



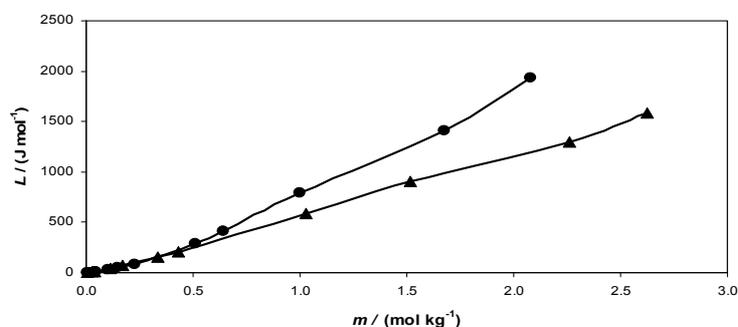
SOLUTION MOLAR ENTHALPIES FOR 1-BUTYL-3-METHYLIMIDAZOLIUM CHLORIDE + 1-PROPANOL SYSTEM AT 303.56 AND 318.68 K

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Enthalpies of solution for 1-butyl-3-methylimidazolium chloride ([bmim]Cl) + 1-propanol system have been measured in a SETARAM C80 3D calorimeter with reversal mixing mechanism over the composition range from $m = 0.0048$ to $2.6224 \text{ mol kg}^{-1}$ of [bmim]Cl at temperatures of 303.56 K and 318.68 K and atmospheric pressure. The data have been correlated adequately with Archer and Rard (1998) model for electrolyte systems. The mean relative deviations in absolute value obtained in molar enthalpy of solution correlation were situated between 5.9 % and 11.2 %. The molar enthalpies of solution at



infinite dilution, the apparent relative molar enthalpies for the solutes and relative molar enthalpies L for the mixtures were determined according to this model. The latter thermodynamic property is endothermic throughout the whole composition range of studied homogenous mixtures, and at constant mole fraction decreases with increasing temperature. The negative solution molar enthalpy at infinite dilution confirmed that within low concentration range of the IL, the interactions which appear at mixing of the two compounds are strongly attractive and they are most likely dominated by the packing of unlike molecules.

INTRODUCTION

Ionic liquids (ILs), a new class of green solvents with low melting point ($< 373 \text{ K}$), exhibit unique physicochemical properties.¹⁻⁴ Due to their negligible vapor pressures, they have been suggested as replacements for volatile organic compounds (VOC) (which are flammable and toxic) and in a growing number of applications such as in separations, catalysis, chemical reactions, nanoscience, and electrochemistry.⁴⁻⁷ 1-Butyl-3-methylimidazolium chloride is known as prototype IL, used for the synthesis of other more complicated ILs.

The multi-purpose utilization of pure ILs or of their mixtures with organic solvents requires

reliable thermodynamic data of phase equilibria, activity coefficients including those at infinite dilution, heat and excess heat capacities, heats of solution and excess molar enthalpies and thermophysical data such as density, surface tension, viscosity, speed of sound, refractive index and conductivity.

To date, for the 1-propanolic system of [bmim]Cl only two types of experimental data have been reported:⁸ vapor-liquid equilibria and activity coefficients at infinite dilution (pure solvents).

The experimental data of apparent and relative molar enthalpies (that approximate excess molar enthalpies in terms of Pitzer's theory, *e.g.*⁹) and enthalpies of solution at infinite dilution for the selected IL + 1-propanol system presented in this

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paper represent a continuation of our study on thermodynamic and thermophysical properties on prototype ILs with organic solvents (alcohols, water) systems.¹⁰⁻¹⁵ In the available literature^{8,16} for the [bmim]Cl + 1-propanol system no data on solution and excess molar enthalpies have been found. These data together with above mentioned measured properties for this system offer a better understanding of the nature of the interactions between the IL cations and anions and the other compound which is 1-propanol. But most importantly, for a better understanding of solutions behavior, it is recommended to evaluate the derivative excess properties at infinite dilution, where a single solute molecule is surrounded only by solvent molecules. Since solute-solute interactions are no longer present, infinite dilution excess properties reflect almost completely unlike pair interactions and yield information about such intermolecular forces.¹⁷

The ILs and electrolyte systems and the infinite dilution concentration range are very important for industry from both experimental and modeling viewpoints.¹⁸ There is an increasing need for enthalpic-thermodynamic properties estimation and experimentally - based improved electrolyte models in a wide range of industries.¹⁸

EXPERIMENTAL

The ionic liquid [bmim]Cl was purchased from Fluka with stated purity of >0.998 mass fraction and 0.20 mass percents of water content. It was dried until constant mass under vacuum at 316.15 K and 0.1 kPa for three weeks and stored afterwards at 298.15 K under the same vacuum conditions, during all experiments. The water content was reduced to 0.05 mass percent. The additional purification consisted in successive vacuum drying and weighing steps, until a constant mass of the sample was reached. As the total mass loss was less than the one corresponding to certified water content, the difference was ascribed to residual water (not possible to remove at 0.1 kPa). A significant decrease of the producer's certified water content was thus obtained. 1-Propanol was also purchased from Fluka, with stated purity of 0.998 mass fraction, and it was dried by storing it on molecular sieves before use. The fusion temperature of the IL and its fusion enthalpy are reported elsewhere.¹⁴⁻¹⁵

The calorimetric measurements for the enthalpy of solution measurements were carried out by using a SETARAM C80 3D computer-controlled mixing and reaction calorimeter by means of the reversal mixing cells made of stainless steel. Details on the measuring and reference cells as well as on the heat measuring procedure and the method of calibration can be found in our previous paper¹³ and in literature, for a similar calorimeter.^{19,20} The amount of

[bmim]Cl weighted in the lower recipient of the measuring cell was between 1 and 401.3 mg. The same amount of 1-propanol was added volumetrically by means of special syringes in the lower container of the reference cell. In the larger, upper container of each cell the 1-propanol sample was weighted in amounts between 0.8761 and 1.1902 g. The temperature was measured by means of a 100 Ω platinum resistance thermometer located between the two vessels, and it remained constant to within ± 0.05 K during each measurement. The thermal equilibrium was reached in 2-3 hours. The complete isotherm for 303.56 K was measured first, then the one for 318.68 K, following a similar protocol with that reported for the [bmim]Cl + water system measurements.¹³ It is worth mentioning that the rocking device of the calorimeter was running continuously until reaching of the peak baseline.

The accuracy of the calorimeter was checked for temperature and enthalpy measurements by melting high purity indium (>0.9999 mass fraction) by means of standard cells made of stainless steel, with very good results (deviations against standards of 0.02 K for temperature and 1% for the melting enthalpy) and by performing test measurements of the enthalpies of solution in the high dilution region for KCl (crystals) in double-distilled and deionized water. The acquired values for the latest case at molality $m = 0.0673$ mol kg^{-1} were 2.5% lower than literature values²¹ and 0.6% lower than calculated literature value at infinite dilution²¹, determined at 303.15 K. The corresponding enthalpy of mixing $\Delta_s H_{m,mix}$ obtained in this study was 8% higher than the reference value²¹. Our mixing enthalpy reproducibility was of 0.1% of the measured value. The KCl samples (Merck > 0.995 mass fraction) were carefully conditioned as recommended in literature²¹. Samples were weighed on a GH-252 A&D Japan electronic balance with uncertainty of ± 0.1 mg. The estimated uncertainty of the molality is ± 0.0001 mol kg^{-1} .

The solution molar enthalpy for [bmim]Cl + 1-propanol system was measured at 303.56 and 318.68 K and atmospheric pressure in the range from 0.0048 to 2.6224 mole kg^{-1} of [bmim]Cl. The room temperature was 298 K and kept constant by air conditioning system during all measurements.

THEORY AND CORRELATIONS

The ILs are organic salts with low melting points (<373 K) containing positive and negative ions which in solution with a proton donor organic solvent can be regarded as electrolyte mixtures.³ For the evaluation of the thermodynamic data, the available semi-empirical electrolyte models can be used. For [bmim]Cl + 1-propanol system, due to complex molar enthalpies of solution behavior and the high number of experimental points available, the 7-parameters Archer and Rard²² model has been chosen. Relevant literature²³ states that "The number of the parameters used to represent the experimental data depends on the molecular complexity of the excess molar enthalpy behavior, the quality of the data, and the number of data points available."

**Archer and Rard model²²
for the molar enthalpy of solution
at infinite dilution determination**

Archer and Rard model²² is an extension of Pitzer - type model⁹ and allows for a better correlation when a larger amount of experimental data is available for electrolyte solutions.

According to this model, the molar solution enthalpy for the solute, $\Delta_s H_m$, at constant

temperature T and pressure P may be expressed as:

$$\Delta_s H_m = \Delta_s H_m^0 + \phi L \quad (1)$$

where $\Delta_s H_m^0$ is the molar solution enthalpy for the solute at infinite dilution and ϕL is its apparent relative molar enthalpy. According to the model²², for 1-1 electrolytes, as is the case for the investigated systems here, ϕL has the following expression:

$$\phi L = \frac{2A_H}{2b} \ln(1 + bI^{1/2}) - 2RT^2(mB'_{MX} + m^2C'_{MX}) \quad (2)$$

where

$$B'_{MX} = \left(\frac{\partial \beta_{MX}^{(0)}}{\partial T} \right)_P + 2 \left(\frac{\partial \beta_{MX}^{(1)}}{\partial T} \right)_P j(\alpha I^{1/2}) + 2 \left(\frac{\partial \beta_{MX}^{(2)}}{\partial T} \right)_P j(\alpha_2 I^{1/2}) + \frac{kI^{1/2} A_H}{2RT^2} \beta_{MX}^{(2)} j'(\alpha_2 I^{1/2}) \quad (3)$$

$$C'_{MX} = \left(\frac{\partial C_{MX}^{(0)}}{\partial T} \right)_P + 4 \left(\frac{\partial C_{MX}^{(1)}}{\partial T} \right)_P \left[6 - (6 + 6\alpha_3 I^{1/2} + 3\alpha_3^2 I + \alpha_3^3 I^{3/2}) \exp(-\alpha_3 I^{1/2}) \right] / (\alpha_3^4 I^2) \quad (4)$$

and

$$j(x) = [1 - (1+x)\exp(-x)] / x^2 \quad (5)$$

$$\alpha_2 = kA_\phi \quad (6)$$

$$j'(x) = -(2/x^3) [1 - (1+x+x^2/2)\exp(-x)] \quad (7)$$

where m is molality, I ionic strength, R is the gas constant (8.3145 J mol⁻¹ K⁻¹), $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$ are the model parameters (terms of the second virial coefficient which accounts for non-ideality of the vapor phase) and reflect the short-range interactions between the positive and negative ions (M-X) in solution and indirect forces arising from the solvent; $C_{MX}^{(1)}$, $C_{MX}^{(2)}$ are the two terms of the third virial coefficient (which accounts for non-ideality of the vapor phase) and reflect triple-ionic interactions that are important at higher concentrations. For 1-1 electrolytes the ionic strength is equal to molality m .^{9,22} $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$, $C_{MX}^{(1)}$, $C_{MX}^{(2)}$ exact values can be determined from osmotic coefficient measurements and correlation of data by the same model²² in the same

range of temperatures and atmospheric pressure. A_ϕ represents the Debye-Hückel coefficient for osmotic coefficient of 1-propanol calculated in this work by using experimental density data from literature²⁴ and static dielectric constants of 1-propanol²⁵ at the temperatures of this work (Table 1). A_H is the Debye-Hückel coefficient for 1-propanol enthalpy in J mol⁻¹ and it was calculated in this work (Table 1). The following equations have been used:^{26,27}

$$A_\phi = (1/3)(2\pi N_A \rho)^{1/2} (e^2 / 4\pi DK T)^{3/2} \quad (8)$$

$$A_H = 4RT^2 \left(\frac{\partial A_\phi}{\partial T} \right)_P \quad (9)$$

Table 1

Input constant values for the Archer and Rard model²² used in the correlation of the enthalpy of solution, $\Delta_s H_m$, vs. molality, m , data at isothermal conditions

T / K	A_ϕ	$A_H / (J \text{ mol}^{-1})$	b	α	α_2	α_3	k
303.56	2.6775	-25204.9	3.2	2	7	1	2.6144
318.68	2.7122	42484.1	3.2	2	7	1	2.5809

The model constants b , a , a_2 and a_3 , in $\text{kg}^{1/2} \text{mol}^{-1/2}$, are the same as those used in literature^{26,27} for the best correlation of the osmotic coefficients data with the same model for ILs + water or ethanol systems.

$$\Delta_s H_m^0, \left(\frac{\partial \beta_{MX}^{(0)}}{\partial T} \right)_P, \left(\frac{\partial \beta_{MX}^{(1)}}{\partial T} \right)_P, \left(\frac{\partial \beta_{MX}^{(2)}}{\partial T} \right)_P, \beta_{MX}^{(2)}, \left(\frac{\partial C_{MX}^{(1)}}{\partial T} \right)_P, \left(\frac{\partial C_{MX}^{(2)}}{\partial T} \right)_P \text{ model parameters are}$$

obtained from the correlation of experimental data of $\Delta_s H_m$ vs. m , at constant T , with Eqs. (1-2) by non-linear least-squares fitting.

From the isothermal molar enthalpy of solution data only $\beta_{MX}^{(2)}$ is evaluated directly.

The objective function (O.F.) used for the parameters optimization was standard deviation (SD):

$$O.F. = SD = \sqrt{\frac{\sum_i^N (\Delta_s H_{m,i,\text{exp}} - \Delta_s H_{m,i,\text{cal}})^2}{N - n}} \quad (10)$$

where N is the number of experimental points from an isothermal data set and n represent the number of the model parameters.

Using the $\Delta_s H_m$ calculated values, the mixing molar enthalpies $\Delta_s H_{m,\text{mix}}$ have been calculated as:

$$\Delta_s H_{m,\text{mix}} = x \Delta_s H_m \quad (11)$$

where x is the mole fraction of the IL in solution. The relative molar enthalpies L of the mixtures are then calculated as:

$$L = \Delta_s H_{m,\text{mix}} - x \Delta_s H_m^0 \quad (12)$$

RESULTS AND DISCUSSION

The experimental values of molar solution enthalpy of [bmim]Cl in 1-propanol, $\Delta_s H_m$, at various molalities and 303.56 K and 318.68 K together with the corresponding mixing molar enthalpies $\Delta_s H_{m,\text{mix}}$ and integral heats of the mixing $\Delta_s H$ are presented in Table 2. In Table 3 the results of the correlation of experimental molar enthalpies of solution, $\Delta_s H_m$, vs molality, m , data for the IL + 1-propanol system by means of Archer and Rard (1998) model are presented.

Table 2

Experimental heats of solution, $\Delta_s H$, for 1-butyl-3-methylimidazolium chloride (1) + 1-propanol (2) system, the molar enthalpy of solution of 1-butyl-3-methylimidazolium chloride, $\Delta_s H_m$, and mixing molar enthalpy, $\Delta_s H_{m,\text{mix}}$, at $T = (303.56 \text{ and } 318.68) \text{ K}$ at various pure components initial weights w_1 , w_2 and final molalities m of the solutions and atmospheric pressure of $101.22 \pm 0.26 \text{ kPa}$

w_1 / g	w_2 / g	$m / (\text{mol kg}^{-1})$	$\Delta_s H / \text{J}$	$\Delta_s H_m / (\text{J mol}^{-1})$	$\Delta_s H_{m,\text{mix}} / (\text{J mol}^{-1})$
$T = 303.56 \text{ K}$					
0.0010	1.1902	0.0048	-0.022	-3842.7	-1.11
0.0035	1.1785	0.0170	-0.032	-1597.0	-1.63
0.0099	1.1795	0.0481	0.001	10.6	0.03
0.0205	1.1790	0.0995	0.217	1848.9	11.00
0.0293	1.1334	0.1480	0.247	1472.5	12.98
0.0452	1.1359	0.2278	0.542	2094.5	28.29
0.0986	1.1055	0.5106	2.872	5087.8	151.49
0.1236	1.1031	0.6415	4.847	6849.7	254.28
0.1826	1.0434	1.0019	10.044	9607.8	545.68
0.2827	0.9664	1.6748	17.947	11088.8	1014.05
0.3357	0.9230	2.0822	24.979	12997.0	1445.57
$T = 318.68 \text{ K}$					
0.0013	1.1829	0.0063	-0.040	-5374.5	-2.03
0.0054	1.1759	0.0263	-0.098	-3169.9	-5.00
0.0083	1.1464	0.0414	-0.158	-3325.0	-8.26
0.0233	1.1757	0.1135	-0.138	-1034.5	-7.01

Table 2 (continued)

0.0347	1.1534	0.1722	0.016	80.5	0.83
0.0661	1.1292	0.3351	0.301	795.4	15.70
0.0850	1.1238	0.4330	0.336	690.5	17.51
0.1882	1.0475	1.0286	2.982	2767.6	161.13
0.2625	0.9918	1.5153	5.718	3804.8	317.57
0.3619	0.9173	2.2587	7.090	3422.0	409.00
0.4013	0.8761	2.6224	10.273	4471.4	608.78

Standard uncertainties u are: $u(w) = 0.0001$ g, $u(m) = 0.0001$ mol kg⁻¹, $u(\Delta_s H) = 0.005$ J, $u(\Delta_s H_m) = 0.025 \Delta_s H_m$ J mol⁻¹, $u(\Delta_s H_{m,mix}) = 0.025 \Delta_s H_{m,mix}$ J mol⁻¹

Table 3

Results of the correlation of the molar enthalpy of solution for 1-butyl-3-methylimidazolium chloride ([bmim]Cl) in 1-propanol, $\Delta_s H_m$ vs. m , with the Archer and Rard model²² together with average relative deviations in absolute value (AARD), absolute average (AAD), and standard (SD) deviations of the fits and coefficients of determination, R^2

Parameters	T / K	
	303.56	318.68
$\Delta_s H_m^0 / (\text{J mol}^{-1})$	-4366.0	-7253.6
$\left(\frac{\partial \beta_{MX}^{(0)}}{\partial T} \right)_P$	-0.2521	-0.2323
$\left(\frac{\partial \beta_{MX}^{(1)}}{\partial T} \right)_P$	0.4624	0.5908
$\left(\frac{\partial \beta_{MX}^{(2)}}{\partial T} \right)_P$	-0.6660	-0.1741
$\beta_{MX}^{(2)}$	27.78	77.87
$\left(\frac{\partial C_{MX}^{(1)}}{\partial T} \right)_P$	-0.0179	-0.0050
$\left(\frac{\partial C_{MX}^{(2)}}{\partial T} \right)_P$	0.2993	0.2256
¹ AARD / %	5.9	11.2
² AAD / (J mol ⁻¹)	146	208
³ SD / (J mol ⁻¹)	340	411
R^2	0.99	0.99

$$\text{Note: } ^1 AARD = \frac{\sum_{i=1}^N 100 \frac{|\Delta_s H_{m,i,\text{exp}} - \Delta_s H_{m,i,\text{cal}}|}{|\Delta_s H_{m,i,\text{exp}}|}}{N}; \quad ^2 AAD = \frac{\sum_{i=1}^N |\Delta_s H_{m,i,\text{exp}} - \Delta_s H_{m,i,\text{cal}}|}{N}; \quad ^3 SD = \sqrt{\frac{\sum_{i=1}^N (\Delta_s H_{m,i,\text{exp}} - \Delta_s H_{m,i,\text{cal}})^2}{N-n}}$$

N = total number of experimental points at constant T ; $n = 7$ (total number of model parameters).

These are better evidenced in Fig. 1. The comparison of the experimental and calculated data for molar mixing enthalpies $\Delta_s H_{m,mix}$ vs. m is presented in Fig. 2.

From these Figures a good agreement between experimental and calculated data is observed. In Figs. 3 and 4, the calculated apparent relative molar enthalpies for the solutes and relative molar enthalpies for [bmim]Cl mixture

with 1-propanol against composition are presented.

Based on the results obtained, the following aspects can be pointed out:

From Table 3, it is evident that molar enthalpy of solution at infinite dilution is negative at both temperatures, with a higher absolute value at upper temperature. This means that the solute-solvent interactions are strongly attractive and dominated by packing between unlike molecules.

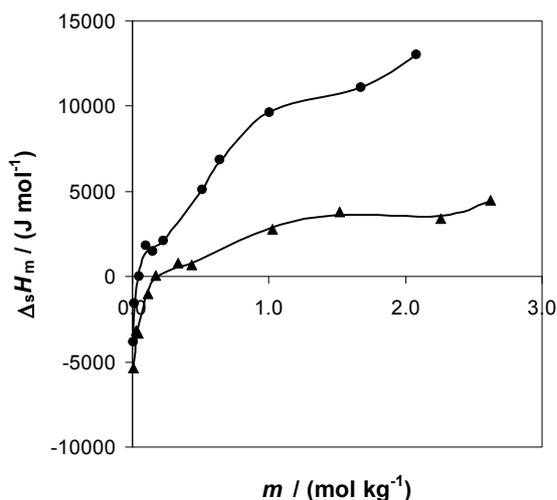


Fig. 1 – Molar enthalpy of solution of 1-butyl-3-methylimidazolium chloride in 1-propanol, $\Delta_s H_m$ vs. molality m at $T = 303.56 \text{ K}$ (●) and 318.68 K (▲). Filled symbols represent experimental data and solid lines represent the calculated values by the Archer and Rard model²² using the parameters from Table 3.

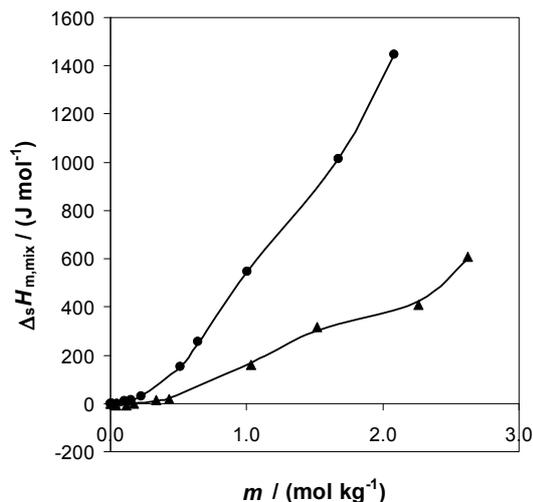


Fig. 2 – Mixing molar enthalpy $\Delta_s H_{m,mix}$ vs. molality m for 1-butyl-3-methylimidazolium chloride + 1-propanol system at $T = 303.56 \text{ K}$ (●) and 318.68 K (▲). Filled symbols represent experimental data and solid lines represent the calculated values by the Archer and Rard model²² using parameters from Table 3.

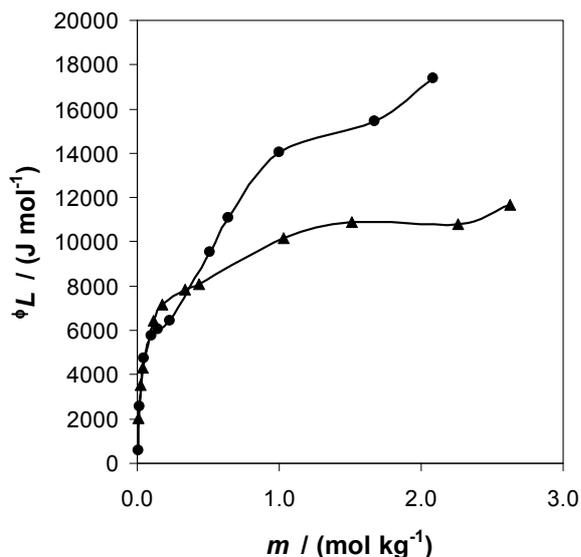


Fig. 3 – Calculated apparent relative molar enthalpies of 1-butyl-3-methylimidazolium chloride in 1-propanol, ϕL , vs. molality, m , at $T = 303.56 \text{ K}$ (●) and 318.68 K (▲) with the Archer and Rard model²² using parameters from Table 3.

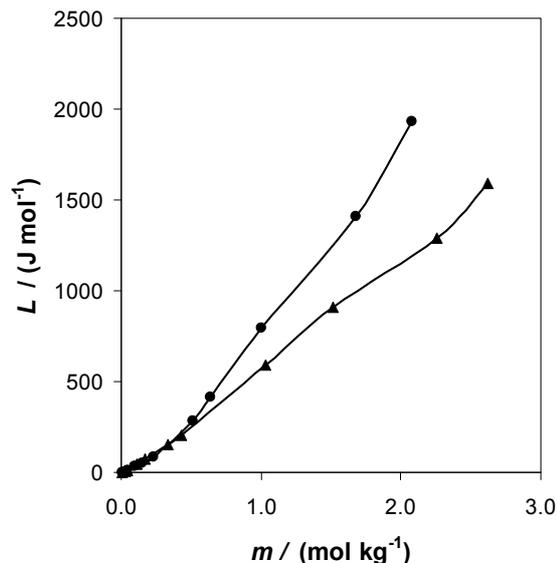


Fig. 4 – Calculated relative molar enthalpies of the mixtures, L , vs. molality, m , for 1-butyl-3-methylimidazolium chloride + 1-propanol at $T = 303.56 \text{ K}$ (●) and 318.68 K (▲) with the Archer and Rard model²² using parameters from Table 3.

From Fig. 1, it can be observed that the solute-solvent interactions decrease with increasing amounts of the IL; in this case, the solute-solute and solvent-solvent endothermic disruption between like molecules became dominant; at constant composition, the solute-solvent interactions are stronger when temperature increases, since molar enthalpy of solution decreases by increasing temperature. The same behavior is displayed in Fig. 2 by the variation of the molar enthalpy of mixing with molality.

A combined analysis of Fig. 1 and Fig. 3 reveals four distinct regions in the variation of molar enthalpy of solution and apparent molar relative enthalpy of the [bmim]Cl in 1-propanol vs. molality. This type of dependence was observed also for the same IL in 1-butanol¹⁵ and it was ascribed to an effect of solid-solid phase transition of the pure IL in the alcoholic solution. In the 1-propanol solution this effect is diminished comparing with the 1-butanol-solution, but still it is present, and it is more evident at 303.56 K.

From Fig. 4 it can be observed that the relative molar enthalpy variation with molality for [bmim]Cl + 1-propanol system is similar with that of the same IL with 1-butanol¹⁵: it is endothermic on the whole interval of the investigated composition and decrease with increasing temperature at constant molality. This is due to the fact that the solute-solute and solvent-solvent interactions are dominant and with increasing temperature the solute-solvent interactions increase. Up to 1.2 mol kg⁻¹ molality (see maximum investigated composition at Fig. 8 from¹⁵), at constant concentration, the relative molar enthalpy for [bmim]Cl + 1-propanol system is smaller than that for [bmim]Cl + 1-butanol mixture proving that the solvent-solvent interactions in 1-propanol are stronger than those from 1-butanol.

CONCLUSIONS

Enthalpies of solution for 1-butyl-3-methylimidazolium chloride + 1-propanol system have been measured at temperatures of 303.56 and 318.68 K and low concentration of the solid IL solute. The excess molar enthalpies L have been evaluated. They are endothermic over the whole composition range of studied homogenous mixtures and decrease with increasing temperature. At the same time, solution molar enthalpy at infinite dilution has been determined and it was found that it

decreases when temperature increases. The solution molar enthalpy vs. molality data have been successfully correlated with Archer and Rard model²² by means of non-linear least squares fitting. It is confirmed that within low concentration range of the IL the interactions which appear at mixing of the two compounds are strongly attractive and they are most likely dominated by the packing of unlike molecules. At higher concentrations, the contribution of the solute/solute and solvent/solvent interactions becomes dominant. The apparent and relative molar enthalpies are positive and, at constant composition, they generally decrease with increasing temperature. This proves that the unlike molecules interactions increase in intensity by increasing temperature and/or the solvent-solvent interactions in 1-propanol are stronger than those from 1-butanol when the same IL solute is used.

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