# SOLUTION MOLAR ENTHALPIES FOR 1-BUTYL-3-METHYLIMIDAZOLIUM BROMIDE AND 1-BUTYL-3-METHYLIMIDAZOLIUM CHLORIDE + 1-BUTANOL BINARY SYSTEMS IN THE RANGE OF (303.15 - 318.15) K

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Experimental mixing enthalpies of solutions for 1-butyl-3-methylimidazolium bromide ([bmim]Br) and 1-butyl-3-methylimidazolium chloride ([bmim]Cl) + 1-butanol binary systems measured by using a SETARAM C80 3D calorimeter with reversal mixing mechanism over the composition range from m 0.0075 to 1.1625 mol kg^{-1} of ionic liquid (IL) at temperatures of 303, 310 and 318 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 molar enthalpy of solution correlation were situated between 2.3 % and 5.1 % for the bromide compound, while for the chloride one they were between 15.8 % and 21.8 %. 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 physical interactions in the two ionic liquids (ILs) alcoholic solutions are briefly analyzed, based on the obtained results.
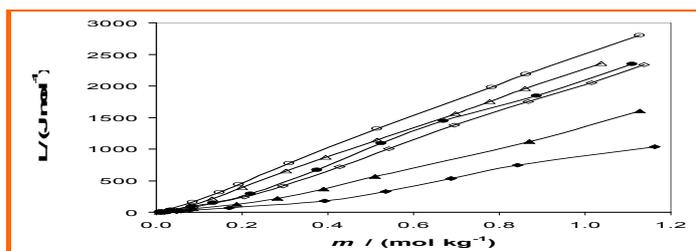
INTRODUCTION

In the last thirty years, the ionic liquids (ILs), greener alternatives to the classical organic solvents, got an increased importance in various applications.[1-5]

The [bmim]Br and [bmim]Cl, which are the basis of the synthesis of other derivatives, are known as prototype ILs. Their high hygroscopicity is important in understanding the nature of their interactions with water[6,7] and other classical solvents (e.g. alcohols), involved in the design of synthesis of derived ILs and in drying procedures.

The multiple utilizations of pure ILs or of their mixtures with alcohols require accurate thermodynamic data on phase equilibria and related thermophysical properties, including those at infinite dilution, such as enthalpies of solution. The absence of data on solution heats is a significant hurdle for the design of chemical reactors and heat transfer systems.[8]

Until now, for [bmim]Br and [bmim]Cl + 1-butanol systems no heats of solution and excess molar enthalpies data exist in the literature.[9]

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

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calorimetry. Advances in calorimetry[11] resulted in vastly improved instruments, capable of rapid and precise measurements.[12] Previous attempts to carry out these measurements for the infinite dilution region have been hampered mostly by 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.[10] The 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 high sensitive batch calorimeter like SETARAM C80 3D with reversal mixing mechanism[7] 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 weighting 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[13] and enthalpies of solution at infinite dilution for the two selected ILs + 1-butanol 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 SECTION

Source, 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 at those conditions before next sampling measurement. 1-Butanol of Riedel-de-Haën provenience with stated purity >0.995 mass fraction was dried before use by storing it on 4Å molecular sieves.

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 papers[7,15] and in literature, for a similar calorimeter[16,17]. A very small amount of IL was charged (between 1.6 and 251.6 mg) in the lower container of the measuring cell. The same amount of 1-butanol 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-butanol sample was weighed in amounts between 1.0105 and 1.1936 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 or 310.43) K, following a similar protocol with that reported for the same ILs with water systems measurements.[7,15] 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 doubly-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 values[18] and 0.6% lower than calculated literature value at infinite dilution[18] determined at 303.15 K. The corresponding mixing molar enthalpy $\Delta_s H_{m,mix}$ obtained by us was 8% higher than reference value from[18]. Our mixing molar enthalpy reproducibility was of 0.1% of the measured value. The KCl samples (Merck with stated purity >0.995 mass fraction) were carefully conditioned as recommended in literature[18]. Samples were weighed on a GH-252 A&D Japan electronic balance with uncertainty of ±0.1 mg. The estimated uncertainty of the molality m is ± 0.0001 mol kg^{-1}.

The solution molar enthalpies for [bmim]Br and [bmim]Cl + 1-butanol systems were measured at (303.15, 310.15 or 310.43 and 318.15) K and atmospheric pressure in the range from 0.0075 to 1.1625 mol kg^{-1} of IL. The room temperature was about 298 K and kept constant during all measurements.

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 fraction)	Method of further purification	Water content after purification (mass fraction)	T_{fus} (K)	$\Delta_s H_{m,fus}$ (J mol^{-1})
[bmim]Br	Fluka	0.999, with 0.0005 water content	23 days till constant mass of the sample at T = 318 K and P = 0.1 kPa	0.0001	350	26500
[bmim]Cl	Fluka	0.998, with 0.0022 water content	8 days till constant mass of the sample at T = 316 K and P = 0.1 kPa	0.0005	343	13800

Standard uncertainties u are: $u(T_{fus})$= 1K; $u(\Delta_s H_{m,fus})$= 0.01 $\Delta_s H_{m,fus}$ J mol^{-1}.

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 thermal program was the following: 90 minutes 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 sated rate of 2 K min^{-1}.

The fusion temperatures for the two ILs, presented in Table 1, agree well with those from literature.[19-23] As for the fusion enthalpies from this work, $\Delta_{fas} H_m$, determined as horizontal last point integration of the endothermic melting peak, they are slightly smaller than literature reported values[19-21] 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 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]Br and [bmim]Cl + 1-butanol systems, due to complex molar enthalpies of solution behavior and the high number of experimental points available, the 7-parameters Archer and Rard[24] model has been chosen. Relevant literature[12] show 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 model[24]
for the molar enthalpy of solution
at infinite dilution determination**

Archer and Rard model[24] is an extension of Pitzer type model[13] 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:

$$\Delta_s H_m = \Delta_s H_m^0 + {}^\phi L \tag{1}$$

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 the model[24], for 1-1 electrolytes, as is the case for the investigated systems here, ${}^\phi L$ has the following expression:

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

where

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

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

and

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

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

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

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.[13,24] $\beta_{MX}^{(0)}, \beta_{MX}^{(1)}, \beta_{MX}^{(2)}, C_{MX}^{(1)}, C_{MX}^{(2)}$ exact values can be determined from osmotic coefficient measurements and correlation of data by the same model[24] in the same range of temperatures and atmospheric pressure. A_ϕ represents the Debye-Hückel coefficient for osmotic coefficient of 1-butanol calculated in this work by using own experimental density data and static dielectric constants of 1-butanol[25] at the temperatures of this work (Table 2). A_H is the Debye-Hückel coefficient for 1-butanol enthalpy in J mol^{-1} and it was calculated in this work (Table 2). The following equations have been used[26,27]:

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

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

The model constants b, α, α_2 and α_3, in kg$^{1/2}$ 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.

$\Delta_s H_m^0$, $\left(\frac{\partial \beta_{MX}^{(0)}}{\partial T}\right)_P$, $\left(\frac{\partial \beta_{MX}^{(1)}}{\partial T}\right)_P$, $\left(\frac{\partial \beta_{MX}^{(2)}}{\partial T}\right)_P$, $\beta_{MX}^{(2)}$, $\left(\frac{\partial C_{MX}^{(1)}}{\partial T}\right)_P$, $\left(\frac{\partial C_{MX}^{(2)}}{\partial T}\right)_P$ 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 the least-squares method.

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):

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

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 $\Delta_s H_{m,mix}$ have been calculated as:

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

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

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

Table 2

Imputed constant values for the Archer and Rard model[24] 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 mol^{-1})	b	α	α_2	α_3	k
303.15	3.3685	62844.4	3.2	2	7	1	2.0781
310.15 (310.43)	3.5042	65780.2	3.2	2	7	1	1.9976
318.15	3.6766	69217.5	3.2	2	7	1	1.9039

RESULTS AND DISCUSSION

The experimental values of molar solution enthalpy of [bmim]Br in 1-butanol, $\Delta_s H_m$, at various molalities and 303.15 K, 310.15 K, and 318.15 K together with the corresponding mixing molar enthalpies $\Delta_s H_{m,mix}$ and integral heats of the mixing $\Delta_s H$ are presented in Table 3. Similar experimental data for [bmim]Cl + 1-butanol system are shown in Table 4. In Table 5 the results of the correlation of experimental molar enthalpies of solution, $\Delta_s H_m$, vs molality, m, data for the two systems by means of Archer and Rard (1998) model are presented. These are better evidenced in Fig. 1 for bromide derivative system and in Fig. 2 for chloride derivative mixture. The comparison of the experimental and calculated data for molar mixing enthalpies $\Delta_s H_{m,mix}$ vs m is presented in Fig. 3 for bromide and in Fig. 4 for chloride. From these Figures a good agreement between experimental and calculated data is observed. In Figs. 5 to 8, the calculated apparent relative molar enthalpies for the solutes and relative molar enthalpies for their mixtures with 1-butanol against composition are presented. Based on the results obtained, the following aspects can be pointed out:

The obtained values of enthalpies of solution for the two ILs in 1-butanol at infinite dilution are negative and roughly decrease with increasing temperature indicating strong H-bonding and/or packing solute/solvent interactions;

As expected, these are stronger for chloride/1-butanol. They are dominated in this case by those of the H-bond type because $\Delta_s H_m^0$ is less negative with increasing temperature due to breaking of H-bonds between unlike molecules; For bromide/1-butanol, after certain temperature they are dominated by packing effects since $\Delta_s H_m^0$ for 318.15 K is more negative than that at 310.15 K;

The thermal effect of Br-Br derivatives bonds breaking is larger than that of Cl-Cl ones, supported by the higher $\Delta_s H_{m,fus}$ and T_{fus} of pure bromide derivative;

At higher concentrations of the solutions, the breaking of the solute/solute and solvent/solvent interactions became dominant since relative (excess) molar enthalpies, L, are positive. They are decreasing with increasing temperature in both cases which sign for consistent modeling because the two ILs are differing only by the nature of the halogen anion;

The higher deviations obtained in both $\Delta_s H_m$ vs. m correlation and $\Delta_s H_{m,mix}$ vs. m prediction for [bmim]Cl + 1-butanol system are due to the solid-solid phase transition which takes place in the pure chloride derivative around 0.2 mol kg^{-1} at all investigated temperatures of the mixtures. The exact transition temperature corresponds to 303.15 K as can be seen clearly in Figure 2. This confirms the findings from literature[19,20] and it agrees with our previous measurements[7,15] and their correct interpretation.[15] An alternative interpretation is that around 0.2 mol kg^{-1} the solid-liquid transition occurs but this hypothesis is contradicted by the solubility data from literature.[21]

Table 3

Experimental heats of solution, $\Delta_s H$, for 1-butyl-3-methylimidazolium bromide (1) + 1-butanol (2) system, the molar enthalpy of solution of 1-butyl-3-methylimidazolium bromide, $\Delta_s H_m$, and mixing molar enthalpy, $\Delta_s H_{m,mix}$, at T = (303.15, 310.15 and 318.15) K at 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		
0.0020	1.1860	0.0092	0.018	1643.4	1.12
0.0020	1.1923	0.0115	0.047	3432.9	2.92
0.0200	1.1828	0.0857	1.533	15131.1	95.46
0.0350	1.1617	0.1469	3.045	17840.1	192.19
0.0500	1.1544	0.1933	4.654	20854.5	294.60
0.0750	1.1506	0.3102	8.368	23447.5	526.94
0.1250	1.0985	0.5152	14.224	25135.2	924.45
0.1800	1.0610	0.7820	21.276	25643.5	1404.88
0.2000	1.0552	0.8628	23.023	25287.2	1519.99
0.2500	1.0110	1.1272	29.073	25512.5	1967.10

Table 3 (continued)

			$T = 310.15$ K		
0.0035	1.1901	0.0134	-0.034	-2128.6	-2.12
0.0038	1.1890	0.0146	-0.041	-2364.2	-2.55
0.0106	1.1795	0.0410	0.174	3596.9	10.90
0.0204	1.1852	0.0786	0.711	7637.0	44.21
0.0337	1.1832	0.1300	2.362	15357.9	146.55
0.0511	1.1617	0.2007	4.211	18057.0	264.74
0.0758	1.1421	0.3029	7.603	21978.5	482.59
0.0966	1.1183	0.3942	9.822	22279.5	632.51
0.1239	1.0982	0.5149	13.278	23482.4	863.22
0.1662	1.0858	0.6986	17.698	23333.2	1148.65
0.1803	1.0578	0.7779	20.086	24410.7	1330.70
0.1961	1.0393	0.8611	22.252	24864.1	1491.74
0.2291	1.0080	1.0372	25.945	24814.8	1771.58
0.2491	1.0143	1.1208	28.152	24763.8	1899.42
			$T = 318.15$ K		
0.0023	1.1924	0.0088	-0.032	-3048.6	-1.99
0.0099	1.1783	0.0383	0.052	1150.9	3.26
0.0221	1.1763	0.0857	0.351	3480.1	21.98
0.0529	1.1815	0.2043	1.782	7381.3	110.12
0.0743	1.1472	0.2956	3.213	9475.5	203.14
0.1041	1.1130	0.4268	6.916	14557.5	446.44
0.1307	1.1002	0.5422	10.254	17190.9	664.12
0.1659	1.0905	0.6943	13.792	18216.4	891.55
0.1993	1.0484	0.8676	18.023	19815.4	1197.21
0.2278	1.0255	1.0138	21.031	20229.6	1413.82
0.2516	1.0105	1.1363	23.766	20698.0	1607.82

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 4

Experimental heats of solution, $\Delta_s H$, for 1-butyl-3-methylimidazolium chloride (1) + 1-butanol (2) system, the molar enthalpy of solution of 1-butyl-3-methylimidazolium chloride, $\Delta_s H_m$, and mixing molar enthalpy, $\Delta_s H_{m,mix}$, at $T = $ (303.15, 310.43 and 318.15) K at 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		
0.0018	1.1936	0.0086	-0.042	-4075.6	-2.61
0.0067	1.2117	0.0317	0.001	31.3	0.07
0.0073	1.1817	0.0354	0.045	1076.7	2.82
0.0170	1.1730	0.0830	0.223	2291.3	14.00
0.0266	1.1552	0.1318	0.355	2331.1	22.56
0.0447	1.1601	0.2206	0.525	2051.5	33.00
0.0741	1.1331	0.3744	5.598	13195.7	356.30
0.1013	1.1048	0.5249	8.336	14373.6	538.31
0.1270	1.0844	0.6705	11.591	15941.7	754.75
0.1677	1.0805	0.8886	15.717	16370.2	1011.53
0.2036	1.0495	1.1106	19.485	16716.3	1271.44
			$T = 310.43$ K		
0.0016	1.2169	0.0075	-0.034	-3711.7	-2.07
0.0045	1.2139	0.0212	-0.021	-815.1	-1.28
0.0101	1.1952	0.0484	0.003	45.8	0.16
0.0177	1.1909	0.0851	0.050	493.4	3.09
0.0385	1.1758	0.1875	0.378	1714.9	23.50
0.0572	1.1636	0.2814	0.885	2702.5	55.22
0.0775	1.1353	0.3908	1.835	4135.7	116.43
0.1001	1.1243	0.5097	4.693	8189.1	298.12
0.1666	1.0953	0.8708	9.768	10241.2	620.93
0.2046	1.0397	1.1266	14.994	12800.6	986.54

Table 4 (continued)

		$T = 318.15$ K			
0.0020	1.1950	0.0096	-0.032	-2794.7	-1.98
0.0055	1.1964	0.0263	-0.057	-1810.2	-3.52
0.0098	1.1732	0.0478	-0.065	-1158.5	-4.09
0.0118	1.1709	0.0577	-0.038	-562.5	-2.40
0.0157	1.1621	0.0773	-0.028	-311.5	-1.78
0.0346	1.1568	0.1712	0.019	95.9	1.20
0.0776	1.1307	0.3929	0.399	898.1	25.42
0.1042	1.1152	0.5349	2.264	3795.1	144.73
0.1323	1.1012	0.6878	4.109	5424.9	263.15
0.1609	1.0938	0.8422	6.986	7583.9	445.58
0.2110	1.0391	1.1625	9.461	7832.0	621.32

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 5

Results of the correlation of the molar enthalpy of solution for 1-butyl-3-methylimidazolium chloride ([bmim]Cl) and bromide ([bmim]Br) in 1-butanol, $\Delta_s H_m$ vs. m, with the Archer and Rard model[24] together with absolute average relative (AARD), absolute average (AAD), standard (SD) deviations of the fits and coefficients of determination, R^2

	[bmim]Cl			[bmim]Br		
T (K) Parameters	303.15	310.43	318.15	303.15	310.15	318.15
$\Delta_s H_m^0$ (J mol^{-1})	-14020	-8061	-5226	-10847	-7921	-9309
$\left(\dfrac{\partial \beta_{MX}^{(0)}}{\partial T} \right)_P$	-0.6630	-2.3877	-1.6267	3.6248	1.0311	-0.9097
$\left(\dfrac{\partial \beta_{MX}^{(1)}}{\partial T} \right)_P$	0.6231	4.8253	3.6399	-7.9673	-1.9136	1.6940
$\left(\dfrac{\partial \beta_{MX}^{(2)}}{\partial T} \right)_P$	-0.8758	-2.3467	-1.4950	3.0126	1.1003	-0.9009
$\beta_{MX}^{(2)}$	-201.17	206.14	268.03	-570.77	-8.5674	29.91
$\left(\dfrac{\partial C_{MX}^{(1)}}{\partial T} \right)_P$	-0.2492	-0.3000	-0.0988	0.3025	0.1563	-0.1378
$\left(\dfrac{\partial C_{MX}^{(2)}}{\partial T} \right)_P$	1.4578	3.1861	1.8308	-4.3112	-1.4698	1.3060
Deviations of the fits and coefficients of determination.						
[1]AARD (%)	21.3	21.8	15.8	2.4	5.1	2.3
[2]AAD (J mol^{-1})	835	362	152	169	441	223
[3]SD (J mol^{-1})	1832	824	334	464	665	562
R^2	0.98	0.99	0.98	0.99	0.99	0.99

Note: $^1 AARD = \dfrac{\sum\limits_{i=1}^{N} 100 \dfrac{\left| \Delta_s H_{m,i,\exp} - \Delta_s H_{m,i,cal} \right|}{\left| \Delta_s H_{m,i,\exp} \right|}}{N}$; $^2 AAD = \dfrac{\sum\limits_{i=1}^{N} \left| \Delta_s H_{m,i,\exp} - \Delta_s H_{m,i,cal} \right|}{N}$;

$^3 SD = \sqrt{\dfrac{\sum\limits_{i}^{N} \left(\Delta_s H_{m,i,\exp} - \Delta_s H_{m,i,cal} \right)^2}{N - n}}$; N = total number of experimental points at constant T; $n = 7$ (total number of model parameters).
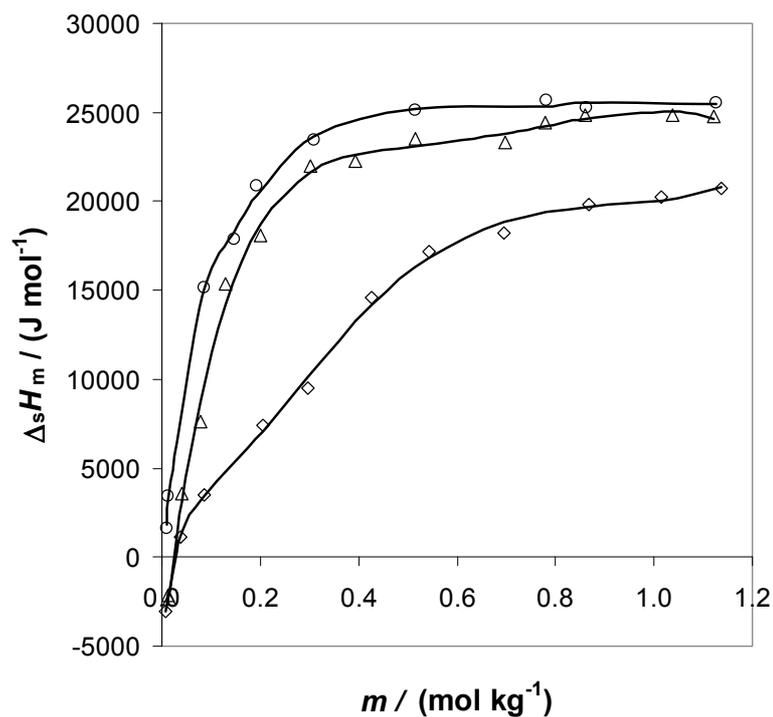
Fig. 1 – Molar enthalpy of solution of 1-butyl-3-methylimidazolium bromide in 1-butanol, $\Delta_s H_m$ vs. molality m at T = 303.15 K (○), 310.15 K (Δ) and 318.15 K (◊). Empty symbols represent experimental data and solid lines represent the calculated values by the Archer and Rard model[24] using the parameters from Table 5.
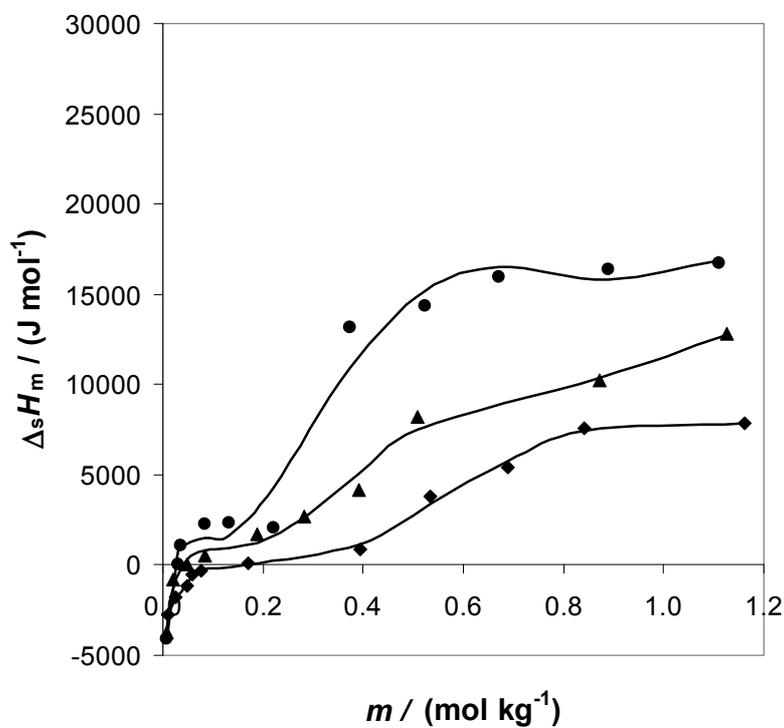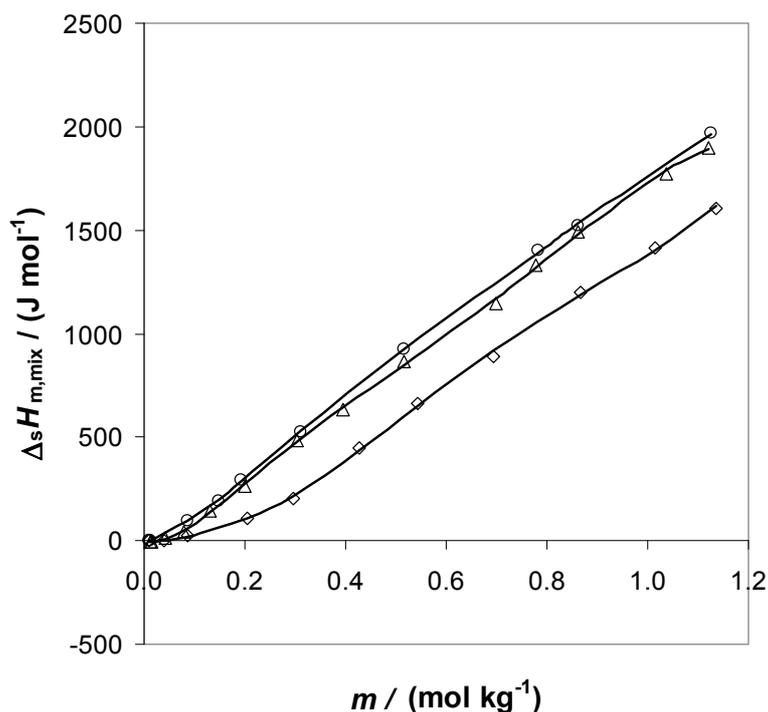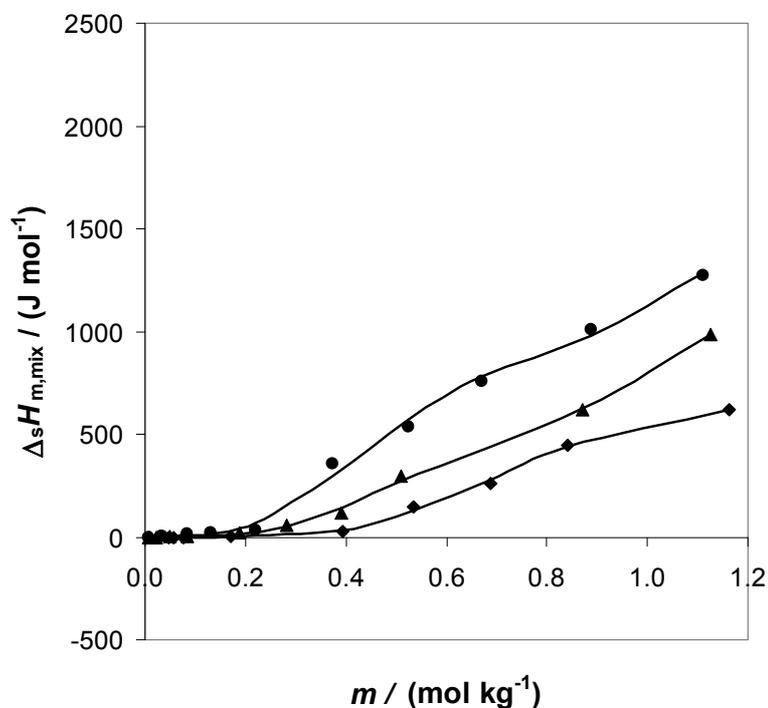

Fig. 2 – Molar enthalpy of solution of 1-butyl-3-methylimidazolium chloride in 1-butanol, $\Delta_s H_m$ vs. molality m at T = 303.15 K (●), 310.43 K (▲) and 318.15 K (♦). Full symbols represent experimental data and solid lines represent the calculated values by the Archer and Rard model[24] using the parameters from Table 5.

Fig. 3 – Mixing molar enthalpy $\Delta_s H_{m,mix}$ vs. molality m for 1-butyl-3-methylimidazolium bromide + 1-butanol system at T = 303.15 K (○), 310.15 K (Δ) and 318.15 K (◊). Empty symbols represent experimental data and solid lines represent the calculated values by the Archer and Rard model[24] using the parameters from Table 5.

Fig. 4 – Mixing molar enthalpy $\Delta_s H_{m,mix}$ vs. molality m for 1-butyl-3-methylimidazolium chloride + 1-butanol system at T = 303.15 K (●), 310.43 K (▲), and 318.15 K (♦). Full symbols represent experimental data and solid lines represent the calculated values by the Archer and Rard model[24] using the parameters from Table 5.
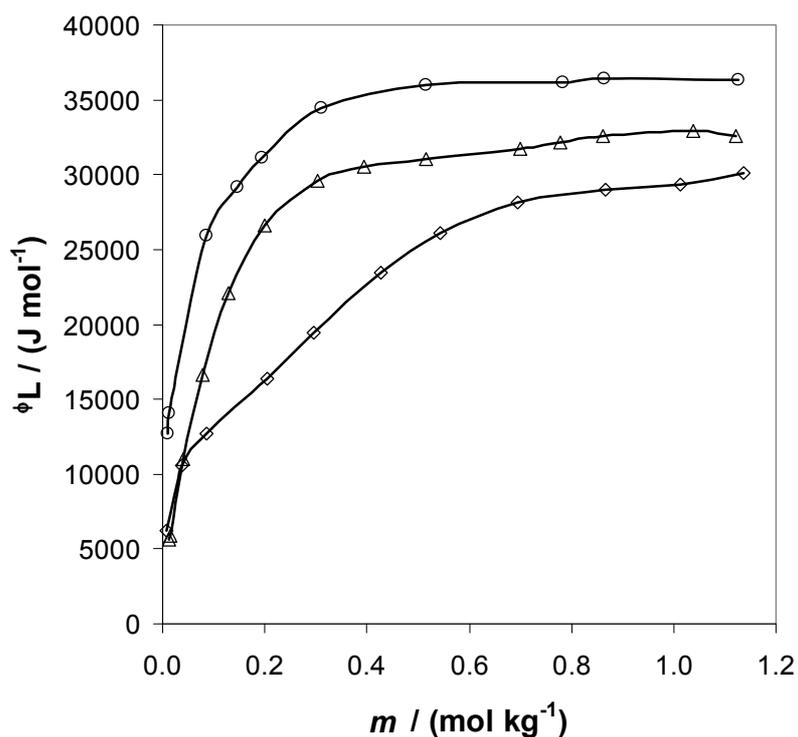
Fig. 5 – Calculated apparent relative molar enthalpies of 1-butyl-3-methylimidazolium bromide in 1-butanol, $^{\phi}L$, *vs.* molality, *m*, at T = 303.15 K (○), 310.15 K (Δ) and 318.15 K (◊) with the Archer and Rard model[24] using the parameters from Table 5.
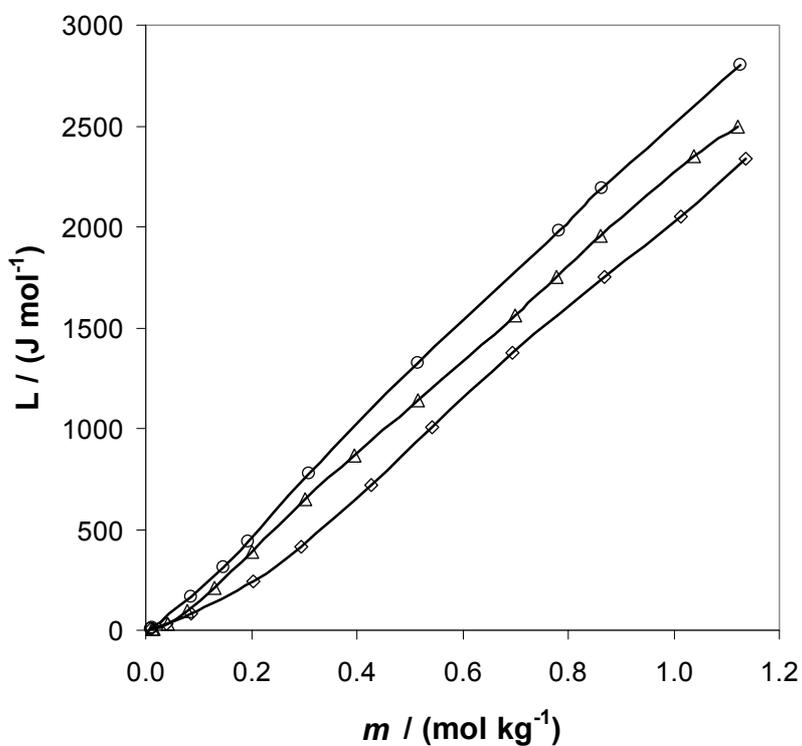

Fig. 6 – Calculated relative molar enthalpies of the mixtures, *L*, *vs.* molality, *m*, for 1-butyl-3-methylimidazolium bromide + 1-butanol at T = 303.15 K (○), 310.15 K (Δ) and 318.15 K (◊) with the Archer and Rard model[24] using the parameters from Table 5.
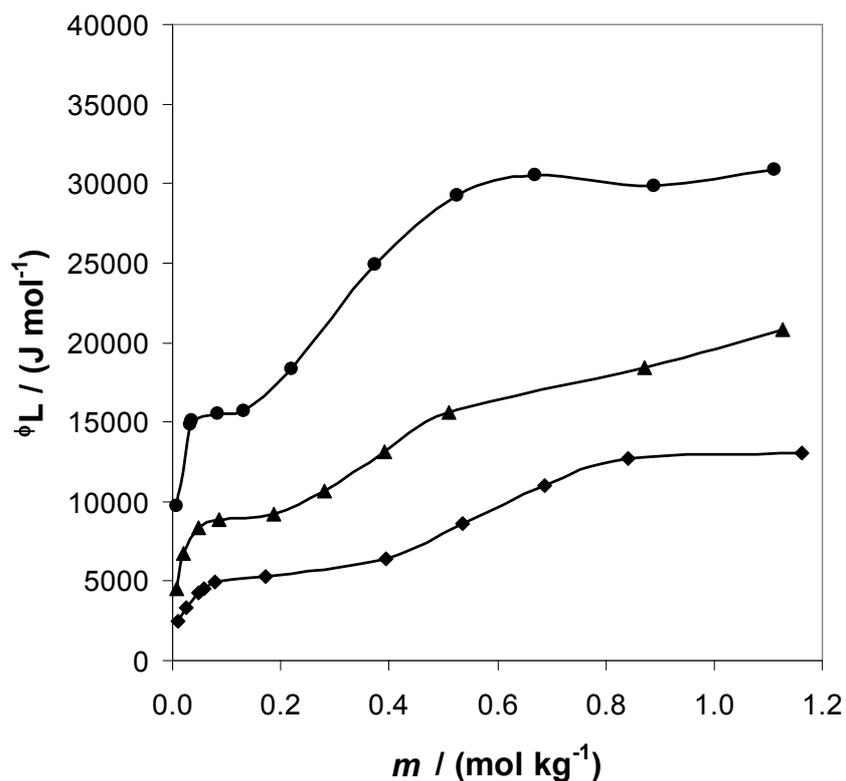
Fig. 7 – Calculated apparent relative molar enthalpies of 1-butyl-3-methylimidazolium chloride in 1-butanol, $^{\phi}L$, vs. molality, m, at T = 303.15 K (●), 310.43 K (▲) and 318.15 K (♦) with the Archer and Rard model[24] using the parameters from Table 5.
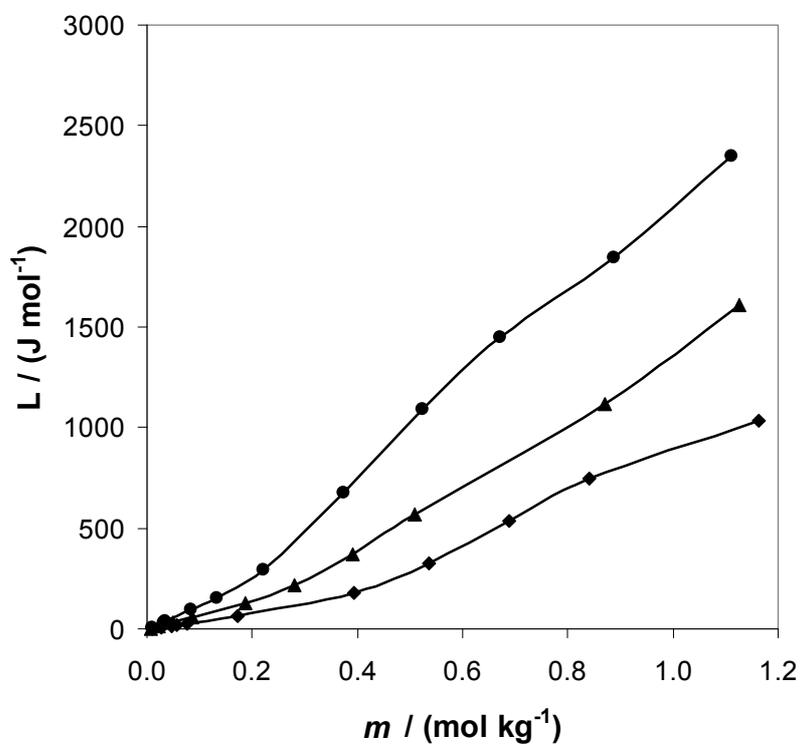

Fig. 8 – Calculated relative molar enthalpies of the mixtures, L, vs. molality, m, for 1-butyl-3-methylimidazolium chloride + 1-butanol at T = 303.15 K (●), 310.43 K (▲) and 318.15 K (♦) K with the Archer and Rard model[24] using the parameters from Table 5.

Table 6

The molar enthalpies of solid-solid phase transitions for [bmim]Cl, $\Delta_s H_{m,tr}$, in the solutions with 1-butanol or water at the corresponding molalities of phase transitions, m_{tr}, and 303.15, 310.43 and 318.15 K and atmospheric pressure of 101.22±0.26 kPa

T (K)	m_{tr} (mol kg^{-1})	$\Delta_s H_{m,tr}$ (J mol^{-1})
	1-butanol	
303.15	0.2975	7624
310.43	0.4503	6162
318.15	0.4639	2347
	water	
303.15	0.1427	5094
318.15	0.2235	2462

Standard uncertainties u are: $u(m_{tr}) = 0.0001$ mol kg^{-1}, $u(\Delta_s H_{m,tr}) = 0.025 \, \Delta_s H_{m,tr}$ J mol^{-1}

Analyzing experimental data pertaining to Fig. 3, we finally can conclude that the molar enthalpies of solid-solid phase transition for [bmim]Cl in the solution with 1-butanol $\Delta_s H_{m,tr}$ can be evaluated.

They are shown in Table 6 in comparison with the molar enthalpies of solid-solid phase transition of the same compound in the solution with water derived from literature[7] data, at various molalities and (303.15, 310.43 and 318.15) K.

CONCLUSIONS

New experimental data on molar solution enthalpies are reported for [bmim]Br and [bmim]Cl + 1-butanol systems at high dilution concentration region, three temperatures and atmospheric pressure. The experimental data for both systems have been correlated satisfactorily with an available semi-empirical electrolytes model within the complexity of the investigated ILs, inherent experimental errors and limitations of the model used. The predicted mixing molar enthalpies are in good agreement with experimental values demonstrating that the composition of the mixtures is measured accurately. The obtained values of enthalpies of solution for the two ILs in 1-butanol at infinite dilution are negative and roughly decrease with increasing temperature indicating strong solute/solvent interactions. They are more important for [bmim]Cl + 1-butanol system. At higher concentrations, the breaking of the solute/solute and solvent/solvent interactions became dominant. The apparent and relative molar enthalpies are positive and, at constant composition, they generally decrease with increasing temperature being a bit higher for bromide derivative system. This proves that the

molecular interactions increase in intensity by increasing temperature and the thermal effect of Br-Br derivatives bonds breaking is larger than that of Cl-Cl ones. The molar enthalpies of solid-solid phase transitions for [bmim]Cl in 1-butanol solution have been evaluated and they agree with those for the same IL in water solutions[7,15].

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