# SOLUTION, APPARENT AND RELATIVE MOLAR ENTHALPIES FOR TWO MODEL IONIC LIQUID + WATER SYSTEMS IN THE RANGE OF 303.15 - 318.15 K AND OF HIGH DILUTION

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Experimental enthalpies of solution, $\Delta_s H_{m,mix}$, for 1-butyl-3-methylimidazolium bromide ([bmim]Br) + water system measured by using a SETARAM C80 3D calorimeter with reversal mixing mechanism over the composition range from $m = 0.0059$ to 0.9646 mol kg^{-1} of [bmim]Br at temperatures of 303.15, 310.15 and 318.15 K and atmospheric pressure are reported. The data have been correlated adequately with Archer and

Rard (1998) model for electrolyte systems. The absolute mean relative deviations obtained in the ionic liquid (IL) molar enthalpy of solution correlation were situated between 6.8% and 22.0%, decreasing with increasing temperature. The molar enthalpies of solution at infinite dilution, the apparent relative molar enthalpies for the solute and relative molar enthalpies for the mixtures were determined according to this model. The results are compared with those obtained for the 1-butyl-3-methylimidazolium chloride ([bmim]Cl) + water system for which the experimental data with inadequate modeling were published recently (Teodorescu and Popa (2016)) and that are adequately correlated in the present work with 3.8% absolute mean relative deviations by Silvester and Pitzer (1977) electrolytes model. The physical interactions in the two ionic liquids (ILs) aqueous solutions are briefly analyzed, based on the obtained results.
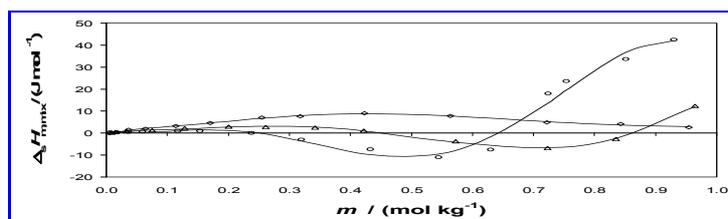
INTRODUCTION

In the last thirty years, the ILs, greener alternatives to the classical organic solvents, got an increased importance in various applications.[1-5] The thermodynamic understanding of the IL + water mixtures is important.[6]

The [bmim]Br and [bmim]Cl are known as prototype ILs. These ILs, which are the basis of the synthesis of others, are very hydroscopic, which makes the understanding of their interactions with water most important in synthesis route design and drying procedures.

The multiple utilizations of pure ILs or of their mixtures require accurate thermodynamic data on phase equilibria and related thermophysical properties, particularly those at infinite dilution, among which the enthalpies of solution. The absence of data on solution heats is a significant hurdle for the design of chemical reactors and heat transfer systems.[7]

Up to now, for [bmim]Br + water system no heats of solution and excess molar enthalpies data exist in the literature.[8] For [bmim]Cl + water system the heats of solution experimental data at 303.15 and 318.15 K and high dilution concentration range have been reported by us recently, but the modeling of the data was not adequate.[9] For the same system, similar data at 298.15 K were also reported by Guan *et al.* in 2006.[7]

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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.[10]

Excess molar enthalpies including those at infinite dilution are determined directly by calorimetry. Advances in calorimetry[11] resulted in vastly improved instruments, capable of rapid and precise measurements, e.g.[12]. Previous attempts to carry out these measurements for the infinite dilution region have suffered mostly due to imprecise values of the composition, the demanding sensitivity requirements of measuring such small heats of mixing, and the presence of the vapor space in batch calorimeters. Modifications of existing methods have allowed sufficiently precise values by using an isothermal flow calorimeter with asymmetric pumps as described by Trampe and Eckert in 1991.[10] This type of system is also amenable to measurements of heats of dilution which provide directly excess molar enthalpies when the solute is solid at room temperature and atmospheric pressure, but it requires high quantities of solid, which is a problem in the case of the ILs, due to the high costs of the pure chemicals. The direct measurement of the molar enthalpy of the solute at infinite dilution is not possible by this method.

The highly sensitive batch calorimeter like SETARAM C80 3D with reversal mixing mechanism[9] is suitable for such measurements. This calorimeter has three advantages: the heat due to the vaporization of the solvent is eliminated by introduction of about the same amount of solvent in the measurement and reference cells at the same volume of the vapor phase in the two cells; the composition in the dilute region is determined accurately by measuring the amounts of the two components to be mixed at desired temperature by their weighing directly in the compartments of the cells at precise analytical balance; the consumption of pure IL is small.

The experimental data of apparent and relative molar enthalpies (that approximate excess molar enthalpies in terms of Pitzer's theory e.g.[13]) and enthalpies of solution at infinite dilution for the two selected ILs + water systems reported here offer a better understanding of the nature of the interactions between the two components in solution. The ILs and electrolyte systems and the infinite dilution concentration range are very important for industry from both experimental and modeling viewpoints.[14] There is an increasing need for enthalpic properties and experimentally based improved electrolyte models in a wide range of industries.[14]

EXPERIMENTAL

Provenience, provider certified purity, method of further purification in our laboratory, water content of the ILs after purification, and their thermo-physical properties obtained in this work are reported in Table 1.

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) and given in the 4th column of Table 1. A significant decrease of the producer's certified water content was thus obtained.

During all molar enthalpy of solution measurements, after each sampling of the IL from the bulk sample, the well covered container with bulk sample was vacuumed at 0.1 kPa and 298 K for several hours and stored under those conditions before next sampling measurement. Water was double distilled and deionized before use.

Table 1

Provenience, provider certified purity, method of further purification, water content after purification, and thermo-physical properties of the ILs

IL	Provenience	Certified purity (mass %)	Method of further purification	Water content after purification (mass %)	T_{fus} (K)	$\Delta_{fus}H_m$ (J mol^{-1})
[bmim]Br	Fluka	99.9, with 0.05 water content	23 days till constant mass of the sample at $T = 318$ K and $P = 0.1$ kPa	0.01	350	26500
[bmim]Cl	Fluka	99.8, with 0.20 water content	8 days till constant mass of the sample at $T = 316$ K and $P = 0.1$ kPa	0.05	343	13800

Standard uncertainties σ: $\sigma(T_{fus}) = 1$ K, $\sigma(\Delta_{fus}H_m) = 1\%$ from measured value, J mol^{-1}

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 way of calibration can be found in our previous paper[9] and in literature, for a similar calorimeter.[15,16] The amount of [bmim]Br weighted in the lower recipient of the measuring cell was between 2 and 260 mg. The same amount of water 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 water sample was weighted in amounts between 1.23 and 1.49 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 3 - 4 hours. The complete isotherm for 303.15 K was measured first, then the one for 318.15 K and finally that for 310.15 K, following a similar protocol with that reported for the [bmim]Cl + water system measurements.[9] It is worth mentioning that the rocking device of the calorimeter was running continuously till reaching 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 bidistilled and deionized water. The acquired values for the latest case at molality $m = 0.0673$ mol kg^{-1} were 2.5% lower than literature values[17] and 0.6% lower than calculated literature value at infinite dilution[17] determined at 303.15 K. The corresponding $\Delta_s H_{m,mix}$ obtained by us was 8% higher than the referenced value from.[17] 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 literature.[17] 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]Br + water system was measured at 303.15, 310.15 and 318.15 K and atmospheric pressure in the range from 0.0059 to 0.9646 mole kg^{-1} of [bmim]Br. The room temperature was about 298 K and kept constant during all measurements.

Thermal analysis of the two pure ILs by using the same Setaram C80 3D calorimeter with standard cells and proper sealed aluminum crucibles of 20 μL in volume (reference empty sealed crucible) has been performed. These measurements were carried out after those of the enthalpies of solution by using the original samples (well preserved for avoiding water contamination). Samples were weighed on a Mettler-Toledo electronic microbalance with uncertainty of ±0.002 mg.

The following thermal program was applied: 90 minutes at constant temperature of 294 K, heating from 294 K to 393 K with the rate of 2 K min^{-1} and cooling with air of 291 K to about 323 K with the same rate of 2 K min^{-1}. No peak was observed in the 294 K isothermal range to be associated with a solid-solid phase transition.

The fusion or on-set temperatures for the two ILs, presented in Table 1, agree well with those from literature.[18,19] As for the fusion enthalpies from this work, $\Delta_{fus} H_m$, determined as horizontal last point integration of the endothermic melting peak, they are slightly smaller than literature reported values[18,19] probably due to the smaller water content of our pure compounds samples. Normally, the vaporization enthalpy of water traces is hidden in the so-called melting enthalpy.

THEORY AND CALCULATION

The ILs are organic salts with low melting points (<373 K) containing positive and negative ions which in solution with water or proton donor organic solvents can be regarded as electrolyte mixtures. For the evaluation of the thermodynamic data, the available semi-empirical electrolyte models can be used. The 4-parameters Silvester and Pitzer (1977) model[13] has been utilized for the [bmim]Cl + water system, due to the small number of experimental points and a reasonable behavior of molar enthalpies of solution.[9] For [bmim]Br + water system, due to the more complex behavior of molar enthalpies of solution and to the higher number of experimental points available, the 7-parameters Archer and Rard (1998)[14] model has been chosen. Relevant literature (e.g. Gmehling et al (2003)[12]) state 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."

Silvester and Pitzer (1977) model for the molar enthalpy of solution at infinite dilution determination

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:

$$\Delta_s H_m = \Delta_s H_m^0 + {}^\phi L \qquad (1)$$

where $\Delta_s H_m^0$ is the molar solution enthalpy for the solute at infinite dilution and ${}^\phi L$ is its apparent relative molar enthalpy. According to Pitzer's theory, e.g.,[13] for 1-1 electrolytes studied here ${}^\phi L$ has the following expression:

$$^{\phi}L = \frac{2A_H}{3b}\ln\left(1 + bI^{1/2}\right) - 2RT^2\left(mB'_{MX} + m^2 C'_{MX}\right) \tag{2}$$

where:

$$B'_{MX} = \left(\frac{\partial B_{MX}}{\partial T}\right)_{P,I} \tag{3}$$

$$B_{MX} = \beta_{MX}^{(0)} + \left(\frac{2\beta_{MX}^{(1)}}{\alpha^2 I}\right)\left[1 - \left(1 + \alpha I^{1/2}\right)\exp(-\alpha I^{1/2})\right] \tag{4}$$

$$C'_{MX} = 1/2\left(\frac{\partial C_{MX}^{\phi}}{\partial T}\right)_{P,I} \tag{5}$$

$$\Delta_s H_m^0, \left(\frac{\partial \beta_{MX}^{(0)}}{\partial T}\right)_{P,I}, \left(\frac{\partial \beta_{MX}^{(1)}}{\partial T}\right)_{P,I}, \left(\frac{\partial C_{MX}^{\phi}}{\partial T}\right)_{P,I} \text{ are}$$

where m is molality, I ionic strength, R is the gas constant, $\beta_{MX}^{(0)}, \beta_{MX}^{(1)}$ are the Pitzer's 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}^{ϕ} (third virial coefficient which accounts for non-ideality of the vapor phase) and reflects triple-ionic interactions that is important at higher concentrations. For 1-1 electrolytes, the ionic strength is equal to molality m. A_H is the Debye-Huckel coefficient for water enthalpy in J mol^{-1} and was interpolated at desired temperatures from the data presented in;[13] b=1.2 kg$^{1/2}$ mol$^{-1/2}$ and α=2 kg$^{1/2}$ mol$^{-1/2}$ are temperature independent constants in Silvester and Pizer model.[13]

the parameters obtained from correlation of experimental data of $\Delta_s H_m$ at constant T with Eqs. (1-2) by least-squares method. TableCurve 2D v5.01. software has been used.

Archer and Rard (1998) model for the molar enthalpy of solution at infinite dilution determination

Archer and Rard model[20] is an extension of Pitzer model[13] for a better correlation where a larger amount of experimental data is available for electrolyte solutions. Eq. (1) is valid but for the $^{\phi}L$ and parameters functions the following expressions are used:

$$^{\phi}L = \frac{2A_H}{2b}\ln\left(1 + bI^{1/2}\right) - 2RT^2\left(mB'_{MX} + m^2 C'_{MX}\right) \tag{6}$$

$$B'_{MX} = \left(\frac{\partial \beta_{MX}^{(0)}}{\partial T}\right)_P + 2\left(\frac{\partial \beta_{MX}^{(1)}}{\partial T}\right)_P j\left(\alpha I^{1/2}\right) + 2\left(\frac{\partial \beta_{MX}^{(2)}}{\partial T}\right)_P j\left(\alpha_2 I^{1/2}\right) + \frac{kI^{1/2}A_H}{2RT^2}\beta_{MX}^{(2)} j'\left(\alpha_2 I^{1/2}\right) \tag{7}$$

$$C'_{MX} = \left(\frac{\partial C_{MX}^{(0)}}{\partial T}\right)_P + 4\left(\frac{\partial C_{MX}^{(1)}}{\partial T}\right)_P \left[6 - \left(6 + 6\alpha_3 I^{1/2} + 3\alpha_3^2 I + \alpha_3^3 I^{3/2}\right)\exp\left(-\alpha_3 I^{1/2}\right)\right]/\left(\alpha_3^4 I^2\right) \tag{8}$$

$$j(x) = \left[1 - \left(1 + x\right)\exp(-x)\right]/x^2 \tag{9}$$

$$\alpha_2 = kA_{\phi} \tag{10}$$

$$j'(x) = -\left(2/x^3\right)\left[1 - \left(1 + x + x^2/2\right)\exp(-x)\right] \tag{11}$$

where A_{ϕ} represents the Debye-Huckel coefficient for osmotic coefficient of water. Its values at desired temperatures were interpolated from the data presented in[13] and the constants b=3.2, α=2,

α_2=7, α_3=1, in kg$^{1/2}$ mol$^{-1/2}$, are the same as those used by Gonzales et al. (2008)[21] and Calvar et al. (2009)[22] for the best correlation of the osmotic coefficients data with the same model for ILs + water or ethanol systems.

$\Delta_s H_m^0$, $\left(\dfrac{\partial \beta_{MX}^{(0)}}{\partial T}\right)_P$, $\left(\dfrac{\partial \beta_{MX}^{(1)}}{\partial T}\right)_P$, $\left(\dfrac{\partial \beta_{MX}^{(2)}}{\partial T}\right)_P$, $\beta_{MX}^{(2)}$,

$\left(\dfrac{\partial C_{MX}^{(1)}}{\partial T}\right)_P$, $\left(\dfrac{\partial C_{MX}^{(2)}}{\partial T}\right)_P$ parameters are obtained from the correlation of experimental data of $\Delta_s H_m$ vs. m, at constant T, with Eqs. (1-2) by least-squares method. TableCurve 2D v5.01. software has been used. The $\beta_{MX}^{(2)}$ is an extra-term for the second virial coefficient; $C_{MX}^{(1)}$, $C_{MX}^{(2)}$ are two terms of the third virial coefficient in the Archer and Rard (1998)[20] model with the same meaning given above.

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:

$$O.F. = \sqrt{\frac{\sum_i^N \left(\Delta_s H_{m,i,\exp} - \Delta_s H_{m,i,cal}\right)^2}{N-n}} \qquad (12)$$

RESULTS AND DISCUSSION

The experimental values of molar solution enthalpy of [bmim]Br in water, $\Delta_s H_m$, at various molalities and 303.15 K, 310.15 K, and 318.15 K are listed in Table 2 together with the corresponding mixing molar enthalpies $\Delta_s H_{m,mix}$ and integral heats of the mixing $\Delta_s H$.

Table 2

Experimental heats of solution, $\Delta_s H$, for 1-butyl-3-methylimidazolium bromide (1) + water (2) system, the molar enthalpy of solution of 1-butyl-3-methylimidazolium bromide, $\Delta_s H_m$, and molar enthalpy of the mixture, $\Delta_s H_{m,mix}$, at $T = 303.15$, 310.15 and 318.15 K and various pure components initial weights w_1, w_2 and final molalities m of the solutions and atmospheric pressure of 101.22±0.26 kPa.

w_1 (g)	w_2 (g)	m (mol kg^{-1})	$\Delta_s H$ (J)	$\Delta_s H_m$ (J mol^{-1})	$\Delta_s H_{m,mix}$ (J mol^{-1})
			$T = 303.15$ K		
0.0022	1.4892	0.0067	0.025	2490.0	0.30
0.0049	1.2612	0.0177	0.027	1207.4	0.39
0.0118	1.4767	0.0365	0.035	649.9	0.43
0.0191	1.4617	0.0596	0.051	585.1	0.63
0.0363	1.4114	0.1174	0.077	464.8	0.98
0.0491	1.4537	0.1541	0.078	348.1	0.96
0.0725	1.3917	0.2377	0.005	14.5	0.06
0.0971	1.3824	0.3206	-0.234	-528.1	-3.03
0.1282	1.3500	0.4334	-0.555	-948.6	-7.35
0.1588	1.3307	0.5446	-0.826	-1139.8	-11.07
0.1808	1.3092	0.6302	-0.550	-666.6	-7.48
0.2043	1.2883	0.7237	1.297	1391.1	17.90
0.2111	1.2772	0.7543	1.695	1759.4	23.59
0.2333	1.2506	0.8514	2.370	2226.0	33.62
0.2537	1.2442	0.9306	2.973	2567.8	42.34
			$T = 310.15$ K		
0.0029	1.4733	0.0090	0.015	1133.4	0.18
0.0051	1.4571	0.0160	0.039	1675.6	0.48
0.0106	1.4606	0.0331	0.066	1364.3	0.81
0.0236	1.4371	0.0749	0.106	984.2	1.33
0.0401	1.4299	0.1280	0.173	945.3	2.17
0.0626	1.4247	0.2005	0.232	812.1	2.92
0.0812	1.4186	0.2612	0.221	596.4	2.79
0.1030	1.3737	0.3422	0.192	408.5	2.50
0.1269	1.3717	0.4222	0.080	138.1	1.04
0.1695	1.3523	0.5720	-0.287	-371.0	-3.78
0.2030	1.2819	0.7227	-0.485	-523.5	-6.73
0.2302	1.2576	0.8354	-0.192	-182.8	-2.71
0.2617	1.2382	0.9646	0.861	720.9	12.31

Table 1 (continued)

T = 318.15 K

0.0019	1.4796	0.0059	0.008	965.3	0.10
0.0054	1.4605	0.0169	0.034	1379.6	0.42
0.0118	1.4556	0.0370	0.121	2246.9	1.50
0.0206	1.4697	0.0640	0.160	1701.9	1.96
0.0363	1.4503	0.1142	0.255	1539.3	3.16
0.0537	1.4408	0.1701	0.368	1501.6	4.59
0.0780	1.3954	0.2551	0.545	1531.0	7.00
0.0975	1.3983	0.3182	0.593	1332.7	7.60
0.1267	1.3684	0.4226	0.691	1195.0	9.03
0.1653	1.3380	0.5638	0.583	772.8	7.77
0.2007	1.2678	0.7225	0.347	378.9	4.87
0.2317	1.2545	0.8429	0.291	275.2	4.12
0.2591	1.2392	0.9542	0.188	159.0	2.69

Standard uncertainties σ: $\sigma(w)$ = 0.0001 g, $\sigma(m)$ = 0.0001 mol kg^{-1}, $\sigma(\Delta_s H)$ = 0.005 J, $\sigma(\Delta_s H_m)$ = 2.5% from measured value, J mol^{-1}, $\sigma(\Delta_s H_{m,mix})$ = 2.5% from measured value, J mol^{-1}.

Table 3

Results of the correlation of the molar enthalpy of solution for 1-butyl-3-methylimidazolium bromide in water, $\Delta_s H_m$ vs. m, with Archer and Rard (1998) model[20] together with absolute mean and absolute mean relative deviations

T (K)	$\Delta_s H_m^0$ (J mol^{-1})	$\left(\dfrac{\partial \beta_{MX}^{(0)}}{\partial T}\right)_P$	$\left(\dfrac{\partial \beta_{MX}^{(1)}}{\partial T}\right)_P$	$\left(\dfrac{\partial \beta_{MX}^{(2)}}{\partial T}\right)_P$	$\beta_{MX}^{(2)}$	$\left(\dfrac{\partial C_{MX}^{(1)}}{\partial T}\right)_P$	$\left(\dfrac{\partial C_{MX}^{(2)}}{\partial T}\right)_P$	amd^1 (J mol^{-1})	$amrd^2$ (%)
303.15	3140.84	2.8597	-5.5690	2.8289	-462.768	0.4709	-4.1412	187	22.0
310.15	175.74	0.8151	-1.7818	0.7861	-257.863	0.0539	-0.9413	70	9.2
318.15	-421.20	0.6845	-1.5113	0.5928	-227.387	0.0540	-0.8050	83	6.8

$$^1\; amd = \frac{\sum_{i=1}^{N}\left|\Delta_s H_{m,i,\exp} - \Delta_s H_{m,i,cal}\right|}{N}$$

$$^2\; amrd = \frac{\sum_{i=1}^{N}100\frac{\left|\Delta_s H_{m,i,\exp} - \Delta_s H_{m,i,cal}\right|}{\left|\Delta_s H_{m,i,\exp}\right|}}{N}$$; At 303.15 K, the experimental point for m=0.0725 has been excluded.

The $\Delta_s H_m$ *vs. m* data have been correlated with the above described Archer and Rard (1998) model at each constant temperature. The values of the molar enthalpy for [bmim]Br at infinite dilution and the model parameters obtained are shown in Table 3 together with the absolute mean *amd* and absolute mean relative *amrd* deviations of the fits. The obtained coefficients of determination, R^2, are: 0.96 for 303.15 K, 0.98 for 310.15 K and 0.95 for 318.15 K. The comparison of the experimental and calculated values of $\Delta_s H_m$ *vs. m* for [bmim]Br are shown in Fig. 1.

One may notice in Fig. 1 that within our experimental conditions a saturation region is evidenced. This corresponds to the almost constant trend of $\Delta_s H_m$ in a small range of composition: 0.11-0.25 mol kg^{-1} for 318.15 K, 0.07-0.13 mol kg^{-1} for 310.15 K and about 0.12 mol kg^{-1} for 303.15 K. These data can be a good approximation of solubilities or solid-liquid equilibria liquidus curve at atmospheric pressure for [bmim]Br + water system. Good classical static visual technique for solid-liquid equilibria determination[23] can be an option for confirming or infirming the approximate values reported here. An alternative hypothesis is that the above-mentioned data corresponds to solid-solid phase transition in [bmim]Br pure compound.

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

$$\Delta_s H_{m,mix} = x\Delta_s H_m \qquad (13)$$

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

$$L = \Delta_s H_{m,mix} - x\Delta_s H_m^0 \qquad (14)$$

The calculated mixing molar enthalpies are compared with the experimental values in Fig. 2. The absolute mean deviations *amd* in J mol^{-1} between experimental and calculated values of $\Delta_s H_{m,mix}$ are: 1.5 for 303.15 K, 0.2 for both 310.15 and 318.15 K while the *amrd*'s are the same as those obtained in correlation of $\Delta_s H_m$ *vs m* shown in Table 3.
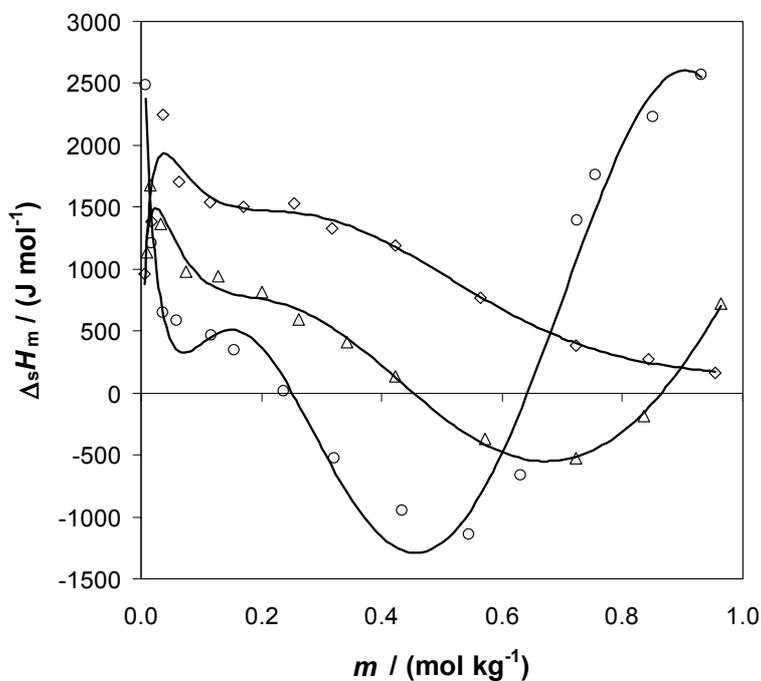

Fig. 1 – Molar enthalpy of solution of 1-butyl-3-methylimidazolium bromide, $\Delta_s H_m$ vs. molality *m* at *T* = 303.15 (○), 310.15 (Δ) and 318.15 (◊) K. Empty symbols represent experimental data and solid lines represent the calculated values by Archer and Rard model[20] using the parameters from Table 3.
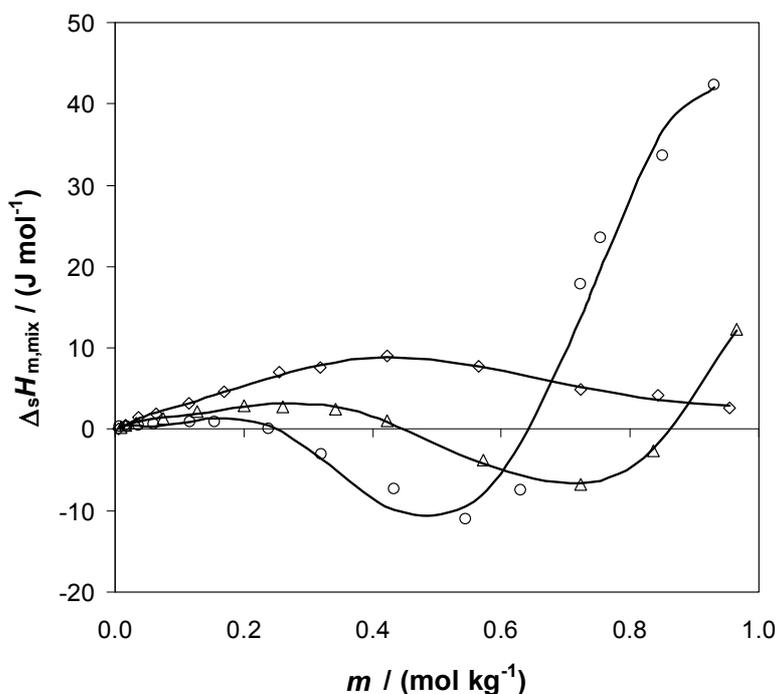
Fig. 2 – Mixing molar enthalpy $\Delta_s H_{m,mix}$ *vs.* molality *m* for 1-butyl-3-methylimidazolium bromide + water system at *T* = 303.15 (○), 310.15 (Δ) and 318.15 (◊) K. Empty symbols represent experimental data and solid lines represent the calculated values by Archer and Rard model[20] using the parameters from Table 3.

The correlation results for 303.15 K can be improved substantially by excluding the last 2 experimental points (m=0.2333 and 0.2537 mol kg^{-1}). The *amrd* decreases from 22% to 8.2% in $\Delta_s H_m$ and the model parameters obtained are shown in Table 4, case b).

Unfortunately, in this case, the consistent evolution of the model parameters with temperature observed in Table 3 is obviously disturbed. The parameter $\beta_{MX}^{(2)}$ turned from high negative to high positive. There is no reason to believe that ion-ion interaction is completely opposite to that observed in this parameter at 310.15 and 318.15 K. Excluding only the last experimental point (m=0.2537 mol kg^{-1}), the results of the correlation (Table 4, case a)) are a bit worse than in the case of considering all 15 experimental points in correlation. The experimental data of $\Delta_s H_m$ and $\Delta_s H_{m,mix}$ vs. m from Figs. 1-2 show that around m=0.7 mol kg^{-1} there is an inflection point at 303.15 K. It might be due to a) a solid-solid phase transition in the solute or b) changing of conformation of [bmim]$^+$ ion in the liquid state. No solid-liquid equilibria or solubility data are reported in literature for [bmim]Br + water system[8] to confirm a clear phase transition of the solute. A melting/crystallization study for the pure [bmim]Br does not show a phase change in the range of our studied temperatures,[18] but the existence of polymorphism and a coexistence of the *trans-trans* (TT) and *gauche-trans* (GT) conformations in the liquid and super-cooled states of [bmim]Br and [bmim]Cl at room temperature have been discussed by Holbrey *et al.*[24] and Ozawa *et al.*[25] Therefore, we consider that all our 15 experimental data points from Table 1 of enthalpy of solution for [bmim]Br + water system at 303.15 K should be considered equally in further calculations.

The experimental values of molar solution enthalpy of [bmim]Cl in water reported previously by us[9] at the converted molalities and 303.15 K and 318.15 K have been correlated with the above described Silvester and Pitzer (1977) model. The values of the molar enthalpy for [bmim]Cl at infinite dilution and the model parameters obtained are shown in Table 5 together with the absolute mean *amd* and absolute mean relative *amrd* deviations of the fits.

Table 4

Results of the correlation of the molar enthalpy of solution for 1-butyl-3-methylimidazolium bromide in water, $\Delta_s H_m$ *vs. m*, with Archer and Rard (1998) model[20] together with absolute mean and absolute mean relative deviations at 303.15 K in two cases: a) excluding the last experimental point; b) excluding the last two experimental points from Table 2

Case	$\Delta_s H_m^0$ (J mol^{-1})	$\left(\dfrac{\partial\beta_{MX}^{(0)}}{\partial T}\right)_P$	$\left(\dfrac{\partial\beta_{MX}^{(1)}}{\partial T}\right)_P$	$\left(\dfrac{\partial\beta_{MX}^{(2)}}{\partial T}\right)_P$	$\beta_{MX}^{(2)}$	$\left(\dfrac{\partial C_{MX}^{(1)}}{\partial T}\right)_P$	$\left(\dfrac{\partial C_{MX}^{(2)}}{\partial T}\right)_P$	amd^1 (J mol^{-1})	$amrd^2$ (%)
a)	3088.33	3.0301	-5.9117	2.9870	-499.952	0.4980	-4.3822	210	22.3
b)	4442.15	-2.5059	5.0723	-2.0804	625.268	-0.4793	3.7033	76	8.2

$$^1\ amd = \frac{\sum\limits_{i=1}^{N}\left|\Delta_s H_{m,i,\exp} - \Delta_s H_{m,i,cal}\right|}{N}$$

$$^2\ amrd = \frac{\sum\limits_{i=1}^{N}100\dfrac{\left|\Delta_s H_{m,i,\exp} - \Delta_s H_{m,i,cal}\right|}{\left|\Delta_s H_{m,i,\exp}\right|}}{N}$$; The experimental point for m=0.0725 has been excluded.

Table 5

Results of the correlation of the molar enthalpy of solution for 1-butyl-3-methylimidazolium chloride in water[9], $\Delta_s H_m$ *vs. m*, with Silvester and Pitzer (1977) model[13] together with absolute mean and absolute mean relative deviations

T (K)	$\Delta_s H_m^0$ (J mol^{-1})	$\left(\dfrac{\partial\beta_{MX}^{(0)}}{\partial T}\right)_{P,I}$	$\left(\dfrac{\partial\beta_{MX}^{(1)}}{\partial T}\right)_{P,I}$	$\left(\dfrac{\partial C_{MX}^{\phi}}{\partial T}\right)_{P,I}$	amd^1 (J mol^{-1})	$amrd^2$ (%)
303.15	-2037.33	0.0133	0.0027	-0.0207	151	3.8
318.15	-1277.06	-0.0007	0.0137	0.0016	100	3.8

$$^1\ amd = \frac{\sum\limits_{i=1}^{N}\left|\Delta_s H_{m,i,\exp} - \Delta_s H_{m,i,cal}\right|}{N}$$

$$^2\ amrd = \frac{\sum\limits_{i=1}^{N}100\dfrac{\left|\Delta_s H_{m,i,\exp} - \Delta_s H_{m,i,cal}\right|}{\left|\Delta_s H_{m,i,\exp}\right|}}{N}$$
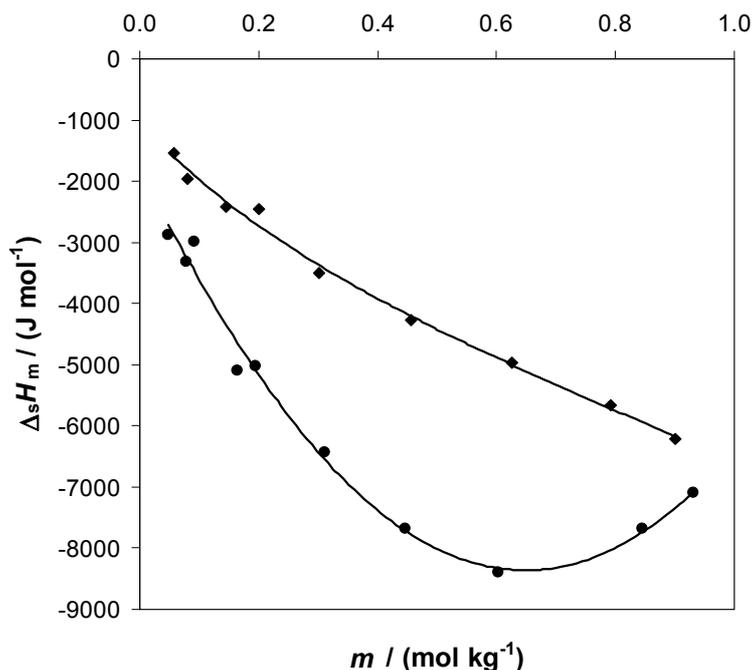
Fig. 3 – Molar enthalpy of solution of 1-butyl-3-methylimidazolium chloride, $\Delta_s H_m$ *vs.* molality m at T = 303.15 (●) and 318.15 (♦) K. Full symbols represent experimental data[9] and solid lines represent the calculated values by Silvester and Pitzer model[13] using the parameters from Table 5.

The obtained coefficients of determination, R^2, are 0.99 for both temperatures. The comparison of the experimental and calculated values of $\Delta_s H_m$ *vs.* m for [bmim]Cl are shown in Fig. 3 and for $\Delta_s H_{m,mix}$ *vs.* m for the same compound are visible in Fig. 4.

Following the procedure described above for bromide system, the $\Delta_s H_{m,mix}$ and L were calculated for aqueous chloride mixture, according to the Silvester and Pitzer model. The obtained *amd*'s between experimental and calculated values of $\Delta_s H_{m,mix}$ are 0.5 J mol⁻¹ for both temperatures while the *amrd*'s are the same as those obtained in correlation of $\Delta_s H_m$ shown in Table 5. A solid-solid phase transition is reported at 303 K for pure [bmim]Cl by Efimova *et al.*[18] A small peak at about 315 K together with uncountable solid-solid transition for pure [bmim]Cl was observed also by Domanska *et al.*[19] This small effect has been viewed as a characteristic inflection in the liquidus curve in [bmim]Cl + 1-octanol and + water solubility experimental data at atmospheric pressure.[19] For [bmim]Cl + water system this inflection point appears at around 0.92 mole fraction of IL and 331 K. It should be mentioned that our molalities include this saturation composition, *e.g.* in[9] the number of moles of [bmim]Cl are in the range of about $7 \cdot 10^{-5}$ to $1.2 \cdot 10^{-3}$.

To reach the saturation from ref.,[19] a number of moles of water between $6 \cdot 10^{-6}$ and $1.2 \cdot 10^{-4}$ is required, which is much smaller that those used in[9] for the enthalpy of solution measurements. Following an idea of Cassel and Wood[26] we can represent *e.g.* the $\Delta_s H_m/m$ for [bmim]Cl + water system. This is shown in Fig. 5. It is almost obvious that we deal with a phase transition in the solute at both temperatures: at 303.15 K it takes place at about 0.16 mol kg⁻¹ and at 318.15 K at about 0.30 mol kg⁻¹. Therefore, the apparent scattering of the experimental data represented in Figs. 3 and 4 for [bmim]Cl + water system can be associated with the phase transition in the solid solute in the aqueous solution. The enthalpy of transition is even quantifiable from Fig. 5. Due to this complexity, the deviations between experimental and calculated data reported in Table 5 can be considered acceptable.

For the sake of completeness, in Fig. 6 the representation $\Delta_s H_m/m$ for [bmim]Br + water system is presented with a detail in the range of interest. It can clearly be observed that there is an inflection point at around m=0.7 mol kg⁻¹.
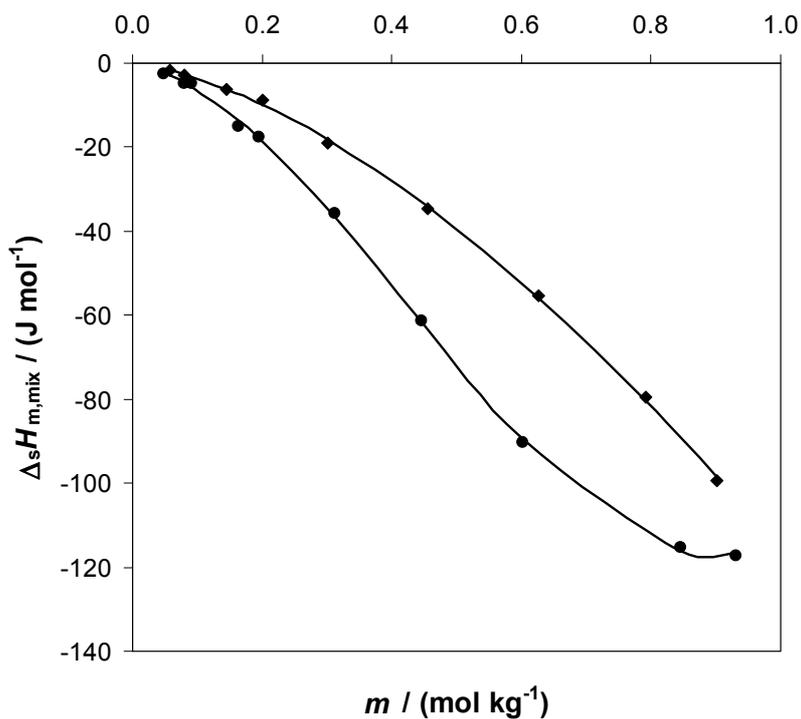
Fig. 4 – Mixing molar enthalpy $\Delta_sH_{m,mix}$ *vs.* molality *m* for 1-butyl-3-methylimidazolium chloride + water system at *T* = 303.15 (●) and 318.15 (♦) K. Full symbols represent experimental data[9] and solid lines represent the calculated values by Silvester and Pitzer model[13] using the parameters from Table 5.
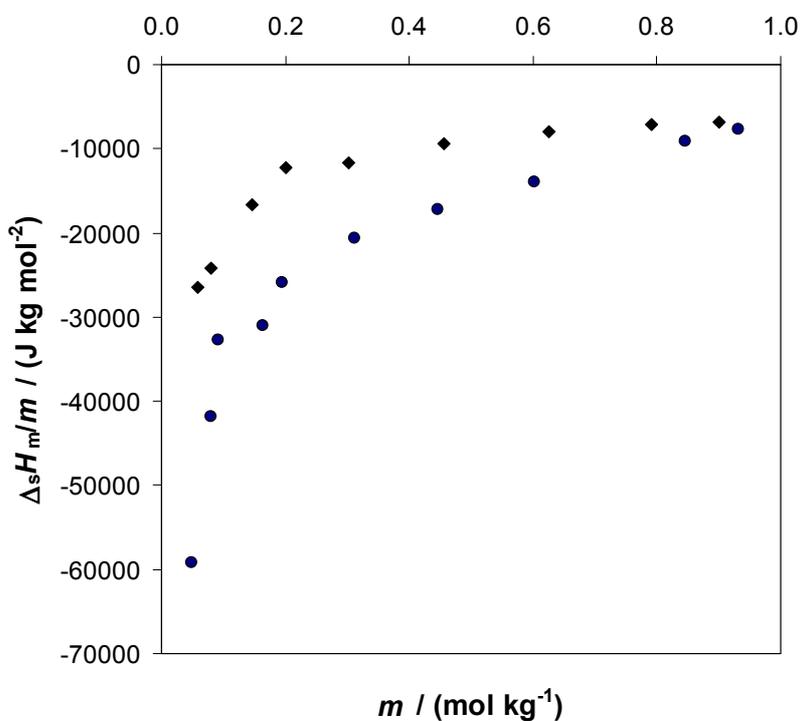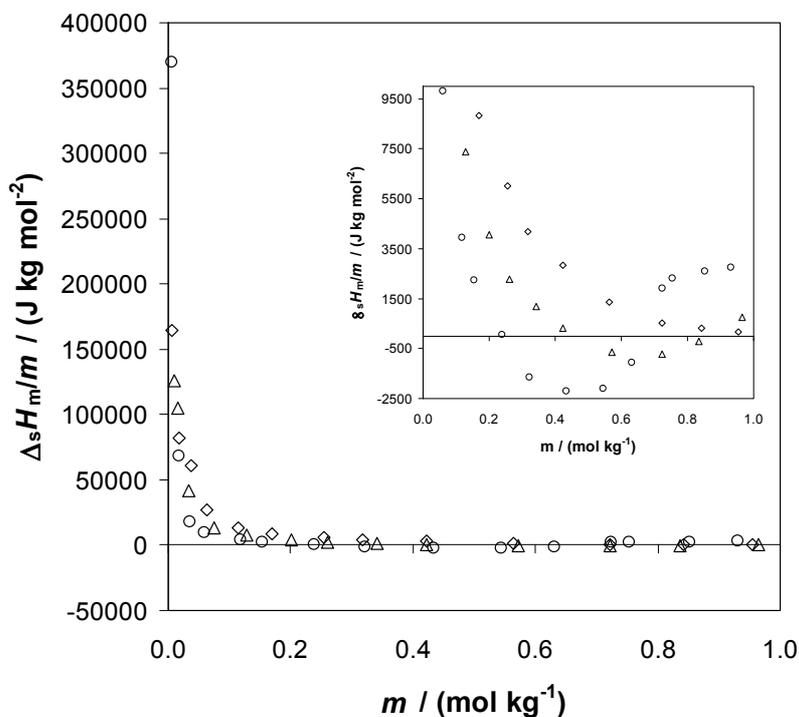

Fig. 5 – Experimental molar enthalpy of solution of 1-butyl-3-methylimidazolium chloride divided by molality *m*, Δ_sH_m/m *vs. m* at *T* = 303.15 (●) and 318.15 (♦) K[9].

The variation of the apparent and relative molar enthalpies for the two solutes and for their binary aqueous mixtures with temperature and composition are shown in Table 6 and Figs. 7 – 8.

The obtained values of enthalpies of solution for the two ILs at infinite dilution (Tables 3 and 5) show that the solute-solvent interactions are stronger for chloride/water. They are dominated by those of the H-bond type in this case: $\Delta_s H_m^0$ is less negative with increasing temperature (breaking of the H-bonds between unlike molecules with increasing temperature). These persist even at higher concentrations of the solutions and it is visible in Fig. 7. L is an approximation of the excess molar enthalpy.[13] The bromide/water H-bond interactions are very weak but still exist because the relative molar enthalpy L (Fig. 7) is negative for certain ranges of concentration. They are weaker with increasing temperature. At the infinite dilution, $\Delta_s H_m^0$ is positive at lower temperature and slightly negative at higher temperature. This evolution can be associated with domination of the packing between unlike molecules. The conclusions are supported by the values of the apparent molar volumes at infinite dilution for the two ILs in water[27] which are higher for bromide and increase with increasing temperature in both cases. The $\beta_{MX}^{(2)}$ parameter evolution with temperature in Table 3 indicates a strong ion-ion interaction in the vapor phase of the [bmim]Br aqueous solutions and these interactions are stronger at lower temperature.

Due to complexity of the investigated ILs, the results of the correlation of experimental data reported in this work for [bmim]Br + water system can be considered as satisfactory.

Data concerning molar enthalpies of aqueous solutions, $\Delta_s H_m$, were reported in a series of papers of the same research group for 1-ethyl-3-methylimidazolium chloride[28], 1-butyl-3-methylimidazolium chloride,[7] 1-pentyl-3-methylimidazolium chloride[29] and 1-hexyl-3-methylimidazolium chloride,[30] at 298.15 K and atmospheric pressure and higher dilution region, but only up to 0.1 mol kg^{-1}. The reported molar enthalpies of solution at infinite dilution for the ILs, $\Delta_s H_m^0$ in kJ mol^{-1}, in the original papers containing the experimental data, are the following: -8.97[28] for –ethyl- (C2), +16.03[7] for –butyl- (C4), -17.85[29] for –penthyl- (C5) and -17.30[30] for –hexyl- (C6). Seeking for the evolution of $\Delta_s H_m^0$ with the number of carbon atoms of n-alkyl chain connected to the 1-methylimidazolium group in chloride derivatives, in the paper[30] two of these values were corrected: -19.15 instead -8.97 citing[28] for C2 and -18.13 instead of +16.03 citing[7] for C4. With these changes, a linear variation was obtained.[30] No explanation was given for the corrections. At least for C4 there is a dramatic change, in agreement with our presented data. Assuming the values from[30] as the correct ones, for comparison with our current data the solvent mass used in the above-cited works and the present one should be taken into consideration.

Table 6

Calculated apparent relative molar enthalpies for [bmim]Br and [bmim]Cl, $^{\phi}L$, and relative molar enthalpies, *L,* for their aqueous mixtures at experimental molalities *m* from Table 2 and *T* = 303.15, 310.15 and 318.15 K using the Archer and Rard model[20] for bromide with parameters from Table 3 and Silvester and Pitzer model[13] for chloride with the parameters from Table 5

m (mol kg^{-1})	$^{\phi}L$ (J mol^{-1})		L (J mol^{-1})	
	[bmim]Br	[bmim]Cl	[bmim]Br	[bmim]Cl
		T = 303.15 K		
0.0067	-769		-0.1	
0.0177	-1694		-0.5	
0.0365	-2484	-470	-1.6	-0.3
0.0596	-2793	-877	-3.0	-0.9
0.1174	-2685	-1866	-5.7	-3.9
0.1541	-2632	-2455	-7.3	-6.8
0.2377	-3026	-3647	-12.9	-15.6
0.3206	-3762	-4617	-21.6	-26.5
0.4334	-4409	-5591	-34.2	-43.3
0.5446	-4115	-6154	-40.0	-59.8
0.6302	-3285	-6319	-36.9	-70.9
0.7237	-2070	-6232	-26.6	-80.2

Table 6 (continued)

0.7543	-1673	-6143	-22.4	-82.4
0.8514	-706	-5663	-10.7	-85.5
0.9306	-589	-5049	-9.7	-83.2
		T = 310.15 K		
0.0090	1084		0.2	
0.0160	1274		0.4	
0.0331	1277		0.8	
0.0749	903		1.2	
0.1280	666		1.5	
0.2005	581		2.1	
0.2612	497		2.3	
0.3422	268		1.6	
0.4222	-50		-0.4	
0.5720	-593		-6.1	
0.7227	-690		-8.9	
0.8354	-332		-4.9	
0.9646	533		9.1	
		T = 318.15 K		
0.0059	1300		0.1	
0.0169	2066		0.6	
0.0370	2350	-152	1.6	-0.1
0.0640	2251	-393	2.6	-0.6
0.1142	2009	-817	4.1	-1.8
0.1701	1910	-1243	5.8	-3.8
0.2551	1877	-1815	8.6	-8.3
0.3182	1817	-2194	10.4	-12.5
0.4226	1600	-2761	12.1	-20.9
0.5638	1196	-3445	12.0	-34.6
0.7225	823	-4146	10.6	-53.3
0.8429	666	-4653	10.0	-69.6
0.9542	591	-5114	10.0	-86.4

Fig. 6 – Experimental molar enthalpy of solution of 1-butyl-3-methylimidazolium bromide divided by molality m, $\Delta_s H_m/m$ vs. m at T = 303.15 (○), 310.15 (△) and 318.15 (◊) K.
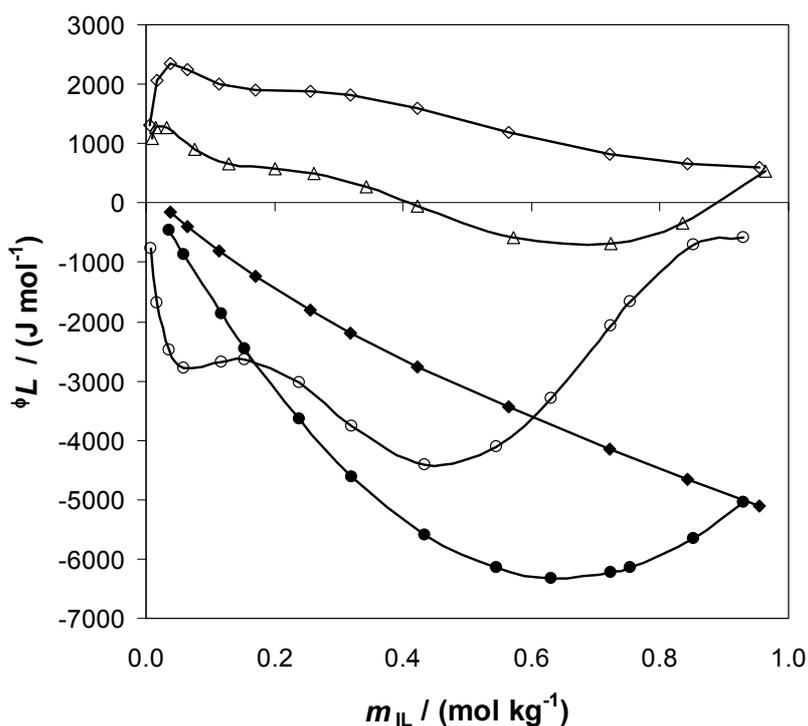
Fig. 7 – Calculated apparent relative molar enthalpies of solution, $^{\phi}L$, vs. molality, m_{IL}, for 1-butyl-3-methylimidazolium bromide at T = 303.15 (○), 310.15 (Δ) and 318.15 (◊) K and for 1-butyl-3-methylimidazolium chloride at T = 303.15 (●) and 318.15 (♦) K with Archer and Rard model[20] for bromide using the parameters from Table 3 and Silvester and Pitzer model[13] for chloride using the parameters from Table 5.
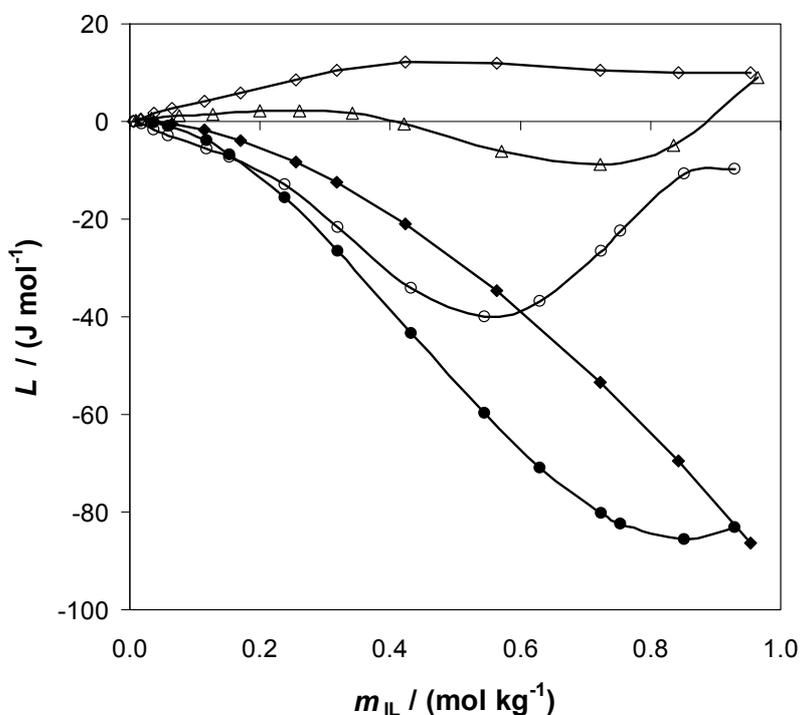

Fig. 8 – Calculated relative molar enthalpies of the mixtures, L, vs. molality, m_{IL}, for 1-butyl-3-methylimidazolium bromide + water at T = 303.15 (○), 310.15 (Δ) and 318.15 (◊) K and for 1-butyl-3-methylimidazolium chloride + water at T = 303.15 (●) and 318.15 (♦) K with Archer and Rard model[20] for bromide using the parameters from Table 3 and Silvester and Pitzer model[13] for chloride using the parameters from Table 5.
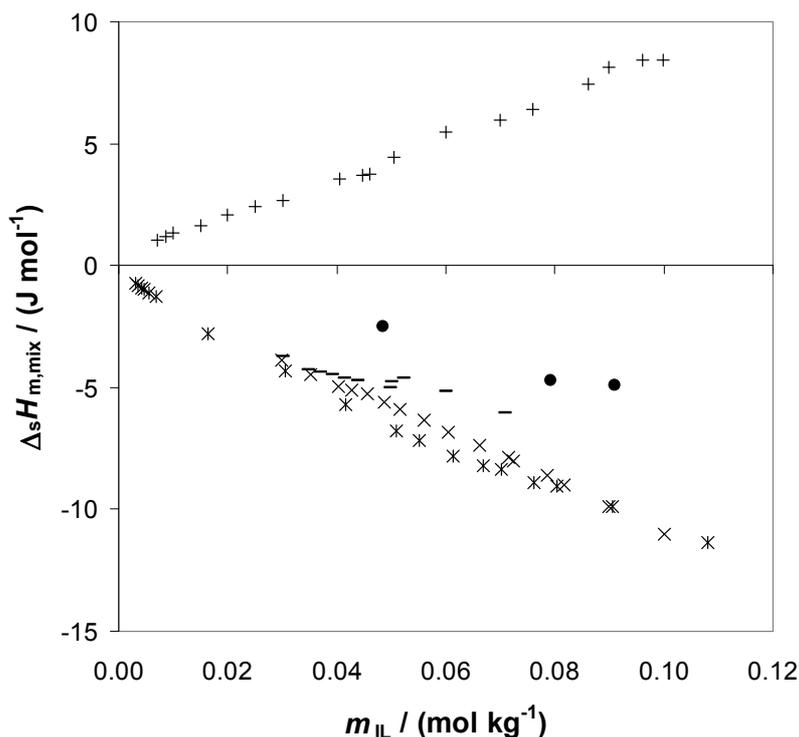
Fig. 9 – Experimental mixing molar enthalpy $\Delta_s H_{m,mix}$ vs. molality of the IL, m_{IL}, for 1-alkyl-3-methylimidazolium chloride + water systems. Full symbols (●): our data for 1-butyl-3-methylimidazolium chloride (C4) at T = 303.15 K[9]; Open symbols - literature data and 298.15 K: (−) 1-ethyl-3-methylimidazolium chloride (C2)[28], (+) 1-butyl-3-methylimidazolium chloride (C4)[7], (×) 1-pentyl-3-methylimidazolium chloride (C5)[29] and (∗) 1-hexyl-3-methylimidazolium chloride[30].

In Fig. 9, our experimental data on $\Delta_s H_{m,mix}$ vs. molality of the IL, m_{IL}, for [bmim]Cl + water system at T = 303.15 K[9] are compared with literature experimental data[7,28-30] at 298.15 K from above mentioned homologous series. No sizable differences are to be expected in such a narrow composition interval of 0-0.1 mol kg⁻¹ and temperature range of 5 K. For [bmim]Cl + water system this can be seen in our data representation in Fig. 4. In Fig. 9, it can be observed that the experimental data for C2[28] are not very accurate and the data for C4 from the literature[7] are totally in disagreement as sign with our data[9] and other data of the same group.[28-30] Causes of discrepancies could be multiple,[31] but the main one may come from different water content of the samples, or simply from the wrong sign assigning of the data from ref.[7]

CONCLUSION

New experimental data on molar solution enthalpies are reported for [bmim]Br + water system at high dilution concentration region, three temperatures and atmospheric pressure. Previously published similar data for [bmim]Cl + water system[9] have been reevaluated and afforded some qualitative conclusions regarding the molecular solute/solvent interactions at infinite dilution in these two systems. The experimental data for both systems have been satisfactorily correlated with available semi-empirical electrolytes models within the complexity of the investigated ILs, inherent experimental errors and limitations of the utilized models. The data for [bmim]Cl + water system are in reasonable agreement with similar data reported in literature for aqueous 1-alkyl-1-methylimidazolium chloride solutions.

List of symbols

T: temperature (K)
T_{fus}: fusion temperature of the IL (K)
P: atmospheric pressure (kPa)
m, m_{IL}: molal concentration of the final solution after mixing (mol kg⁻¹)
w_1, w_2: mass of the [bmim]Br and of the water samples, respectively (g)
x: mole fraction concentration of the final solution after mixing
$\Delta_s H$: heat of mixing (J)

$\Delta_s H_m$: molar enthalpy of solution defined as enthalpy of mixing divided by the number of moles of solute in the solution (J mol^{-1})

$\Delta_{fus} H_m$: molar enthalpy of fusion of the IL (J mol^{-1})

$\Delta_s H_{m,mix}$: molar enthalpy of mixing defined as enthalpy of mixing divided by total number of moles of the two components in the solution (J mol^{-1})

$\Delta_s H_m^0$: molar enthalpy of solution at infinite dilution (J mol^{-1})

$^\phi L$: apparent relative molar enthalpy reported to the number of moles of solute (J mol^{-1})

L: relative molar enthalpy reported to the total number of moles of the two components in the solution (J mol^{-1})

A_H: Debye-Huckel coefficient for enthalpy of water as solvent (J mol^{-1}) in molal scale: at $T = 303.15$ K is 3208.624 J mol^{-1}; at $T = 310.15$ K is 3610.072 J mol^{-1}; at $T = 318.15$ K is 4068.870 J mol^{-1}

A_φ: Debye-Huckel coefficient for the osmotic coefficient of water as solvent (J mol^{-1}) in molal scale: at $T = 303.15$ K is 0.395; at $T = 310.15$ K is 0.400; at $T = 318.15$ K is 0.406

b, α, α_2, α_3: constants used for Silvester and Pitzer (1977) and Archer and Rard (1998) models (kg$^{1/2}$ mol$^{-1/2}$)

k: constant of the Archer and Rard (1998) model (Eq. (10)) connecting α_2 by A_φ at each constant T: at $T = 303.15$ K is 17.78; at $T = 310.15$ K is 17.56; at $T = 318.15$ K is 17.32

$$\left(\frac{\partial \beta_{MX}^{(0)}}{\partial T}\right)_P, \quad \left(\frac{\partial \beta_{MX}^{(1)}}{\partial T}\right)_P, \quad \left(\frac{\partial \beta_{MX}^{(2)}}{\partial T}\right)_P, \quad \beta_{MX}^{(2)},$$

$$\left(\frac{\partial C_{MX}^{(1)}}{\partial T}\right)_P, \quad \left(\frac{\partial C_{MX}^{(2)}}{\partial T}\right)_P: \quad \text{adjusted constant}$$

parameters for Silvester and Pitzer (1977) and Archer and Rard (1998) models at each constant T

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