapor and the IL (WCR < 0.03 %) had been reached. In this way, 11 different unsaturated solutions of IL in water were made. The hydration equipment was cleaned between experiments by rinsing with acetone and water, followed by heating in a drying oven at 333.15 K for 24 h.

Estimation of Uncertainties. In this work, every expanded uncertainty was evaluated from n independent observations $Z_{i,k}$ of Z_i obtained under the same measurement conditions. The mean of the distribution was calculated using eq 2, and the standard uncertainty $u(Z_i)$ of the mean was estimated by eq 3. The expanded uncertainty was subsequently estimated by multiplying $u(Z_i)$ by the coverage factor ($k_Z = 2$), eq 4.[14,15]

$$Z_i = \bar{Z}_i = \frac{\sum_{k=1}^{n} Z_{i,k}}{n} \tag{2}$$

$$u(Z_i) = \sqrt{\frac{\sum_{k=1}^{n} (Z_{i,k} - \bar{Z}_i)^2}{n(n-1)}} \tag{3}$$

$$u_Z = k_Z \cdot u(Z_i) \tag{4}$$

Density Measurements. The densities of aqueous solutions of [emim][EtSO$_4$] were determined at 298.15 K (± 0.01 K) and at atmospheric pressure using an Anton Paar density meter, model DMA 5000 (Anton Paar GmbH, Graz, Austria). The uncertainty in the experimental measurements was found to be less than $\pm\ 1 \cdot 10^{-6}$ g·cm^{-3}. The density of ultrapure water was determined using the same method, and the measurements are in agreement with literature values.[16]

Dynamic Viscosities. Dynamic viscosities of aqueous solutions of [emim][EtSO$_4$] were determined using an automated microviscometer, model AMVn (Anton Paar GmbH, Graz, Austria). Its measuring ranges of time, viscosity, and temperature values are up to 250 s, 2500 mPa·s, and 408.00 K, respectively. The standard uncertainty in experimental measurements has been found to be less than ± 0.01 mPa·s. The equipment maintains the operating temperature of the capillary and measures time with a resolution of 0.01 K and 0.001 s, respectively. The principle of measurement, on which this microviscometer is based, is a falling ball.[17]

Surface Tension. The surface tension measurements were performed using the pendant drop method[18] and a Dataphysics OCA 15 tensiometer (Dataphysics Instruments GmbH, Filderstadt). The compartment containing the ionic liquid drop was thermostatted using a JULABO F12-EC bath with a temperature stability of ± 0.03 K; a temperature range of (253.15 to 373.15) K was employed. The experimental apparatus includes an experimental cell, an optical system for the illumination and the visualization of the drop shape, and a data acquisition system. Using an electronic injection system, a pendant drop is formed, and the contour of the drop is analyzed from its visualization to infer the surface tension using suitable software (SCA 20 from Dataphysics Instruments GmbH). The uncertainty of the surface tension measurement was estimated to be less than ± 0.05 mN·m^{-1}.

Water Contents. Water contents of the aqueous solutions of [emim][EtSO$_4$] were carried out by employing a Karl Fischer titrator DL31 from Mettler Toledo and using the one-component technique. The polarizing current for potentiometric end-point determination was 20 A, and the stop voltage was 100 mV. The end-point criterion was the drift stabilization (3 μg of H_2O·min^{-1}) or maximum titration time (10 min). The measurement was corrected for the baseline drift, defined as the residual or penetrating water that the apparatus removes per minute. The

Table 3. Comparison of Measured Pure Component Property Data of [emim][EtSO$_4$] with Literature Values at T = 298.15 K.

ρ/g·cm^{-3}		η/mPa·s		γ/mN·m^{-1}		10^6 w_{H_2O}		V_φ/cm^3·mol^{-1}	
exptl	lit.	exptl	lit.	exptl	lit.	exptl	lit.	calcd	lit.
1.23626	1.23737[a]	91.85	95[a]	47.00	46.96[c]	475	45[a]	190.8	192.1[d]
	1.23882[b]		100.4[b]				98[b]		
	1.23763[c]		97.58[c]				300[c]		

[a] Ref 6. [b] Ref 19. [c] Ref 20. [d] Ref 8.

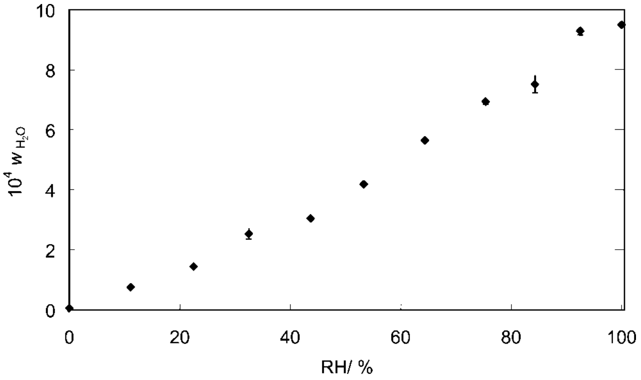

Figure 2. Plot of water mass fraction (w_{H_2O}) of [emim][EtSO$_4$] vs relative humidity of air (RH) at T = 298.15 K.

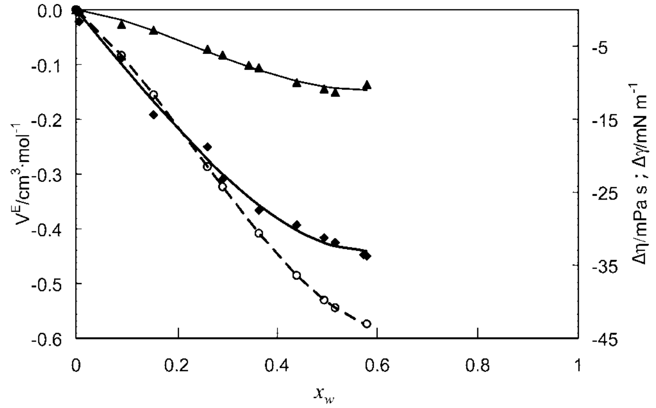

Figure 3. ♦, Excess molar volume and deviations in ○, viscosity and ▲, surface tension of [emim][EtSO$_4$] plotted vs water mole fraction (x_w) at T = 298.15 K. The lines represent the corresponding correlations by the Redlich–Kister equation.

expanded uncertainty decreases with the mass fraction of water. At $w = 3 \cdot 10^{-2}$, $6 \cdot 10^{-2}$, and $9 \cdot 10^{-2}$, the uncertainty decreases by 2.5 %, 0.6 %, and 0.4 %, respectively.

Results and Discussion

The influence of atmospheric moisture on the density, apparent molar volume, viscosity, surface tension, and water content of [emim][EtSO$_4$] is reported in Table 2. The density, apparent molar volume, and viscosity of [emim][EtSO$_4$] all decrease with increasing relative humidity. On the other hand, in the employed RH range, the surface tension and the water content of the IL increased with increasing RH.

As illustrated in Table 3, the density values reported in the literature for pure [emim][EtSO$_4$][16,19,20] are in agreement with data obtained in this work, despite the water contents of these ionic liquid samples varying significantly. Indeed, the largest difference (viz. Arce et al.) is ≈ 0.0026 g·cm^{-3}.[19]

The apparent molar volumes (V_φ) for aqueous solutions of [emim][EtSO$_4$] reported in this work are also in good agreement with literature data (Table 3).[8] For example, the viscosity of the commercial [emim][EtSO$_4$] used in this work differs by < 9 mPa·s from data reported in the literature.[6,19,20] This difference is mainly due to the water content of the IL used in Arce's work (< $98 \cdot 10^{-6}$).[19] Finally, the surface tension for commercial [emim][EtSO$_4$] reported in this work is also in agreement with literature data (Δ = 0.04 mN·m^{-1}).[20]

As shown in Table 3, viscosity values exhibit the largest differences between our work and that available in the literature. This is most likely because, of all the physical properties studied in this work, viscosity is the most sensitive toward water content.[5,21]

Effect of RH on the Water Content of [emim][EtSO$_4$] IL. Relative humidity is the ratio between the partial pressure of water vapor and the vapor pressure of water at a given temperature; i.e., it quantifies the water content of air. High values of RH mean that there is a large amount of water vapor in the air and consequently that hydration of [emim][EtSO$_4$], for example, should be easy.

In this work, at 298.15 K, the water content of [emim][EtSO$_4$] was measured at different RH values (between 0 % and 100 %). Vapor–liquid equilibrium was assumed to be reached once the variation of WCR between two consecutives measurements, eq 1, was less than 0.03 %. As can be seen in Figure 2, there is a linear relationship between RH and water mass fraction of the [emim][EtSO$_4$], eq 5 (correlation coefficient, R^2, higher than 0.99 and the standard deviation, σ, equal to $1.5 \cdot 10^{-3}$ of w_{H_2O}), and the water mass fraction (w_{H_2O}) of this IL increases with increasing RH. These observations are consistent with the hygroscopic nature of [emim][EtSO$_4$].

$$w_{H_2O} = 886.21 \cdot \mathrm{RH} \qquad (5)$$

Effect of RH on Density. The influence of the RH of air on the density of [emim][EtSO$_4$] is shown in Table 2. The density decreases with increasing RH. The change of density with the relative humidity and water content was adequately described by two total derivatives of first order with respect to RH and w_{H_2O} of fitted equations (first-order polynomial, which correlates density of mixture versus RH and w_{H_2O}, R^2 > 0.95, σ = 0.001 g·cm^{-3}, and R^2 > 0.98, σ = 0.0006 g·cm^{-3}, respectively), eqs 6 and 7.

Table 4. Coefficients of the Redlich–Kister Equation[21]

Q	A_0	A_1	A_2	A_3	R^2	rmsd
V^E/cm^3·mol^{-1}	−1.7017	−0.7387	−0.2810	–	0.99	0.012
$\Delta\eta$/mPa·s	−166.304	−77.975	319.286	409.862	0.95	0.5
$\Delta\gamma$/mN·m^{-1}	−53.3176	82.9127	538.621	495.844	0.90	0.6

$$\frac{d\rho}{d\mathrm{RH}}/\mathrm{g\cdot cm^{-3}} = -0.0002 \qquad (6)$$

$$\frac{d\rho}{dw_{\mathrm{H_2O}}}/\mathrm{g\cdot cm^{-3}} = -0.2 \qquad (7)$$

The excess molar volume (V^E) was calculated by eq 8 (Figure 3), and it was fitted by means of the Redlich–Kister polynominal equation, eq 9.[22]

$$V^E = \sum_{i=1}^{N} x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i}\right) \qquad (8)$$

$$Q = x_w(1 - x_w)\sum_{i=0}^{c} A_i \cdot (2x_w - 1)^i \qquad (9)$$

In eqs 8 and 9, N, M_i, ρ, ρ_i, Q, x_w, c, and A_i represent the number of components of the mixture (water and IL), molar mass of component i ($\mathrm{g\cdot mol^{-1}}$), density of mixture ($\mathrm{g\cdot cm^{-3}}$), density of pure component ($\mathrm{g\cdot cm^{-3}}$), excess molar volume (Q represents either the viscosity or surface tension deviations), molar fraction of water in an aqueous solution, the degree of the polynomial expansion, and fit parameters, respectively.

The order of the Redlich–Kister equation was optimized by the correlation coefficient (R^2) and root mean square deviation (rmsd) values, eq 10. The order of this equation was tested from first to sixth. It was found that the second-order Redlich–Kister equation estimates V^E with the least rmsd and the highest R^2 (> 0.99). Therefore, a second-order Redlich–Kister equation was found to be the optimum method to estimate the V^E. The A_i parameters, R^2, and rmsd values calculated in this study are shown in Table 4. As can be seen in Figure 3, there is a negative deviation from ideality, providing an indication of the interactions between water and [emim][EtSO$_4$] molecules resulting in negative excess volumes. This departure from the ideal behavior might be due to hydrogen bonds between water and the IL, and these results are in agreement with the literature.[6,20]

$$\mathrm{rmsd} = \sqrt{\sum_{i}^{n} \frac{(z_i^{\mathrm{exptl}} - z_i^{\mathrm{calcd}})^2}{n_{\mathrm{dat}}}} \qquad (10)$$

In eq 10, z_i^{exptl}, z_i^{calcd}, n, and n_{dat} are the experimental and calculated property, number of estimations, and number of experimental data, respectively.

Apparent molar volumes (V_φ, $\mathrm{cm^3\cdot mol^{-1}}$) for IL solutions were calculated from the experimental density of the aqueous solutions measured in this work. The apparent molar volumes are derived from the density of aqueous solutions of [emim][EtSO$_4$], eq 11.

$$V_\varphi = 1000\left(\frac{\rho_w - \rho}{m\rho_w\rho}\right) + \frac{M_{\mathrm{IL}}}{\rho} \qquad (11)$$

In eq 11, ρ_w, ρ, m, and M_{IL} are the density of water, density of aqueous solutions, molality of IL, and molar mass of [emim][EtSO$_4$], respectively. The derived values were also correlated by a Redlich−Mayer equation, eq 12.[23]

$$V_\varphi = V^0_\varphi + S_v \cdot \sqrt[2]{m} + B_v \cdot m \qquad (12)$$

In eq 12, V^0_φ is the limiting apparent molar volume. S_v and B_v are empirical parameters of the model. These fit parameters and standard deviation are listed in Table 5.

Table 5. Coefficients of the Redlich−Mayer Equation[23]

	$10^6\cdot V^0_\varphi$ / $\mathrm{m^3\cdot mol^{-1}}$	$10^6\cdot S_v$ / $\mathrm{m^3\cdot mol^{-3/2}\cdot kg^{1/2}}$	$10^6\cdot B_v$ / $\mathrm{m^3\cdot mol^{-2}\cdot kg}$	R^2	σ / $\mathrm{cm^3\cdot mol^{-1}}$
V_φ	188.93	0.36	−0.01	0.94	2

Effect of RH on Dynamic Viscosity. The effect of RH and $w_{\mathrm{H_2O}}$ of [emim][EtSO$_4$] IL on its viscosity, η, is shown in Table 2. The viscosity decreases with increasing RH and water content of the IL. The change of viscosity with the RH was described by two total derivatives of first order with respect to RH and $w_{\mathrm{H_2O}}$ of fitted equations (linear regression equation, which correlates viscosity of the mixture against RH (R^2 > 0.97 and σ = 2 mPa·s) and against $w_{\mathrm{H_2O}}$ (R^2 > 0.92 and σ = 4 mPa·s)), eqs 13 and 14.

$$\frac{d\eta}{d\mathrm{RH}}/\mathrm{mPa\cdot s} = -0.807 \qquad (13)$$

$$\frac{d\eta}{dw_{\mathrm{H_2O}}}/\mathrm{mPa\cdot s} = -812 \qquad (14)$$

In aqueous solutions of IL, when x_w increases toward 1 (Figure 4), the ionic liquid density and viscosity approach those of pure water, and therefore, the addition of water to [emim][EtSO$_4$] leads to a decrease in viscosity and density of the mixture.[5] The viscosity deviation was calculated following eq 15 and fits the Redlich–Kister polynomial equation, eq 9.[22]

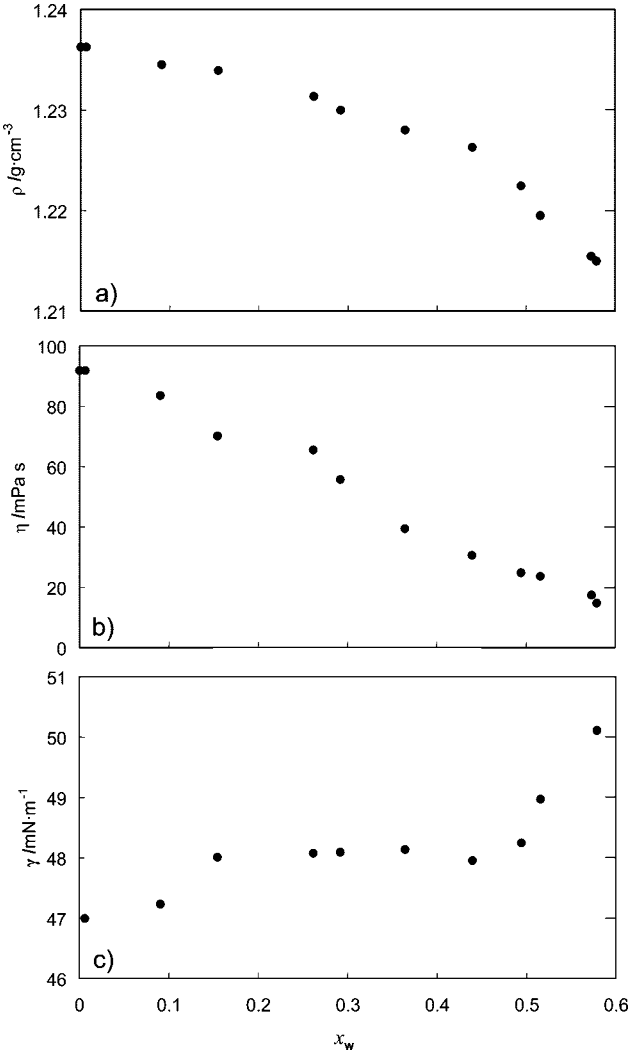

Figure 4. Density (a), viscosity (b), and surface tension (c) values of [emim][EtSO$_4$] as a function of its water mole fraction (x_w) at T = 298.15 K.

$$\Delta\eta = \eta - \sum_{i=1}^{N} \eta_i x_i \qquad (15)$$

In eq 15, N, x_i, η, and η_i represent the number of components of the mixture, mole fraction of component i, viscosity of mixture, and viscosity of pure components, respectively. As has been described in the effect of RH on density subsection and taking into account the statistical parameter values shown in Table 4, a Redlich–Kister equation of third degree was found to be optimum to estimate the $\Delta\eta$. The fit parameters, R^2 and rmsd, are shown in Table 4. The relatively small rmsd value of the fits shows that $\Delta\eta$ could be adequately reproduced by the third-order Redlich–Kister equation.

Effect of RH on Surface Tension. The effect of RH and w_{H_2O} of [emim][EtSO$_4$] IL on the surface tension γ is shown in Table 2. In the studied range, γ increases with increasing RH and water content. The change of surface tension with the relative humidity was described by two total derivatives of first order with respect to RH and w_{H_2O} of fitted equations (third-order polynomial, which correlates surface tension of mixture versus RH and w, $R^2 > 0.97$, $\sigma = 2$ mN·m^{-1} and $R^2 > 0.92$, $\sigma = 0.1$ mN·m^{-1}, respectively), eqs 16 and 17.

$$\frac{d\gamma}{d\mathrm{RH}}/\mathrm{mN\cdot m^{-1}} = 3\cdot 10^{-5}\cdot \mathrm{RH}^2 - 3.4\cdot 10^{-3}\cdot \mathrm{RH} + 7.9\cdot 10^{-2} \qquad (16)$$

$$\frac{d\gamma}{dw_{H_2O}}/\mathrm{mN\cdot m^{-1}} = 4\cdot 10^{4}\cdot w_{H_2O}^2 - 3.4\cdot 10^{-3}\cdot w_{H_2O} + 79 \qquad (17)$$

The experimental γ value of [emim][EtSO$_4$] (47 mN·m^{-1}) is higher than that of conventional organic solvents such as methanol (22.07 mN·m^{-1}) and acetone (23.5 mN·m^{-1}) but less than that of water (71.98 mN·m^{-1}).[24] Taking into account the hydrophilic features of [emim][EtSO$_4$], the surface tension increases (Table 2) as the water content approaches that of pure water (Figure 4). [25,26]

The surface tension deviation was calculated by eq 18 and fitted by means of the Redlich–Kister polynominal equation, eq 9.[22] A Redlich–Kister equation of third degree was found to be optimum to estimate the $\Delta\gamma$. Table 4 gives the fit parameters, R^2 and rmsd.

$$\Delta\gamma = \gamma - \sum_{i=1}^{N} \gamma_i x_i \qquad (18)$$

In eq 18, $\Delta\gamma$, x_i, and γ_i represent the surface tension deviation (mN·m^{-1}), mole fraction of component i, and surface tension of pure component i (mN·m^{-1}), respectively.

As can be seen in Figure 5, comparing the derivative of every regression equation (eqs 6, 13, and 16) with respect to RH, the viscosity is the most sensitive property to the relative humidity of air. This effect is also notable in 1-hexyl-3-methylimidazolium chloride and 1-octyl-3-methylimidazolium chloride ionic liquids.[21]

Conclusions

In this work, the effect of relative humidity of air on the water content, density, apparent molar volume, viscosity and surface tension of the ionic liquid, 1-ethyl-3-methylimidazolium ethylsulfate, was studied. The density, apparent molar volume, and viscosity decrease, and the water content and surface tension of the IL increase as the relative humidity of air increases.

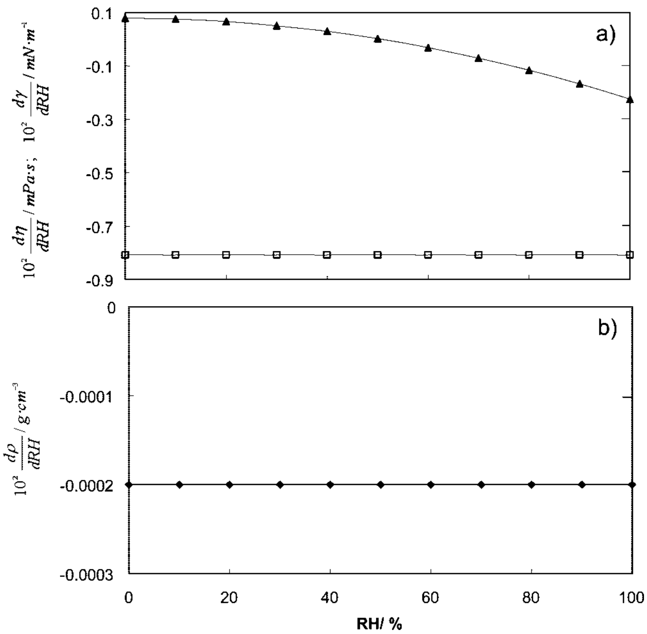

Figure 5. First derivative of regression equations vs relative humidity of air: (a) viscosity (■, eq 13) and surface tension (▲, eq 16) and (b) density of [emim][EtSO$_4$] (♦, eq 6) at $T = 298.15$ K.

As expected, the absorption of atmospheric moisture by the ionic liquid affects its chemical structure, and as a result, noticeable changes to the investigated physical properties (vide supra) occur. Of the studied physical properties, viscosity exhibits the greatest sensitivity to RH.

The apparent molar volume was established by applying the Redlich—Mayer equation. The calculated excess molar volume, the viscosity, and surface tension deviations were found to be negative over the whole studied RH range. They were fitted by the Redlich–Kister equation. The order of the Redlich–Kister equation was optimized by statistical analysis (root-mean-square deviation and correlation coefficient between real and predicted values).

Literature Cited

(1) Nelson, W. *Green solvents for chemistry: Perspectives and practice*; Oxford University press: New York, 2003.

(2) Freemantle, M. Designer solvents - Ionic liquids may boost clean technology development. *Chem. Eng. News.* **1998**, *76*, 32–37.

(3) Palomar, J.; Ferro, V. R.; Torrecilla, J. S.; Rodríguez, F. Density and Molar Volume Predictions using COSMO-RS for Ionic Liquids. An Approach to Solvents Design. *Ind. Eng. Chem. Res.* **2007**, *46*, 6041–6048.

(4) Seddon, K. R.; Stark, A.; Torres, M. J. Influence of chloride, water, and organic solvents on the physical properties of ionic liquids. *Pure Appl. Chem.* **2000**, *72*, 2275–2287.

(5) Widegren, J. A.; Laesecke, A.; Magee, J. W. The effect of dissolved water on the viscosities of hydrophobic room-temperature ionic liquids. *Chem. Commun.* **2005**, 1610–1612.

(6) Rodríguez, H.; Brennecke, J. F. Temperature and composition dependence of the density and viscosity of binary mixtures of water + ionic liquid. *J. Chem. Eng. Data* **2006**, *51*, 2145–2155.

(7) Yang, J. Z.; Lu, X. M.; Gui, J. S.; Xu, W. G. A new theory for ionic liquids—the Interstice Model Part 1. The density and surface tension of ionic liquid EMISE. *Green Chem.* **2004**, *6*, 541–543.

(8) Yang, J. Z.; Lu, X. M.; Gui, J. S.; Xu, W. G.; Li, H. W. Volumetric properties of room temperature ionic liquid 2: The concentrated aqueous solutions of {1-methyl-3-ethylimidazolium ethyl sulphate + water} in a temperature range of 278.2 to 338.2 K. *J. Chem. Thermodyn.* **2005**, *37*, 1250–1255.

(9) Lu, X. M.; Xu, W. G.; Gui, J. S.; Li, H. W.; Yang, J. Z. Volumetric properties of room temperature ionic liquid. 1. The system {1-methyl-3-ethylimidazolium ethyl sulfate + water} at temperature in the range (278.15 to 333.15) K. *J. Chem. Thermodyn.* **2005**, *37*, 13–19.

(10) Zafarani-Moattar, M. T.; Shekaari, H. Apparent molar volume and isentropic compressibility of ionic liquid 1-butyl-3-methylimidazolium bromide in water, methanol, and ethanol at T = (298.15 to 318.15) K. *J. Chem. Thermodyn.* **2005**, *37*, 1029–1035.

(11) Li, W.; Zhang, Z.; Han, B.; Hu, S.; Xie, Y.; Yang, G. Effect of Water and Organic Solvents on the Ionic Dissociation of Ionic Liquids. *J. Phys. Chem. B* **2007**, *111*, 6452–6456.

(12) Wink, W. A. Determining the moisture equilibrium curves of hygroscopic materials. *Ind. Eng. Chem.* **1946**, *18*, 251–252.

(13) Torrecilla, J. S.; Aragón, J. M.; Palancar, M. C. Improvement of Fluidized Bed Dryers for Drying Olive Oil Mill Solid Waste (Olive pomace). *Eur. J. Lipid Sci. Technol.* **2006**, *108*, 913–924.

(14) Chirico, R. D.; Frenkel, M.; Diky, V. V.; Marsh, K. N.; Wilhoit, R. C. ThermoML-An XML-Based Approach for Storage and Exchange of Experimental and Critically Evaluated Thermophysical and Thermochemical Property Data. 2. Uncertainties. *J. Chem. Eng. Data* **2003**, *48*, 1344–1359.

(15) National Institute of Science and Technology (NIST), Physical Reference Data. http://physics.nist.gov/cuu/.

(16) Sieweck, F.; Bettin, H. Review: Solid and liquid density determination. *Technisches Messen* **1992**, *59*, 285–292.

(17) Lim, W. K.; Johnson, H. W.; Wilhelmsen, P. C., Jr.; Stross, F. H. Falling Ball Viscometry. An Instrument for Precise Measurements. *Anal. Chem.* **1964**, *36*, 2482–2485.

(18) Arashiro, E. Y.; Demarquette, N. R. Use of the Pendant drop method to measure interfacial tension between molten polymers. *Mater. Res.* **1999**, *2*, 23–32.

(19) Arce, A.; Rodil, E.; Soto, A. Volumetric and Viscosity Study for the Mixtures of 2-Ethoxy-2-methylpropane, Ethanol, and 1-Ethyl-3-methylimidazolium Ethyl Sulfate Ionic Liquid. *J. Chem. Eng. Data* **2006**, *51*, 1453–1457.

(20) Gomez, E.; Gonzalez, B.; Calvar, N.; Tojo, E.; Dominguez, A. Physical Properties of Pure 1-Ethyl-3-methylimidazolium Ethylsulfate and Its Binary Mixtures with Ethanol and Water at Several Temperatures. *J. Chem. Eng. Data* **2006**, *51*, 2096–2102.

(21) Gomez, E.; Gonzalez, B.; Dominguez, A.; Tojo, E.; Tojo, J. Dynamic Viscosities of a Series of 1-Alkyl-3-methylimidazolium Chloride Ionic Liquids and Their Binary Mixtures with Water at Several Temperatures. *J. Chem. Eng. Data* **2006**, *51*, 696–701.

(22) Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345–348.

(23) Redlich, O.; Mayer, D. M. The molal volume of electrolytes. *Chem. Rev.* **1964**, *64*, 221–227.

(24) The NIST Chemistry webbook, http://webbook.nist.gov/chemistry/name-ser.html, 2005.

(25) Rivera-Rubero, S.; Baldelli, S. Influence of Water on the Surface of Hydrophilic and Hydrophobic Room-Temperature Ionic Liquids. *J. Am. Chem. Soc.* **2004**, *126*, 11788–11789.

(26) Freire, M. G.; Carvalho, P. J.; Fernandes, A. M.; Marrucho, I. M.; Queimada, A. J.; Coutinho, J. A. P. Surface Tensions of Imidazolium Based Ionic Liquids: Anion, Cation, Temperature and Water Effect. *J. Colloid Interface Sci.* **2007**, *314*, 621–630.

Received for review September 12, 2007. Accepted January 15, 2008. The authors are grateful to the Spanish Ministry of Education and Science for their financial support for project CTQ2006-04644 and the Ramón y Cajal research contract of José S. Torrecilla, as well as to Comunidad de Madrid and UCM for the support of 910717 Research Group.

JE700523B