

*Dedicated to Professor Dumitru Oancea  
on the occasion on his 75th anniversary*

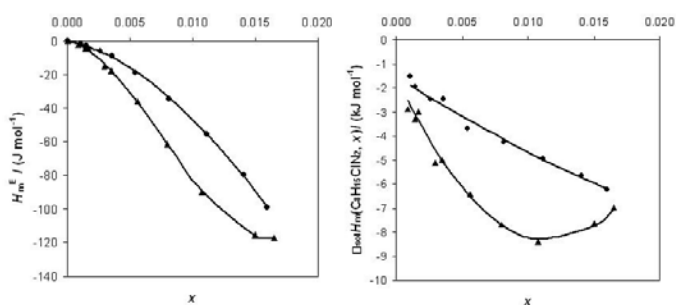
## SOLUTION AND EXCESS MOLAR ENTHALPIES FOR 1-BUTYL-3-METHYLIMIDAZOLIUM CHLORIDE + WATER SYSTEM AT (303.15 AND 318.15) K

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Enthalpies of solution for 1-butyl-3-methylimidazolium chloride ([bmim]Cl) + water system have been measured in a SETARAM C80 3D calorimeter with reversal mixing mechanism over the composition range of 0.0009 to 0.0165 mole fraction of [bmim]Cl at temperatures of 303.15 K and 318.15 K. The results are reported in terms of excess molar enthalpies,  $H_m^E$ , for  $x$  C<sub>8</sub>H<sub>15</sub>ClN<sub>2</sub> + (1- $x$ ) H<sub>2</sub>O system and molar enthalpies of solution for C<sub>8</sub>H<sub>15</sub>ClN<sub>2</sub>. The temperature and concentration dependence of  $H_m^E$ 's, are evaluated by fitting the 3-parameters Redlich-Kister equation to the experimental data. This thermodynamic property is negative in the whole composition range of studied homogeneous mixtures and at constant mole fraction became less negative with increasing temperature. 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 H-bonds type.



### INTRODUCTION

Ionic liquids (ILs), a new class of green solvents with low melting point (< 373 K), exhibit unique physicochemical properties.<sup>1-4</sup> 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.<sup>4-7</sup>

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.

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To date, for the aqueous system of [bmim]Cl, a number of papers have reported some of these properties.<sup>4,8-16</sup>

The solution and excess molar enthalpies data presented in this paper represent a continuation of our study on thermodynamic and thermophysical properties on prototype ILs with various solvents (alcohols, water) systems.<sup>17-19</sup> In the available literature for the [bmim]Cl + water system no data on solution and excess molar enthalpies have been found.<sup>20,21</sup> These data together with the 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 water, the hygroscopic character of the IL having significant practical consequences. The Gibbs-Helmholtz relation together with information on excess enthalpies allows for a temperature dependence estimation of the excess molar Gibbs energy,  $G_m^E$ , (or of the activity coefficients); the obtained data are very useful for fitting reliable  $G_m^E$  model parameters or the required group interaction parameters for group contribution methods. Beyond theoretical importance in developing predictive models, evaluation of the reciprocal temperature dependences of the activity coefficients at infinite dilution is useful for estimation of solvent properties for extraction processes.

## EXPERIMENTAL

The ionic liquid [bmim]Cl was purchased from Fluka with stated purity of >0.98 mass fraction. It was dried till constant mass under vacuum at 316.15 K and 0.1 kPa for 8 days and stored afterwards at 298.15 K under the same vacuum, during all experiments. Water was double distilled and deionized before use.

The calorimetric measurements were carried out in SETARAM C80 3D computer-controlled mixing and reaction calorimeter using reversal mixing cells made of stainless steel. Details on the measuring and reference cells as well as on the heat measuring procedure can be found in literature, for a similar calorimeter.<sup>23</sup> The amount of IL weighted in the lower recipient of the measuring cell was between 12 and 206 mg. In the larger, upper container of each cell the water sample was weighted in the amounts between 1.27 and 1.44 g. The temperature was measured by means of a 100  $\Omega$  platinum resistance thermometer located between the two vessels, and it was held constant to within  $\pm 0.05$  K during each measurement. The thermal equilibrium was reached in *ca.* 3 hours.

The calorimeter was Joule effect calibrated by means of a special cell with calibrated heaters as recommended by IUPAC.<sup>22</sup> The calibration procedure of Dallos *et al.* was applied.<sup>23</sup> The obtained calibration coefficient was  $k / (\mu\text{V} \times \text{mW}^{-1}) = 3.05762 \times 10^1 + 1.3653 \times 10^{-2} \times T - 3.094333 \times 10^{-4} \times T^2 + 8.932 \times 10^{-7} \times T^3 - 1.026667 \times 10^{-9} \times T^4$ .

The accuracy of the calorimeter was checked by performing test measurements of the enthalpies of solution at infinite dilution of KCl (crystals) in bidistilled and deionized water. The acquired value was  $0.097 \text{ kJ mol}^{-1}$  or 0.6 % lower

than literature value determined at 303.15 K.<sup>24</sup> The mixing enthalpy reproducibility was  $\pm 0.020 \text{ kJ mol}^{-1}$  or 0.1 % of the measured value. The KCl samples (Merck > 0.955 mass fraction) were carefully conditioned as recommended in literature.<sup>24</sup> Samples were weighed on a GH-252 A&D Japan balance with uncertainty of  $\pm 0.1 \text{ mg}$ . The estimated uncertainty of the mole fraction is  $\pm 0.0001$ .

The excess molar enthalpy for [bmim]Cl + water system was measured at 303.15 K and 318.15 K in the range of 0.0009 to 0.0165 mole fraction of [bmim]Cl. The composition range was dictated by the small capacity of the lower compartment of the two cells and the form of the solid [bmim]Cl (loose crowded powder). Preliminary measurements for this system at 303.15 K by using [bmim]Cl with small water content (0.005 mass fraction by Karl-Fischer titration) resulted in quite scattered data of excess molar enthalpies ( $0.01 \text{ kJ mol}^{-1}$  standard deviation) and of molar heat of solution for [bmim]Cl ( $2.93 \text{ kJ mol}^{-1}$  standard deviation) when correlated with 3-parameters Redlich-Kister equation.<sup>25</sup> Consistently improved results are reported in the present study.

## RESULTS AND DISCUSSION

The measured enthalpy changes during the dissolution  $\Delta_{sol}H$  are summarized in Table 1 for various mole fractions  $x = n_1 / (n_1 + n_2)$  of [bmim]Cl aqueous solutions consisting in  $n_1$  moles of [bmim]Cl (1) and  $n_2$  moles of water (2). The total molar (integral) enthalpies of solution of [bmim]Cl,  $\Delta_{sol}H_m(\text{C}_8\text{H}_{15}\text{ClN}_2, x)$ , and the excess molar enthalpies,  $H_m^E$ , for  $x \text{ C}_8\text{H}_{15}\text{ClN}_2 + (1-x) \text{ H}_2\text{O}$  calculated from the experimental data as:

$$\Delta_{sol}H_m = \Delta_{sol}H / n_1 \quad (1)$$

$$H_m^E = \Delta_{sol}H / (n_1 + n_2) \quad (2)$$

are also reported in Table 1.

The excess molar enthalpies for  $x \text{ C}_8\text{H}_{15}\text{ClN}_2 + (1-x) \text{ H}_2\text{O}$  are negative over the whole composition range of studied homogeneous mixtures, and became less negative when temperature increases.

The experimental  $H_m^E$ 's for  $x \text{ C}_8\text{H}_{15}\text{ClN}_2 + (1-x) \text{ H}_2\text{O}$  at  $T = 303.15 \text{ K}$  and  $T = 318.15 \text{ K}$  were fitted in TableCurve® V5.01 using the 3-parameters Redlich-Kister equation and assuming that the adjustable  $a_i$  parameters are linear functions of temperature  $T$ :

$$H_m^E = x(1-x)\{a_1 + a_2(1-2x) + a_3(1-2x)^2\} \quad (3)$$

Under the inherent scatter of experimental data obtained at low IL concentrations, the natural fitting alternative to the standard least squares minimization was a Lorentzian robust one, with the following objective function:

$$O.F. = \ln \left[ 1 + \sum_{i=1}^N \left( H_{m,i,exp}^E - H_{m,i,calc}^E \right)^2 \right] \quad (4)$$

Table 1

Experimental enthalpies of solution,  $\Delta_{sol}H$ , for 1-butyl-3-methylimidazolium chloride (1) + water (2) system, the molar enthalpy of solution of 1-butyl-3-methylimidazolium chloride in aqueous solution having a mole fraction of  $C_8H_{15}ClN_2$  equal to  $x$ ,  $\Delta_{sol}H_m(C_8H_{15}ClN_2, x)$ , and excess molar enthalpy,  $H_m^E$ , for  $x C_8H_{15}ClN_2 + (1-x) H_2O$  at  $T = 303.15$  K and  $T = 318.15$  K

$10^4 n_1 / \text{mol}$	$10^2 n_2 / \text{mol}$	$x$	$\Delta_{sol}H / \text{J}$	$\Delta_{sol}H_m(C_8H_{15}ClN_2, x) / (\text{kJ mol}^{-1})$	$H_m^E / (\text{J mol}^{-1})$
$T = 303.15$ K					
0.6927	7.9223	0.0009	-0.20	-2.9	-2.5
1.1622	8.1488	0.0014	-0.39	-3.3	-4.7
1.2939	7.8845	0.0016	-0.39	-3.0	-4.9
2.3416	7.9245	0.0029	-1.19	-5.1	-15.0
2.7309	7.8035	0.0035	-1.37	-5.0	-17.5
4.4198	7.8795	0.0056	-2.84	-6.4	-35.9
6.1945	7.6958	0.0080	-4.76	-7.7	-61.4
8.1124	7.4782	0.0107	-6.82	-8.4	-90.2
10.9349	7.1735	0.0150	-8.41	-7.69	-115.5
11.7937	7.0291	0.0165	-8.37	-7.10	-117.1
$T = 318.15$ K					
0.8359	8.0067	0.0010	-0.13	-1.5	-1.6
1.1507	7.9023	0.0015	-0.23	-2.0	-2.9
2.0668	7.8851	0.0026	-0.50	-2.5	-6.2
2.8797	7.9750	0.0036	-0.71	-2.5	-8.9
4.2308	7.7891	0.0054	-1.48	-3.7	-18.9
6.2117	7.5726	0.0081	-2.65	-4.3	-34.7
8.3529	7.4022	0.0112	-4.15	-5.0	-55.4
10.2765	7.2018	0.0141	-5.82	-5.7	-79.6
11.5589	7.1185	0.0160	-7.19	-6.2	-99.3

Standard uncertainties  $u$ :  $u(n_1) = 0.0001$  mol,  $u(n_2) = 0.0001$  mol,  $u(x) = 0.0001$ ,  $u(\Delta_{sol}H) = 0.05$  J,  $u(\Delta_{sol}H_m) = 0.2$  kJ mol<sup>-1</sup>,  $u(H_m^E) = 0.5$  J mol<sup>-1</sup>

The fitting procedure yielded the temperature dependence of the coefficients of equation (3),  $a_i$ , as follows:

$$a_1 / \text{J mol}^{-1} = 35406225 - 772279.2 (T - 273.15) \quad (5)$$

$$a_2 / \text{J mol}^{-1} = -72252239 + 1572576.9 (T - 273.15) \quad (6)$$

$$a_3 / \text{J mol}^{-1} = 36844545 - 800298.99 (T - 273.15) \quad (7)$$

The obtained parameters reproduce the best currently available experimental data within the low concentration range of [bmim]Cl.

The experimentally determined excess molar enthalpies data and the values calculated by

$$\Delta_{sol}H_m = H_m^E / x = (1-x) \{ a_1 + a_2(1-2x) + a_3(1-2x)^2 \} \quad (8)$$

Fig. 2 shows a comparison of the experimentally obtained  $\Delta_{sol}H_m(C_8H_{15}ClN_2, x)$  results for [bmim]Cl in water at  $T = 303.15$  K and  $T = 318.15$  K with corresponding values calculated by equation (8) (solid lines). The standard deviation of equation (8) is  $\sigma(\Delta_{sol}H_m) = 0.3$  kJ mol<sup>-1</sup>.

The molar enthalpy of solution at infinite dilution for [bmim]Cl  $\Delta_{sol}H_m^\infty(C_8H_{15}ClN_2)$  can be obtained from equation (8) as:

$$\Delta_{sol}H_m^\infty = \lim_{x \rightarrow 0} (\Delta_{sol}H_m) = a_1 + a_2 + a_3 \quad (9)$$

According to equation (9), the calculated molar enthalpies of solution at infinite dilution for [bmim]Cl are:  $\Delta_{sol}H_m^\infty(C_8H_{15}ClN_2, 303.15 \text{ K}) = \Delta_{sol}H_m^\infty(C_8H_{15}ClN_2, 318.15 \text{ K}) = -1.5$  kJ mol<sup>-1</sup>.

equation (3) are compared in Fig. 1. It can be seen that equation (3) is able to describe the measured  $H_m^E$  over the entire composition range at both temperatures. The obtained standard deviation of equation (3) is  $\sigma(H_m^E) = 0.8$  J mol<sup>-1</sup>.

The molar enthalpies of solution of [bmim]Cl,  $\Delta_{sol}H_m(C_8H_{15}ClN_2, x)$ , can be expressed in terms of the system composition variables,  $x$ , and temperature,  $T$ , combining equations (3), (5), (6) and (7):

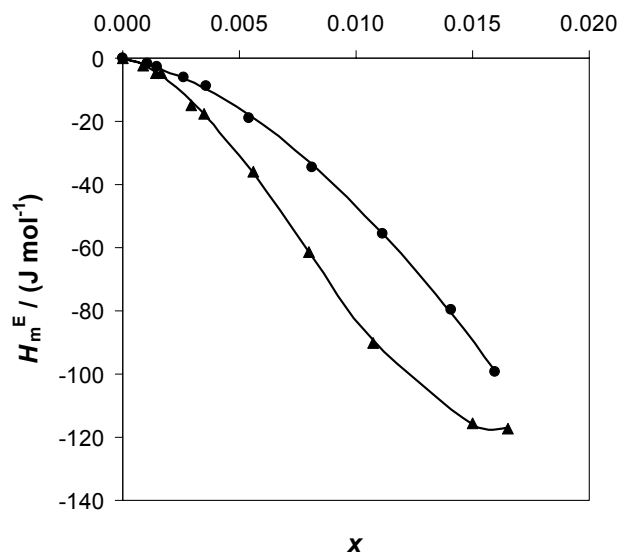


Fig. 1 – Excess molar enthalpies  $H_m^E$  for  $x$   $C_8H_{15}ClN_2 + (1-x)$   $H_2O$  at the temperatures  $T = 303.15$  K ( $\blacktriangle$ ) and  $T = 318.15$  K ( $\bullet$ ). Filled symbols represent experimental data and solid lines represent the Lorentzian fit (equation (3)) of experimental data.

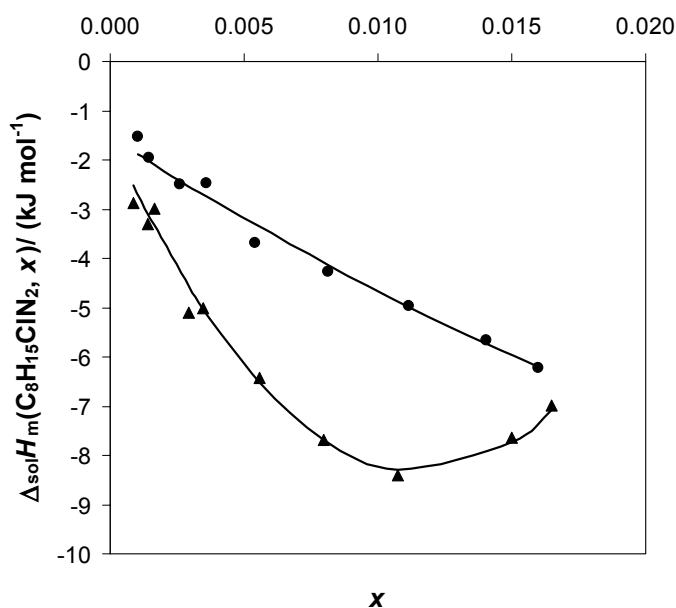


Fig. 2 – Experimental molar enthalpies of solution of 1-butyl-3-methylimidazolium chloride  $\Delta_{sol}H_m(C_8H_{15}ClN_2, x)$  in water as a function of the mole fraction  $x$  of  $C_8H_{15}ClN_2$  at the temperatures  $T = 303.15$  K ( $\blacktriangle$ ) and  $T = 318.15$  K ( $\bullet$ ). Solid lines represent values calculated by equation (8).

From the infinite dilution molar enthalpy of solution, the reciprocal temperature dependence of activity coefficients at infinite dilution can be determined by the following version of the Gibbs-Helmholtz equation:

$$\left( \frac{\partial \ln \gamma_1^\infty}{\partial \frac{1}{T}} \right)_{P,x} = \frac{\Delta_{sol} H_{m,1}^\infty}{R} \quad (10)$$

In eq. (10) the subscript 1 denotes 1-butyl-3-methylimidazolium chloride and  $R$  is the gas constant.

A 3-parameters version for the Redlich-Kister equation was selected because the model is sufficiently flexible in describing any excess property and generally the usual uncertainty of most of the currently available experimental data does not require more parameters for this function.<sup>29</sup> The selected optimization method for

the evaluation of Redlich-Kister adjustable parameters is essential. For the presented data the Lorentzian minimization was proved to be much better than the classical least-squares method. The later did not work properly for fitting, within experimental uncertainties, the molar enthalpy of solution at infinite dilution region.

The classical models developed for non-electrolyte solutions, NRTL, Wilson, UNIQUAC, UNIFAC, Redlich-Kister, etc. were used for modeling different types of experimental data (e.g. vapor-liquid equilibria (VLE)) obtained for IL + alcohol or water systems.<sup>13,14,17-19,27,28</sup> This can be explained by the fact that the ion charge in ILs is usually disperse and the long-range electrostatic forces are so weak, compared with the short-range intermolecular forces, that they can be neglected. Therefore, in the present work the liquid solutions were modeled as mixtures of non-dissociated components.

According to some authors in terms of VLE data, the [bmim]Cl + water system presents negative deviations from ideality (activity coefficients for water  $\gamma_{\text{H}_2\text{O}} < 1$ ), suggesting attractive interactions between the ionic liquid and water.<sup>12,14</sup> The activity coefficients are lower than those for IL + ethanol mixtures pointing to stronger interactions between IL and water than those between IL and ethanol.

Domanska *et al.* demonstrated that the ability of the solute (imidazolium ILs) to form hydrogen bonds with potential solvents (alcohol, water) is an important feature in mixtures behavior.<sup>15</sup> Basically, [C<sub>n</sub>mim][Cl] ILs can act both as a hydrogen-bond acceptor ([Cl]<sup>-</sup>) and donor ([C<sub>n</sub>mim]<sup>+</sup>) and would be expected to interact with solvents which have both accepting and donating sites. As alcohol and water are hydrogen-bonded solvents, with both high enthalpies of association and association constants, they would be expected to stabilize solutes with hydrogen-bonded donor sites (H<sup>+</sup>).

On the other hand, it was proven that in the water + [bmim]Cl system, the apparent molar volume decreases at low molality and then slightly increases with IL concentration.<sup>9,10</sup> This decrease can result from the formation of hydrogen bonds between water and 1-butyl-3-methylimidazolium chloride.

From the present measurements of excess molar enthalpies at two temperatures we can confirm that the interactions at mixing of the two compounds [bmim]Cl + water are strongly attractive in the high dilution region and they are most likely of the

H-bonds type between H<sup>+</sup> of water and Cl<sup>-</sup> of the IL. Physical packing between imidazolium cations cycles [bmim]<sup>+</sup> from IL and OH<sup>-</sup> groups from water and between an ice-like structured water and 1-butyl-3-methyl organic chain are not excluded at mixing due to the bulkier structure of both IL and water. The H-bond type interactions between unlike molecules seem to be dominant since the absolute value of the excess molar enthalpy is decreasing with increasing temperature.

From the VLE measurements, the calculated excess molar Gibbs energy  $G_m^E$  is negative having a minimum value at approximately 0.33 mole fraction of IL. It is -3529 J mol<sup>-1</sup> at 303.15 K and -3703 J mol<sup>-1</sup> at 318.15 K.<sup>14</sup> Molar excess enthalpy estimated from Gibbs-Helmholtz equation (reciprocal temperature dependence of  $G_m^E/T$ ) is -12 J mol<sup>-1</sup> at an average temperature of 310.65 K. It is known that  $H_m^E$  calculated in this way is also affected by high uncertainty, therefore the value cannot be compared with the extrapolated value from the present measurements.<sup>30,31</sup> Unfortunately, activity coefficients at infinite dilution for the [bmim]Cl (solute) in water (solvent) are not experimentally available in the literature thus a test of thermodynamic consistency of the present measurements is not (yet) possible.<sup>20</sup> In fact, the activity coefficients at infinite dilution for [bmim]Cl solute in water solvent cannot be easily determined experimentally. As, at least by gas chromatographic method and dilutor gas stripping technique they cannot be measured, the present results represent useful thermodynamic information.<sup>32</sup>

## CONCLUSIONS

Enthalpies of solution for 1-butyl-3-methylimidazolium chloride + water system have been measured at temperatures of 303.15 and 318.15 K and very small concentration of the solid IL solute. The excess molar enthalpies have been evaluated. They are negative over the whole composition range of studied homogeneous mixtures, and became less negative when temperature increases. The data have been correlated successfully with 3-parameters Redlich-Kister equation by using Lorentzian robust optimization method. The molar enthalpy of solution at infinite dilution has been determined. It is not temperature dependent giving therefore the thermodynamic information that variation of the natural logarithm of the activity coefficient at infinite dilution of the IL in water

with reversal temperature is linear with the slope equal with -180.4 K. Negative excess molar enthalpies indicate that the solute/solvent interactions in this region are of H-bond type which decrease in strength with increasing temperature.

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## REFERENCES

1. J. Dupont, R. F. Souza and P. A. Z. Suarez, *Chem. Rev.*, **2002**, *102*, 3667–3692.
2. M. J. Earle and K. R. Seddon, *Pure Appl. Chem.*, **2000**, *72*, 1391–1398.
3. T. Welton, *Chem. Rev.*, **1999**, *99*, 2071–2083.
4. H. Shekaari and S. S. Mousavi, *Fluid Phase Equilib.*, **2009**, *286*, 120–126.
5. J. S. Wilkes, *J. Mol. Catal. A: Chem.*, **2004**, *214*, 11–17.
6. J. F. Brennecke and E. J. Maginn, *AIChE J.*, **2001**, *47*, 2384–2389.
7. P. Wasserscheid and W. Keim, *Angew. Chem. Int. Ed.*, **2000**, *39*, 3772–3789.
8. B. Lal, M. Sahin and E. Ayranci, *J. Chem. Thermodyn.*, **2012**, *54*, 142–147.
9. E. Gomez, B. Gonzalez, A. Dominguez, E. Tojo and J. Tojo, *J. Chem. Eng. Data*, **2006**, *51*, 696–701.
10. N. Calvar, B. Gonzalez, A. Dominguez and J. Tojo, *J. Solution Chem.*, **2006**, *35*, 1217–1225.
11. J. W. Russo and M. M. Hoffmann, *J. Chem. Eng. Data*, **2010**, *55*, 5900–5905.
12. H. Passos, I. Khan, F. Mutelet, M. G. Freire and J. A. P. Continho, *Ind. Eng. Chem. Res.*, **2014**, *53*, 3737–3748.
13. P. J. Carvalho, I. Khan, A. Morais, J. F. O. Granjo, N. M. C. Oliveira, L. M. N. B. F. Santos and J. A. P. Continho, *Fluid Phase Equilib.*, **2013**, *354*, 156–165.
14. N. Calvar, B. Gonzales, E. Gomez and A. Dominguez, *J. Chem. Eng. Data*, **2006**, *51*, 2178–2181.
15. U. Domanska, E. Bogel-Lukasik and R. Bogel-Lukasik, *Chem. Eur. J.*, **2003**, *9*, 3033–3041.
16. H. -C. Hu, A. N. Soriano, R. B. Leron and M. -H. Li, *Thermochim. Acta*, **2011**, *519*, 44–49.
17. M. Teodorescu, *Rev. Chim. (Bucharest)*, **2015**, *66*, 529–536.
18. M. Teodorescu, *Ind. Eng. Chem. Res.*, **2014**, *53*, 13522–13528.
19. M. Teodorescu, *J. Chem. Thermodyn.*, **2015**, *87*, 58–64.
20. DDBST (Software and Separation Technology) GmbH, The Dortmund Data Bank (DDB), Oldenburg, Germany, <http://www.ddbst.com/>, accessed January 2016.
21. Scopus Database, <http://www.scopus.com/>, accessed January 2016.
22. S. M. Sarge, E. Gmelin, W. H. Hohne, H. K. Cammenga, W. Hemminger and W. Eysel, *Thermochim. Acta*, **1994**, *247*, 129–168.
23. A. Dallos, E. Hajos-Szikszay and J. Liszi, *J. Chem. Thermodyn.*, **1998**, *30*, 263–270.
24. A. Sanahuja and E. Cesari, *Thermochim. Acta*, **1985**, *85*, 163–166.
25. M. Teodorescu, Experiments with possible application to the homogenous solutions of solid nanostructures with liquid solvents, (Rom.), Nanoscience and Nanotechnology National Seminar, Romanian Academy, Bucharest, March 26<sup>th</sup>, 2015, [http://www.romnet.net/nano/SNN2015\\_26.03/](http://www.romnet.net/nano/SNN2015_26.03/), accessed May 2015.
26. N. V. Sastry, N. M. Vaghela and P. M. Macwan, *J. Mol. Liq.*, **2013**, *180*, 12–18.
27. R. Kato, M. Krummen and J. Gmehling, *Fluid Phase Equilib.*, **2004**, *224*, 47–54.
28. J. Zhao, X. -C. Jiang, C. -X. Li and Z. -H. Wang, *Fluid Phase Equilib.*, **2006**, *247*, 190–198.
29. J. M. Prausnitz, R. N. Lichtenthaler and E. G. Azevedo, „Molecular thermodynamics of fluid phase equilibria”, 3<sup>rd</sup> Ed., Prentice-Hall Inc., New Jersey, 1999.
30. J. S. Rowlinson and F. L. Swinton, “Liquids and Liquid Mixtures”, 3<sup>rd</sup> Ed., Butterworths, London, 1982.
31. G. Boukais-Belaribi, B. F. Belaribi, J. Lohmann and J. Jose, *Fluid Phase Equilib.*, **2007**, *262*, 180–186.
32. M. Teodorescu, M. Krummen and J. Gmehling, *J. Chem. Eng. Data*, **2003**, *48*, 435–439.