Isothermal Vapour+Liquid Equilibrium and Thermophysical Properties for 1-Butyl-3-methylimidazolium Chloride + 1-Butanol Binary System

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Experimental isothermal vapour+liquid equilibrium (VLE) data are reported for the binary mixture containing 1-butyl-3-methylimidazolium chloride ([bmim]Cl) + 1-butanol at three temperatures: (353.15, 363.15, 373.15) K, in the range of 0-0.17 liquid mole fraction of [bmim]Cl. Additionally, refractive index measurements have been performed at three temperatures: (298.15, 308.15 and 318.15) K in the whole composition range. Densities, excess molar volumes, surface tensions and surface tension deviations of the binary mixture were predicted by Lorenz-Lorentz (n_D-ρ) mixing rule as well as dielectric permittivities and their deviations by known equations. Both types of experimental data were correlated using the Redlich-Kister models by means of maximum likelihood method.

Keywords: Low pressure VLE; refractive index; 1-butyl-3-methylimidazolium chloride ([bmim]Cl); 1-butanol.

Recently, the ionic liquids (IL) have become solvents with large applicability because of their very interesting properties: - low melting points (<100 ^{0}C) and a wide range of temperatures in which they exists in liquid state (about 300 ^{0}C); - reasonable viscosity; - chemical stability up to very high temperatures; - high solubility in nonpolar or polar organic solvents; - high conductivity; - negligible vapour pressure and therefore non-flammable. These make that IL's be used in so-called green chemistry, for partial or total replacement of volatile organic solvents which are, as it is known, flammable and toxic. They can be very interesting solvents for a variety of industrial applications [1]. Beyond these, they are much discussed as selective solvents (entrainers) for various separation processes [2,3]. The methods of their synthesis are well developed [4], but for various scopes it should be well known their properties, in many cases for their mixtures with organic solvents. For a better understanding of their thermodynamic behavior, correlated with the development of predictive thermodynamic models, phase equilibria data and thermodynamic and thermophysical properties are required. As a result, in recent years, various research groups in the world began systematic studies; currently there are more than 12,000 sets of experimental data containing over 58,000 points accumulated in Dortmund Data Bank. They are not far enough, even more many of them are not of satisfactory precision [5] for verifying or development of adequate predictive thermodynamic models involved. Therefore, with our new research project concerning the thermodynamics of IL's with organic solvent mixtures, we aim to enrich the existing data bank and to bring qualitatively original contributions.

It is well known that alcohols form azeotropes with water being difficult to separate and to obtain desired alcohols of high purity without using an appropriate entrainer. It has been shown that new generation green solvent ionic liquids (ILs) can be good in this role. To describe the VLE for the ternary water-alcohol-IL system, VLE for the constituent binary subsystems are required. The VLE experimental data for 1-butanol + water system are known from old literature [6-8] while for [bmim]Cl + water system they were reported recently [9,10]. Here, we determined experimental isothermal VLE data for an IL (1-butyl-3-methylimidazolium chloride, [bmim]Cl) with 1-butanol binary system in the range of (353.15-373.15) K and liquid composition range 0-0.17 mole fraction of [bmim]Cl. The composition range was limited to the reduced quantity of expensive IL which we had at disposal. In addition, refractometric measurements in the range of (298.15-318.15) K have been performed for whole composition range. From refractive index of mixture and densities of the pure components at the same temperatures, the densities, the excess molar volumes, surface tensions and dielectric permittivities and their deviations vs. composition of the binary mixture have been predicted by Lorenz-Lorentz (n_D-ρ) mixing rule [11] or by known equations [12,13]. As far as we know, no experimental data exist in the literature concerning this binary system [14]. The phase equilibria, thermodynamic and thermophysical data reported here will bring new information required for the design of the separation process of 1-butanol using an organic salt as [bmim]Cl and an insight into specific inter and intra molecular interactions or structural arrangements existing in the binary IL + 1-butanol system.

Experimental part

Materials and methods

The chemicals used were of high purity from trustful commercial sources. The characteristics of the used compounds are summarized in table 1. After purification, both chemicals were deposited in closed system to dried atmosphere, on calcium chloride, during all experiments. A good comparison with literature values has been obtained for the density and ultrasonic sound velocity experimental values of the pure compounds. Also a good comparison was found for the refractive index and vapour pressure of 1-butanol. This is shown in table 2.

As for the comparison of our refractive index at 298.15 K for [bmim]Cl, 1.50157, three values were found in the

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Table 1
COMMERCIAL SOURCES, PURITIES AND METHODS OF PURIFICATION OF THE USED CHEMICAL COMPOUNDS

Compound	Commercial source	Purity / mass fraction	Purification method
[bmim]Cl	Fluka	> 0.98	Dried in the oven at 70 ^{0}C and 20 kPa for 48 hours
1-butanol	Riedel de Häen	> 0.995	Dried and stored on molecular sieves 4Å

Table 2
REFRACTIVE INDICES, n_d, DENSITIES, ρ, AND ULTRASONIC SOUND VELOCITY, u, AT ATMOSPHERIC PRESSURE AND VAPOUR PRESSURES, P, OF PURE COMPOUNDS

	n_D[a]		ρ[b] / (g cm^{-3})		u[c] / (m s^{-1})		P[d] / kPa	
Compound / T[e] / K	This work	Lit.	This work	Lit.	This work	Lit.	This work	Lit.
[bmim]Cl /								
298.15	1.50157		1.08104	1.08201[f] 1.07443[g] 1.081[h]	1864.30	1868[g] 1868[h]		
308.15	1.49896		1.07538	1.07651[f] 1.06832[g]	1839.24	1848[g]		
318.15	1.49625		1.06966	1.07104[f] 1.06214[g]	1814.94	1820[g]		
353.15							0.846[l]	
363.15							1.540[l]	
373.15							2.695[l]	
1-butanol /								
298.15	1.39720	1.39747[i]	0.80533	0.80593[i]	1240.56	1239.28[i]		
308.15	1.39308	1.39342[i]	0.79806	0.79821[i]	1206.98	1206.26[i]		
318.15	1.38899	1.3886[j]	0.79021	0.79049[j]	1173.59	1194[j]		
353.15							21.30	21.80[k]
363.15							33.04	34.19[k]
373.15							50.88	51.89[k]

[a] σ_{nD} = 0.0001, [b] σ_ρ =0.00001 g cm^{-3}, [c] σ_u = 0.1 m s^{-1}, [d] σ_P = 0.1% of measured value, and [e] σ_T = 0.1 K. [f][15]; [g][16]; [h] extrapolated value from [17]; [i][18]; [j][19]; [k][20]; [l]calculated values cf. [31].

literature: 1.5057 for a saturated liquid aqueous solution of [bmim]Cl of 45.24 mole % IL concentration [21], 1.52469 for a saturated liquid aqueous solution of 77.87 mole % IL and 1.52564 for a saturated liquid ethanolic solution of 81.26 mole % IL [17]. According to the authors of [21,17], after the above mentioned concentrations, the IL solutions became solids similarly to the state of the pure [bmim]Cl compound. However, the water concentrations of the saturated solutions of [bmim]Cl are in contradiction in [21] and [17]. In our case, the supercooled liquid [bmim]Cl compound [22] with a water content smaller than 0.07 mole % was used.

The vapour pressures measurements of pure 1-butanol and of the binary mixtures were carried out by an ebulliometric method using a Swietoslawski ebulliometer modified according to Rogalski and Malanowski [23]. The apparatus, is described in details elsewhere along with the experimental procedure [24], usually employed [23,25,26].

The equilibrium temperatures in the ebulliometer were measured with an accuracy of ±0.1 K, by means of mercury thermometers (previously calibrated at National Institute of Metrology, Bucharest).

The vapour pressure was measured by means of a mercury manometer. Manometric readings were performed with a cathetometer to an accuracy of ±0.1 mm, and pressure reproducibility was estimated to be better than 50 Pa. The accuracy of the pressure measurements is estimated to be 0.1% of measured values. The composition of the liquid phase in equilibrium with the vapour phase was analyzed by the refractometric method making use of a calibration curve obtained by measurements of the refractive index of weighed samples (accuracy better than ±0.2 mg by GH-252 A&D Japan balance) at 298.15 K and data correlation with Redlich-Kister polynomials [27] with three parameters in the form:

$$n_D^E = n_D - \left[x n_{D,1} + (1-x) n_{D,2}\right] = \\ = x(1-x)\left[a_0 + a_1(1-2x) + a_2(1-2x)^2\right] \qquad (1)$$

The Redlich-Kister parameters a_0, a_1, a_2 of eq. (1) were obtained by maximum likelihood optimization method using the following objective function:

$$OF = \sum_{i=1}^{N}\left[\frac{\left(x_{i,exp} - x_{i,calc}\right)^2}{\sigma_x^2} + \frac{\left(n_{D,i,exp}^E - n_{D,i,calc}^E\right)^2}{\sigma_{n_D^E}^2}\right] \qquad (2)$$

The refractive index was measured by a digital Abbemat RXA 170 from Anton-Paar (Austria) at the wavelength of the D line of sodium, 589.3 nm, with accuracy better than ±0.0001. The temperature of the Safire prism was controlled by a Peltier element to within ±0.01 K and the calibration of the apparatus was carried out with bidistilled and deionized water and by determining refractive indexes at 298.15 K and its deviations for the binary cyclooctane + toluene system at nine compositions. The error resulted from the comparison of our refractive index deviation values, n_D, and those calculated from 2-parameter Redlich-Kister correlation of experimental data from literature [28] was $2 \cdot 10^{-4}$ in mean absolute average, which it means a good comparison.

The estimated error for n_D^E, which is defined as

$$n_D^E = n_D - x n_{D,1} - (1-x) n_{D,2} \qquad (3)$$

is better than $2 \cdot 10^{-4}$. In eqs. (1) and (3), $n_{D,2}$ and $n_{D,A}$ represent the refractive indexes of the pure components 1 and 2, n_D, the refractive index for the mixture 1+2, and x denotes the molar fraction of component 1 in the binary mixture. Each measurement of refractive index consisted in 4 readings for the same sample. Its averaged value is reported here as one experimental point. Special attention

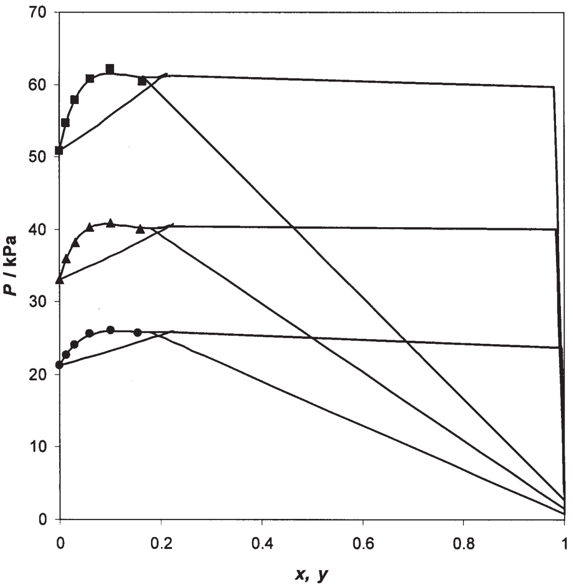

Fig. 1. Isothermal (vapour+liquid) equilibrium data for ([bmim]Cl (1) + 1-butanol (2)) system at 353.15 K (●), 363.15 K (▲), and 373.15 K (■); Solid points: experimental bubble curve (pressure P vs. liquid composition x); (——) 3rd order Redlich-Kister correlation of the bubble curve and calculated dew curve (pressure P vs. vapour composition y) with ideal behaviour assumption of the vapour phase.

Table 3

(VAPOUR+LIQUID) EQUILIBRIUM DATA FOR THE ([BMIM]CL (1) + 1-BUTANOL (2)) SYSTEM. PRESSURE, P_e, TEMPERATURE, T, AND LIQUID PHASE COMPOSITION, x_e, ARE EXPERIMENTAL DATA AND VAPOUR PHASE COMPOSITION, y_c, ACTIVITY COEFFICIENTS, γ_1, γ_2, AND EXCESS GIBBS ENERGY, G^E, ARE CALCULATED DATA WITH 3RD ORDER REDLICH-KISTER MODEL ASSUMING IDEAL VAPOUR PHASE

x_e [a]	y_c [a]	P_e [b] / kPa	γ_1	γ_2	G^E / (J mol^{-1})
T^c = 353.15 K					
0	0	21.31	176	1	0
0.0136	0.0741	22.64	155	1.0008	192
0.0306	0.1392	24.04	131	1.0045	446
0.0603	0.1983	25.57	98	1.0183	867
0.1014	0.2239	26.07	68	1.0524	1391
0.1555	0.2151	25.72	42	1.1284	2009
T^c = 363.15 K					
0	0	33.04	185	1	0
0.0138	0.0926	35.94	157	1.0012	214
0.0311	0.1589	38.20	128	1.0057	468
0.0607	0.2118	40.30	91	1.0224	891
0.1015	0.2250	40.93	59	1.0628	1413
0.1603	0.1999	40.05	33	1.1613	2065
T^c = 373.15 K					
0	0	50.88	141	1	0
0.0136	0.0817	54.73	121	1.0011	207
0.0324	0.1463	57.84	99	1.0058	472
0.0620	0.1967	60.72	71	1.0219	884
0.1019	0.2123	62.17	48	1.0596	1384
0.1654	0.1918	60.44	26	1.1617	2063

[a] σ_{x1} = 0.001, [b] σ_P = 0.1% of measured value, and [c] σ_T = 0.1 K.

was devoted to avoid moisture absorption from the atmosphere in pure chemicals and in their binary mixtures since it is known that water content of the sample has an important effect on refractive index value. By this way, the error in the determination of the liquid phase composition was 0.001 mole fraction.

The VLE apparatus and experimental procedure were successfully verified and used for investigation of different other systems as mentioned previously [29].

The density and ultrasonic sound velocity measurements of the pure compounds at the three temperatures (298.15, 308.15, and 318.15) K were carried out by using a density and sound velocity meter Anton Paar DSA-5000 M with precision of ±0.000005 g·cm^{-3} and ±0.01 m s^{-1}. Dried air and distilled deionized ultra pure water at atmospheric pressure were used as calibration fluids for the cell. The probes thermostating was maintained constant at ±0.01 K. The experimental measurement uncertainty for density was better than 0.0001 g·cm^{-3} and for the sound velocity better than 0.1 m s^{-1}.

Results and discussions

The vapour pressures of pure 1-butanol compound measured in the ebulliometer at the three temperatures are given in table 2 together with literature values. Good agreement can be observed. The differences are acceptable since it is well known that the vapour pressure is dependent on the purity of the chemical used.

The experimental isothermal (P, x) data measured for the binary system at (353.15, 363.15, 373.15) K are shown in figure 1 and are summarized in table 3.

The data were correlated using the 3rd order Redlich-Kister model [27]. The regression was performed by means of maximum likelihood method employing a program described by Hala et al. [30]. In this program, the objective function is defined as follows:

$$S=\sum_{i=1}^{N}\left[(P_{ie}-P_{ic})^2/\sigma_p{}^2+(T_{ie}-T_{ic})^2/\sigma_T{}^2+(x_{ie}-x_{ic})^2/\sigma_x{}^2\right] \quad (4)$$

where N is the number of experimental points, P_{ie}, T_{ie}, and x_{ie} are the experimental data and P_{ic}, T_{ic} and x_{ic} are the corresponding calculated values for pressure, temperature, and liquid composition of component 1, respectively. In this work, the standard deviations for the measured quantities were set to σ_P = 0.1% of measured value, σ_T = 0.1 K, and σ_x = 0.001, respectively.

All standard deviations of correlation were calculated using the expression: $\sigma_Z=\left[\sum(Z_{i,e}-Z_{i,c})^2/(N-m)\right]^{1/2}$, where Z is the value of the property P, T, x, N is the number of experimental points and m = 2 is the number of model parameters.

Table 4
PARAMETERS OF THE 3RD ORDER REDLICH-KISTER CORRELATION EQUATION AND STANDARD DEVIATIONS FOR THE (*P*, *T*, *x*) DATA OF THE ([BMIM]CL (1) + 1-BUTANOL (2)) SYSTEM

T/K	A_0/ (J mol^{-1})	A_1/ (J mol^{-1})	σ_x	σ_P/kPa	σ_T/K
353.15	5.2975	0.1275	0.0005	0.007	0.1
363.15	4.7841	-0.4373	0.0002	0.010	0.1
373.15	4.5559	-0.3938	0.0003	0.032	0.2

Since the experimental data were measured at low pressures, the ideal behaviour of the vapour phase was considered.

The experimentally determined vapour pressures of pure 1-butanol (as given in tables 2-3) and those estimated for [bmim]Cl by Ambrose-Walton method [31] (table 2) were used for the calculations. The required critical temperature and pressure as well as acentric factor for [bmim]Cl have been estimated in [32] and used here as found. The results of fitting are summarized in table 4. In the used program, there are no parameter constraints, and each isotherm is correlated independently. The parameters describe, as best as possible, the particular isotherm till the azeotropic points.

In the range of the liquid composition measurements, in figure 1 and table 4 it can be seen a good agreement between experimental and calculated bubble curves. At this point, in figure 1 and table 3 it can be noticed that the isothermal phase diagrams features a slight non-physical behaviour: at each isotherm, the bubble pressures (*x* vs *P*) has one maximum that is not azeotropic, and the dew pressure (*y* vs *P*) shows a small loop. When this kind of phase diagram is found, the reader immediately may consider that in reality the system features a liquid-liquid phase split that the calculation model cannot make visible, especially when the activity coefficients for [bmim]Cl are high. Therefore, NRTL [33] and Wilson [34] models were tested, too. NRTL gives similar results as 3rd order Redlich-Kister equation, while Wilson model failed in correlation, due probably to some numerical problems.

At the crossing of the two dew lines, it is possible that the vapour phase is in equilibrium with two distinct liquid phases and at higher pressures, a liquid-liquid phase split exists. But firstly, the one should be aware that in figure 1, the temperature *T* is also affected by different uncertainties resulted from correlation and they are not appearing in that figure. Secondly, a liquid-liquid phase stability analysis performed till the azeotropic points (by calculating liquid and vapour total Gibbs energies vs composition and checking the common tangents to these curves) did not indicate any stable vapour-liquid-liquid equilibrium phases. Thirdly, at any of the investigated temperatures no second liquid phase was observed during experiments. The vapour pressures measurements have been performed also for a binary liquid mixture of 0.24-0.25 mole fraction of IL at all temperatures. During the correlation procedure it was found that these measured (*P*, *T*, *x*) values were out of the equilibrium due probably to the fact that a small liquid-liquid phase split was visually observed in the vapour phase condensate at each temperature. Even the high values obtained for the [bmim]Cl activity coefficients (table 3) are indicating a immiscibility in the liquid phase, one should be aware that these values are strongly dependent on the vapour pressure values of the pure [bmim]Cl compound. If these values are in reality a bit higher than those estimated, the afferent activity coefficients will decrease significantly.

Table 5
CALCULATED PRESSURES, *P*, AND VAPOUR PHASE COMPOSITION, $y_{1,AZ}$, AT TEMPERATURES, *T*, OF THE AZEOTROPIC POINTS FOR ([BMIM]CL (1) + 1-BUTANOL (2)) BINARY SYSTEM

T / K	P / kPa	$y_{1,az}$
353.15	25.79	0.203
363.15	40.33	0.206
373.15	61.13	0.199

We can make the conclusion that the small inconsistencies detected in the calculated VLE data are due to rather small number of the experimental data points, to somewhat a bit higher uncertainty in the pressure measurement (which is difficult to evaluate since small quantities of water in [bmim]Br are present) and to the used vapour pressures for the pure [bmim]Cl compound. However, we can say that the binary mixture of [bmim]Cl + 1-butanol shows only an homogenous azeotropic behaviour with the calculated coordinations shown in table 5. A correlation of the experimental VLE data from this work was made also by using the Barker method [35], but the situation did not change significantly.

The experimental isothermal (*x*, n_D) data for the binary system have been determined at (298.15, 308.15 and

Table 6
EXPERIMENTAL REFRACTIVE INDEXES, n_D, AND ITS DEVIATIONS FROM IDEALITY, n_D^E, VS. LIQUID MOLE FRACTION *x*, FOR ([BMIM]CL (1) + 1-BUTANOL (2)) BINARY SYSTEM

x^a	$n_D{}^b$	n_D^E	x^a	$n_D{}^b$	n_D^E
		^cT = 298.15 K			
0	1.39720	0	0.4738	1.46175	0.0152
0.1137	1.41738	0.0083	0.6596	1.47841	0.0124
0.1831	1.42814	0.0118	0.7945	1.48866	0.0086
0.2814	1.44054	0.0139	0.8503	1.49253	0.0066
0.3962	1.45372	0.0151	1	1.50157	0
		^cT = 308.15 K			
0	1.39308	0	0.4738	1.45866	0.0155
0.1137	1.41414	0.0090	0.6596	1.47553	0.0126
0.1831	1.42449	0.0120	0.7945	1.48585	0.0086
0.2814	1.43717	0.0143	0.8503	1.48976	0.0067
0.3962	1.45059	0.0156	1	1.49896	0
		^cT = 318.15 K			
0	1.38899	0	0.4738	1.45556	0.0158
0.1137*	1.41214	0.0109	0.6596	1.47260	0.0129
0.1831	1.42059	0.0120	0.7945	1.48308	0.0089
0.2814*	1.43313	0.0139	0.8503	1.48701	0.0068
0.3962	1.44743	0.0159	1	1.49625	0

$^a\sigma_x$ = 0.0001, $^b\sigma_{nD}$ = 0.0001, and $^c\sigma_T$ = 0.01 K. *partial evaporation of the sample.

Table 7
REDLICH-KISTER COEFFICIENTS A_j [EQ. (1)] AND THE STANDARD DEVIATIONS OF THE COMPOSITION σ_x AND OF THE REFRACTIVE INDEX DEVIATION $\sigma_{n_D^E}$ FOR ([BMIM]CL (1) + 1-BUTANOL (2)) BINARY SYSTEM

T/K	a_0	a_1	a_2	σ_x	$\sigma_{n_D^E}\cdot 10^4$
298.15	0.0593	0.0194	0.0134	0.0010	1.7
308.15	0.0604	0.0209	0.0148	0.0013	1.9
318.15	0.0610	0.0220	0.0194	0.0047	6.9

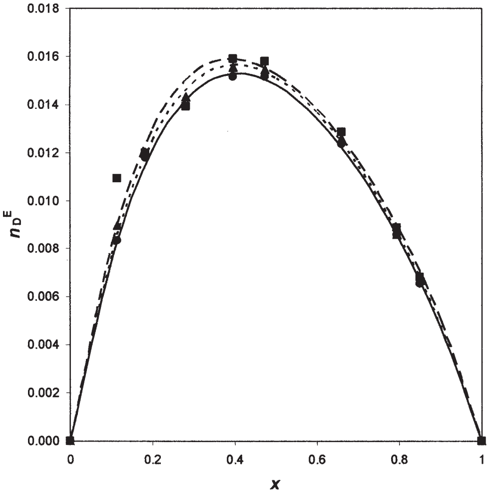

Fig. 2. Refractive index deviations n_D^E vs. liquid composition x for ([bmim]Cl (1) + 1-butanol (2)) system at 298.15 K(●), 308.15 K(▲), and 318.15 K (■); Solid points are calculated values by eq. (3); Lines are 4th order Redlich-Kister correlation for 298.15 K (–), 308.15 K (- - -) and 318.15 K (— —).

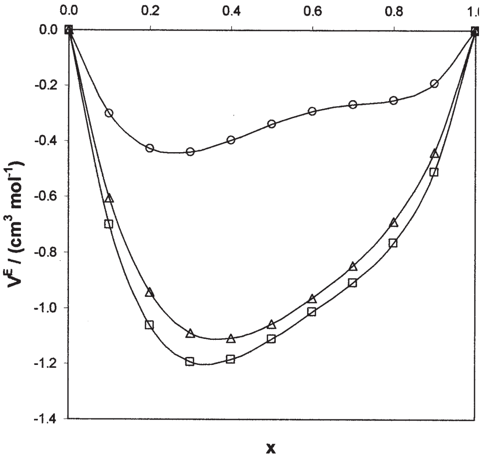

Fig. 4. Excess molar volumes V^E vs. liquid composition x predictions for ([bmim]Cl (1) + 1-butanol (2)) system at 298.15 K (- o -), 308.15 K (- Δ -), and 318.15 K (- □ -)

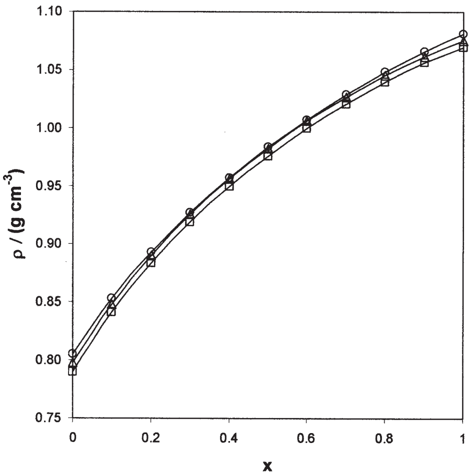

Fig. 3. Density ρ vs. liquid composition x predictions for ([bmim]Cl (1) + 1-butanol (2)) system at 298.15 K (- o -), 308.15 K (- Δ -), and 318.15 K (- □ -).

318.15) K and they are shown in table 6 with the calculated refractive index deviations.

The correlation of these data at each temperature has been made by 3-parameters Redlich-Kister model by using maximum likelihood method, following the procedure described for 298.15 K in the section *Method*. The correlation results are presented in table 7 and the variation of the refractive index deviation vs. composition is shown in figure 2.

Unexpected significant values for the standard deviations of the liquid compositions have been obtained. This can happen either because strong physical interactions take place between the two components of the system (which results in complexes that behave as distinct chemical species [36], or because a very small liquid-liquid split was present in the prepared mixtures. However, a second liquid phase was not observed visually in any of the investigated mixtures. Basically, [bmim]Cl ionic liquid can act both as a hydrogen-bond acceptor ([Cl]$^-$) and donor ([bmim]$^+$) and would be expected to interact with 1-butanol which have both accepting and donating sites. On the other hand, it is well known that 1-butanol is hydrogen-bonded solvent with both high enthalpies of association and association constant. Hence, it should be expected to stabilize [bmim]Cl with hydrogen-bonded donor sites. The [bmim]Cl is a very complicated and highly interacting molecule, especially when the other compound is water or alcohol [36].

The higher deviations obtained for 318.15 K (fig. 2) are due to the partial evaporation on the prism of two samples noted with asterisk in table 6. Since refractive index deviation is situated from one side to another of the curve vs. composition, elimination of these two points does not change much the correlated respective variation.

The refractive index dependence on composition is generally used as calibration curves for phase composition determinations at pressure-temperature equilibrium data sets, by ebulliometry when VLE data are measured, as it was shown here. Since the refractive index of a liquid at sodium D line light, n_D, is a property ease to measure with good accuracy, it was connected with other thermophysical or electrical properties, such as density, surface tension, and dielectric permittivity, by numerous empirical and theoretical equations as referenced in [37].

In this work, from refractive index data vs. composition and densities of the pure compounds at (298.15, 308.15 and 318.15) K, densities, excess molar volumes, surface tensions and dielectric permittivities at optical frequency and their deviations for the binary mixture vs. composition were determined by Lorenz-Lorentz mixing rule [11] or by known equations [12,13]. The selection of the mixing rule was made after analyzing of ten different mixing rules results in giving the refractive indices from experimental densities for twelve binary mixtures of various polarity at 298.15 K [37].

The predicted variation of the densities and excess molar volumes with composition and temperature for the binary ([bmim]Cl (1) + 1-butanol (2)) system are shown in figures 3 and 4.

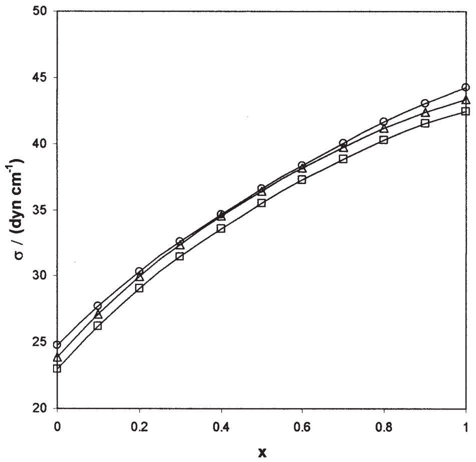

Fig. 5. Surface tensions σ vs. liquid composition x predictions for ([bmim]Cl (1) + 1-butanol (2)) system at 298.15 K (- o -), 308.15 K (- Δ -), and 318.15 K (- □ -)

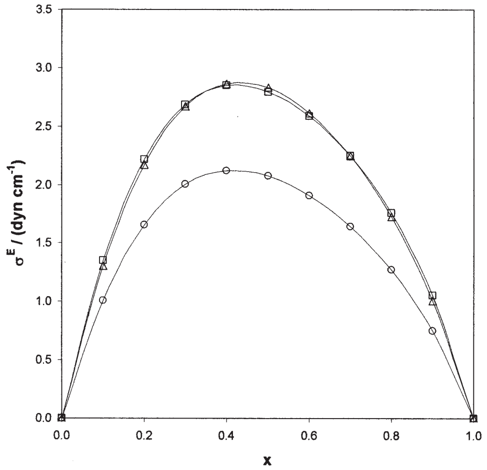

Fig. 6. Excess surface tensions σ^E vs. liquid composition x predictions for ([bmim]Cl (1) + 1-butanol (2)) system at 298.15 K (- o -), 308.15 K (- Δ -), and 318.15 K (- □ -)

As can be observed in figure 4, the V^E is negative on whole composition interval and it is more negative when the temperature increases. Similar behaviour was found also by applying other good mixing rules like Gladstone-Dale, Edwards and Eykman [38]. The temperature effect is not specific to new hydrogen bonds formation between unlike molecules; it is most likely due to the packing between hydrogen acceptor sites of 1-butanol and donor sites of imidazolium ([bmim]$^+$) cycle. These packing effects became more dominant and increase with temperature, as it was observed for other systems in literature [39].

The surface tension of a liquid is a property of great importance in mass transfer processes such as distillation, extraction, or absorption. It is not easily measured, and considerable attention has been paid to the development and analysis of equations allowing its prediction from properties for which data are more readily available. The surface tension σ is related to the densities of the liquid ρ_L and of the vapour ρ_V phases of the substance by using the Macelod [12] equation:

$$\sigma = ct(\rho_L - \rho_V)^4 \qquad (5)$$

For a pure liquid compound, multiplying both sides by the molar mass M and ignoring ρ_V in comparison with ρ_L affords the Sugden equation [13]:

$$\sigma^{1/4} M / \rho_L = \sigma^{1/4} V_m = Parachor \qquad (6)$$

from which it results:

$$\sigma = \left(\frac{Parachor}{V_m}\right)^4 \qquad (7)$$

in which *Parachor* is assumed as mole-wise additive and V_m is calculated from experimental densities of pure compounds and those of the mixtures given by the Lorenz-Lorentz relation [11] (from Redlich-Kister correlated refractive indices). So, we used equation (7) to predict the surface tensions of binary liquid mixtures at three temperatures (298.15, 308.15 and 318.15) K and after that to calculate the surface tension deviation from ideality by applying a similar equation with equation (3). Surface tension variation with composition and temperature is shown in figure 5 and surface tension deviation variation with the same two variables appears in figure 6.

The parachors of the pure compounds have been predicted by additive group contribution methods of Tyn and Calus, 1975 [40]. The surface tensions of pure 1-butanol compares well with those determined experimentally in literature [41] with mean absolute relative deviation of 2.7 % on the three temperatures examined in this work. The calculated surface tensions for pure [bmim]Cl are about 20 % lower than those brutish extrapolated from literature experimental data [42]. As can be seen in figure 6, the surface tensions deviations predicted here are positive on whole composition range and at all three temperatures being higher at higher temperatures. This is explained by the volume expansion resulted from the new H-bonds and packing between unlike molecules in the binary mixture of [bmim]Cl + 1-butanol. It seems that packing of the molecules is dominant since excess surface tension is generally higher at higher temperatures. In the range of about 0.4-0.7 mole fraction of [bmim]Cl the excess surface tension at 318.15 K is slightly lower than that from 308.15 K. The differences are included in the uncertainty of the present predictions of minimum 2.7 %.

From refractive index data, the relative permittivity at optical frequency can be calculated by squaring the refractive index determined at the wavelength of 589.3 nm. For 1-butanol, the relative permittivity agree well with those extrapolated at the three temperatures of (298.15, 308.15 and 318.15) K from experimental literature data [43] with mean absolute relative deviation of 2.6 %. No data have been found for [bmim]Cl for comparison. The dielectric permittivity (fig. 7) at optical frequency is obtained by multiplying relative permittivity by vacuum permittivity. The excess permittivity (fig. 8) calculated by a

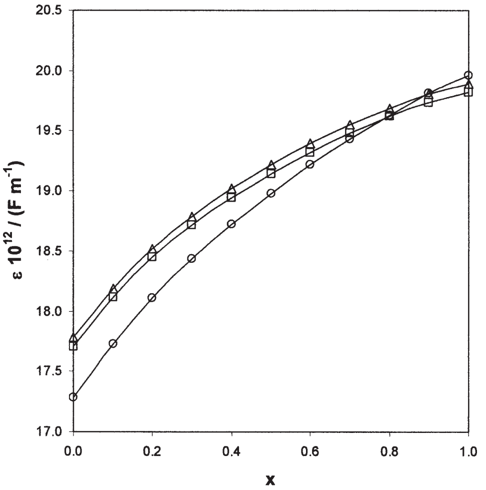

Fig. 7. Dielectric permittivities ε vs. liquid composition x at optical frequency predictions for ([bmim]Cl (1) + 1-butanol (2)) system at 298.15 K (- o -), 308.15 K (- Δ -), and 318.15 K (- □ -)

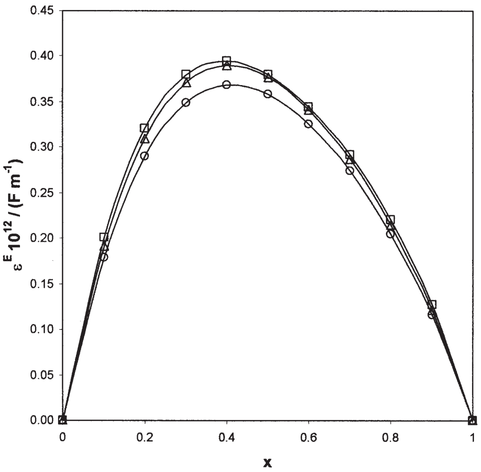

Fig. 8. Excess dielectric permittivities ε^E vs. liquid composition x at optical frequency predictions for ([bmim]Cl (1) + 1-butanol (2)) system at 298.15 K (- o -), 308.15 K (- Δ -), and 318.15 K (- □ -)

similar equation like (3) is found to be positive on whole composition interval and increase with increasing temperature with a maximum around (0.36-0.39) 10^{-12} F m^{-1} and 0.4 mole fraction of [bmim]Cl. This indicates again that both unlike molecular species interact in such a way that they act as more H-bonded structure than those of pure compounds themselves.

Conclusions

The binary 1-butyl-3-methylimidazolium chloride + 1-butanol system has been investigated isothermally at vapour-liquid equilibrium at three temperatures: (353.15, 363.15, and 373.15) K. By correlation of the experimental (P, T, x) data with 3rd order Redlich-Kister like thermodynamic model it was found that the system is azeotropic with high positive deviations from ideality. Excess molar enthalpy calculated from the excess molar Gibbs energy temperature dependence by Gibbs-Helmholtz equation is positive and high (e.g. at an average temperature of 363.15 K and 15 mole % of [bmim]Cl in mixture, it is 2628 J mol^{-1}) indicating again specific interactions between IL and organic solvent molecules. No excess enthalpy value has been found in literature for comparison in order to check the thermodynamic consistency of the reduced VLE data. However, since (P, T, x) experimental data did not show any systematic deviations during the correlation procedure with the two parameters thermodynamic model, we can say that they are thermodynamic consistent. The possible locations of the azeotropic points have been found. For the same system, refractive index measurements have been performed for other three temperatures (298.15, 308.15 and 318.15) K in whole composition interval. Excess refractive index is positive at all temperatures on whole composition range and increase with increasing temperature. Using the Lorenz-Lorentz (n_D-ρ) mixing rule, the densities, excess molar volumes, surface tensions and surface tension deviations have been predicted. By other known relations, dielectric permittivity and its deviations have been calculated, too, at the same temperatures of (298.15, 308.15 and 318.15) K. Structural effects for the binary investigated mixture have been explained in terms of excess thermodynamic and thermophysical properties.

Acknowledgments: This contribution was carried out within the research programme "Chemical thermodynamics and kinetics. Quantum chemistry" of the "Ilie Murgulescu" Institute of Physical Chemistry, financed by the Romanian Academy. Support of the EU (ERDF) and Romanian Government, which allowed for the acquisition of the research infrastructure under POS-CCE O 2.2.1 Project INFRANANOCHEM - Nr. 19/01.03.2009, is gratefully acknowledged.

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Manuscript received: 23.04.2014