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Jan Rotrekl, Pavel Vrbka, Zuzana Sedláková, Zdeněk Wagner, Johan Jacquemin
and Magdalena Bendová*

Solid–liquid equilibria in systems [$C_x$mim][Tf_2N] with diethylamine

Abstract: In the present work, the solid–liquid–liquid equilibrium in the binary system of diethylamine (1) and ionic liquid (2) 1-methyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide and solid–liquid equilibrium in system 1-methyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide was studied. Phase equilibrium was determined experimentally by means of a polythermic method. These data were then used to determine the activity coefficients for both ionic liquids. For the pure diethylamine the enthalpy of fusion was determined by differential scanning calorimetry, because to the best of our knowledge, this data is not yet reported in the open literature, *a contrario* of pure ionic liquids tested during this work.

Keywords: calorimetry; ionic liquids; ISSP-16; solubility.

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Introduction

Accurate experimental data on solubility of ionic liquids and molecular compounds are essential in the successful design and modeling of separation processes and also to test thermodynamic models and theories. This paper is a continuation of a systematic study of thermodynamic properties and phase equilibrium of systems containing organic compounds [1–6].

The growing interest in developing new technologies is both due to a search for cost-effective processes and environmentally friendly compounds. Thanks to their extraordinary properties, increased attention is paid to room-temperature ionic liquids (RTILs). Ionic liquids are considered to be “green chemicals,” as they are mostly non-flammable, with negligible vapor pressure, thermally and chemically very stable, with melting points below 100 °C and often lower than room-temperature [7]. They are used as solvents, with

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***Corresponding author: Magdalena Bendová,** Eduard Hála Laboratory of Separation Processes, Institute of Chemical Process Fundamentals of the ASCR, Rozvojová 135/1, 16502 Prague 6, Czech Republic, e-mail: bendova@icpf.cas.cz
Jan Rotrekl, Zuzana Sedláková and Zdeněk Wagner: Eduard Hála Laboratory of Separation Processes, Institute of Chemical Process Fundamentals of the ASCR, Rozvojová 135/1, 16502 Prague 6, Czech Republic
Pavel Vrbka: Department of Physical Chemistry, Institute of Chemical Technology Prague, Technická 5, 16628 Prague 6, Czech Republic
Johan Jacquemin: The QUILL Research Centre, School of Chemistry and Chemical Engineering, Queen’s University of Belfast, Stranmillis Road, Belfast BT9 5AG, UK

the benefit of almost non-existent volatility, as opposed to the commonly used volatile organic compounds (VOCs) that represent a burden on the environment. Another advantage of ionic liquids lies in the possibility of tuning their chemical and physical properties by a judicious choice of anion and cation and substituent, which allows for preparing solvents for the specific application directly as required. Due to their ionic character they also present good solvating ability and are used as media for Friedel-Crafts [8, 9] or regioselective reactions [10]. Ionic liquids are also used in liquid–liquid separations [11] or in analytical chemistry, such as in chromatographic or electrophoretic methods [12]. Because of their mechanical properties and high thermal stability some ionic liquids are used as lubricants [13]. Ionic liquids 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide can be successfully used for liquid–liquid extraction processes of both aromatic and aliphatic hydrocarbons mixtures [14] or polyhydric alcohols [15].

In a previous article [16] liquid–liquid and vapor–liquid equilibrium in binary systems of imidazolium based ionic liquids with diethylamine and triethylamine were studied. To accomplish the insight into the phase behavior of these systems, solid–liquid equilibrium was measured in the present paper. For these measurements binary systems of the two ionic liquids with diethylamine were selected. The ionic liquids studied in this work were 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (abbr. [emim][Tf_2N]) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (abbr. [bmim][Tf_2N]), that are hydrophobic. The choice of the two members of a homologous series enabled us to estimate the influence of the alkyl chain length on the cation of ionic liquids on their phase behavior in mixtures. On the other hand the choice of diethylamine brings in general new information about the behavior of an industrially important solvent very often used in, e.g., CO_2 capture. Moreover, the experimental data on liquid and solid phase behavior are interesting for the study of intermolecular interactions between the ionic liquid and a non-associating solvent. Most of the literature data about the solid–liquid equilibrium with ionic liquids typically present solubilities of solids in ionic liquids in a limited part of the concentration region [17–19]. Some precise data from solid–liquid equilibrium measurements of ionic liquids with industrially important solvents, e.g., water, alcohols or hydrocarbon are available, but these data are still not comprehensive [20–22]. The present paper thus represents a contribution to the knowledge base of condensed phase behavior of ionic liquids.

Experimental

Materials

All chemicals used were of the highest purity, the overview of their molar masses, temperatures of fusion compared with literature values, and water content is given in Table 1. The studied ionic liquids were synthesized at QUILL, Belfast.

Diethylamine was distilled over calcium chloride to prevent the absorption of moisture. The ionic liquids were dried and degassed under vacuum for at least 48 h. All chemicals were then kept under dry nitrogen atmosphere. Water content was determined by the Karl Fischer titration using a Schott TitroLine KF volumetric titrator.

Table 1: Properties of chemicals used.

	Source	Purity (stated by the manufacturer)	M (g·mol^{-1})	$T^{fus,lit.}$ (K)	$T^{fus, exp.}$ (K)	Water content (wt.%)
diethylamine	Sigma-Aldrich	99.5 %	73.14	223.15 [23]	224.73	0.0119
[emim][Tf_2N]	QUILL	–	391.31	255.10 [24]	257.13	0.0101
[bmim][Tf_2N]	QUILL	–	419.37	270.22 [25]	271.96	0.0105

Liquid phase behavior

All the studied mixtures were prepared by weighing using an analytical balance Sartorius (precision 0.0001 g). The uncertainty in the mole fraction was found to be ± 0.0005.

Solid–liquid equilibrium

Time-temperature cooling and warming curves were recorded using the HP-VEE software. Similarly to previous works [1, 6], warming curves were used to read the liquidus temperatures of measured mixtures with known composition. The temperatures were measured with an uncertainity of ± 0.15 K.

Three types of equilibrium cells were used. Two of the cells used in previous work were used for measurements in system with [emim][Tf_2N]. The first equilibrium cell (Fig. 1a) consists of a double-walled equilibrium cylindrical vessel (180 cm^3), Pt resistance thermometer Pt 100, multimeter Agilent 34401A, a motor-driven Teflon stirrer, thermostat Lauda RL6 CP, and a computer and had been described in detail elsewhere [1]. The thermostat used may reach temperatures as low as 193 K. The optimum rate of the temperature change was found to be 4 $K\cdot h^{-1}$. This cell was used to measure SLE in mixtures rich in diethylamine that have a significantly lower freezing temperature than the ionic liquid [emim][Tf_2N].

The second equilibrium cell (Fig. 1b) used in this work consists of a cylindrical single-walled vessel (30 cm^3), described in detail elsewhere [6] placed on a submersible magnetic stirrer in a Proline clear-view thermostat Lauda DLK 45 (lower temperature limit 233 K), a Pt resistance thermometer Pt 100, an Agilent 34401A multimeter, and a computer. It was possible to observe the measured mixtures through the thermostat window. This cell was used for measurements in mixtures rich in the ionic liquid [emim][Tf_2N]. The optimum heating rate for this apparatus was found to be 2 $K\cdot h^{-1}$.

The third equilibrium cell (Fig. 1c) operated in the before mentioned Lauda RL 6 CP thermostat was used for the measurements with [bmim][Tf_2N] that showed stronger tendency towards subcooling. Thus, experiments had to be performed at lower temperatures (down to 193 K). This double-walled cell equipped with a motor-driven glass stirrer, a Pt resistance thermometer Pt 100, and a multimeter Agilent 34401A combines some advantages of both above-mentioned cells. The internal volume was reduced to approximately 40 cm^3 which resulted in a smaller consumption of ionic liquid. The double wall provides a smooth variation of temperature in the cell, leading in consequence to smoother melting curves and to their more straightforward interpretation. The motor-driven stirrer is more efficient and ensures a permanent and thorough mixing of the solid and liquid phase, as opposed to the magnetic stirrer.

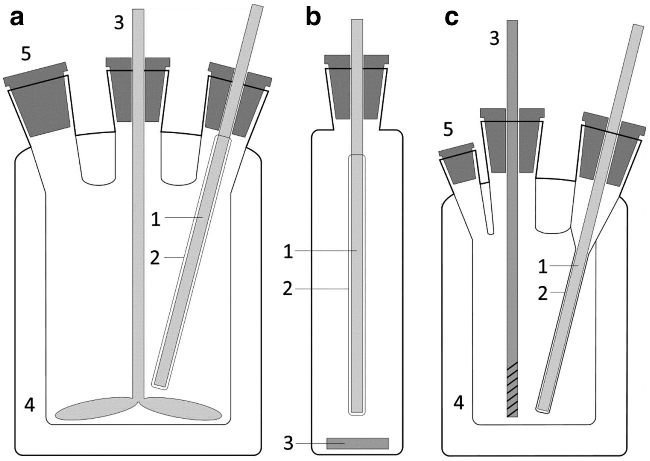

Fig. 1: (a) 1 – Thermometer, 2 – glass tube filled with ethanol, 3 – motor-driven teflon stirrer, 4 – air jacket, 5 – inlet for sample addition; (b) 1 – thermometer, 2 – glass tube filled with ethanol, 3 – magnetic stirrer; (c) 1 – thermometer, 2 – glass tube filled with ethanol, 3 – motor-driven glass stirrer, 4 – air jacket, 5 – inlet for sample addition.

The gold-plated resistance thermometer used in all the experimental setups has an ITS-90 certificate of calibration, this calibration being checked at the triple point of water. The occurrence of rime on the thermometer body, that made homogenization of the mixture more difficult, was reduced by placing the thermometer into a narrow glass tube filled with ethanol. The third equilibrium cell (Fig. 1c) used for measurements in the system with [bmim][Tf_2N] the glass tube was therefore directly integrated in the apparatus.

Temperature changes were recorded in the computer using an HP-VEE program. More than 100 000 values of temperature (resistance) were often collected in one run; temperature was recorded every 2 s. Generally, the determination of temperature was reproducible within 0.15 K in consecutive experiment.

Liquid–liquid equilibrium

The region of limited miscibility was determined by the cloud-point method. The Proline clear-view thermostat was used as previously [4]. Two-phase mixtures of known compositions were placed into a the one-walled cell (Fig. 1b) with a Pt resistance thermometer Pt 100. The mixtures were stirred with a magnetic stirrer. The cell was immersed into the above mentioned Proline clear-view thermostat in solid–liquid equilibrium measurements. Turbidity appearance and disappearance were observed visually. Heating and cooling rate was 0.5 $K \cdot min^{-1}$. The mixture change from heterogeneous to homogeneous was observed easily than the opposite process. The temperature reproducibility was better than 0.2 K on the detection of change of the studied binary liquid mixture from homogenous to heterogeneous and the uncertainty in temperature determination was found to be ± 0.15 K.

DSC measurements

To determine the enthalpy of fusion of diethylamine, calorimetric measurements were carried out by means of a differential scanning calorimeter TA Q1000. Due to the nature of diethylamine, especially its high volatility, a special method for sample preparation had to be developed. To avoid any contamination of the sample, diethylamine was kept under dry nitrogen atmosphere and the sampling was performed in a glove-box. An essential step for a successful preparation of the sample was to fill the calorimetric crucibles at temperature around 253 K. At this temperature the vapor pressure of diethylamine is low enough to prevent evaporation. In addition, wetting of the aluminum walls of the cells by the studied liquid is avoided. Only at such conditions it was possible to fill the crucibles without any loss of substance and to ensure their air-tightness.

Measurement of the enthalpy of fusion was performed using a simple heating program from 193 to 293 K with heating rate 10 $K \cdot min^{-1}$, this program was repeated four times.

The DSC was calibrated for this heating rate using the melting point temperature of the commonly used standards: water, gallium, naphthalene, indium and tin. The enthalpy of fusion was determined with an uncertainty of approx. 2 %.

Calculations

Activity coefficients from solid–liquid equilibrium data

From the solid–liquid equilibrium data the activity coefficients for both components of the studied systems were calculated. For both ionic liquids, for which the isobaric heat capacities are available from literature [24, 25], eq. 1 was used, in which the temperature dependence of enthalpy of fusion is taken into account. For diethylamine no heat capacity data were found in literature, therefore the simpler Schröder–van Laar relation using only temperature-independent the enthalpy of fusion was used (2). Assuming the activity coefficient is equal to unity we can get the eq. 3 for the ideal solubility of component *i* that is independent of the other component of the system. Ideal solubility was then calculated for all the components and was compared with real behavior.

$$\ln\gamma_i = -\ln x_i + \frac{\Delta_{fus}H_i}{R}\left(\frac{1}{T_{fus,i}} - \frac{1}{T}\right) + \frac{\Delta a_i}{RT}\left[T_{fus,i} - T + T\ln\left(\frac{T}{T_{fus,i}}\right)\right] + \frac{\Delta b_i}{2RT}(T - T_{fus,i}) + \frac{\Delta c_i}{6RT}\left(2T_{fus}^3 - T^3 - 3T_{fus}^2 T\right) \quad (1)$$

$$\ln\gamma_i = -\ln x_i + \frac{\Delta_{fus}H_i}{R}\left(\frac{1}{T_{fus,i}} - \frac{1}{T}\right) \quad (2)$$

$$\ln x_i = \frac{\Delta_{fus}H_i}{R}\left(\frac{1}{T_{fus,\mathrm{i}}} - \frac{1}{T}\right) \quad (3)$$

In these relations γ_i and x_i stand for activity coefficient and mole fraction respectively, $\Delta_{fus}H_i$ denotes enthalpy of fusion of component i, $T_{fus,i}$ is the temperature of fusion, T is the measured temperature. The coefficient Δa_i, Δb_i and Δc_i denote the differences between the coefficients of temperature dependence of heat capacity of liquid and solid. R is the universal gas constant (8.314 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$). Standard squared error of the calculated activity coefficients was determined with application of the error propagation law (4). The calculation assumes the error of heat capacity is included in the error of enthalpy of fusion and the errors in temperature, composition and enthalpy are independent. The experiment setup meets this condition.

$$\sigma(\ln\gamma) = \sqrt{\left(\frac{\partial \ln\gamma}{\partial x}\right)^2 \cdot s_x^2 + \left(\frac{\partial \ln\gamma}{\partial T}\right)^2 \cdot s_T^2 + \left(\frac{\partial \ln\gamma}{\partial \Delta H}\right)^2 \cdot s_{\Delta H}^2} \quad (4)$$

In eq. 4 the derivative terms stand for the change of the activity coefficient with mole fraction, temperature and enthalpy, respectively, which are multiplied by the squared accuracy of determination of the corresponding property. The derivatives were determined numerically (5),

$$\sigma_k = \left(\frac{\partial \ln\gamma}{\partial k}\right)_{l,m} = \frac{\ln\gamma(x + s_k) - \ln\gamma(x - s_k)}{2s_k} \quad (5)$$

where σ_k is derivative of the logarithm of activity coefficient (function of k, l, m) with respect to k (l and m are hold constant), s_k is the accuracy of the property k.

Solid–liquid equilibrium prediction using COSMOThermX

In this work, the solid–liquid equilibrium of binary diethylamine + [emim][Tf_2N] and diethylamine + [bmim][Tf_2N] mixtures as a function of the composition were performed within the COSMOThermX software (version C30, release 14.01) by using the same methodology as already reported by our group elsewhere [26, 27]. To conduct these calculations, the prior knowledge of the enthalpy or entropy of fusion (ΔH_{fus} or ΔS_{fus}, respectively) and melting temperature (T_{fus}) is crucial. ΔH_{fus} and T_{fus} values used during this work were taken from literature [24, 25] and from experimental results reported in the Tables 1-SI–3-SI of the supporting information.

Results and discussion

The experimentally obtained data on solid–liquid–liquid equilibrium for the binary system diethylamine (1) + [emim][Tf_2N] (2) (Fig. 2a) and solid–liquid equilibrium for diethylamine (1) + [bmim][Tf_2N] (2) (Fig. 2b) provided simple phase diagrams with eutectic points. The experimental data, as well as literature data used and calculated activity coefficients are in listed in the Supporting Information (Tables 1-SI–4-SI). The two phase diagrams are mainly similar, with an expected eutectic point being very close to the pure

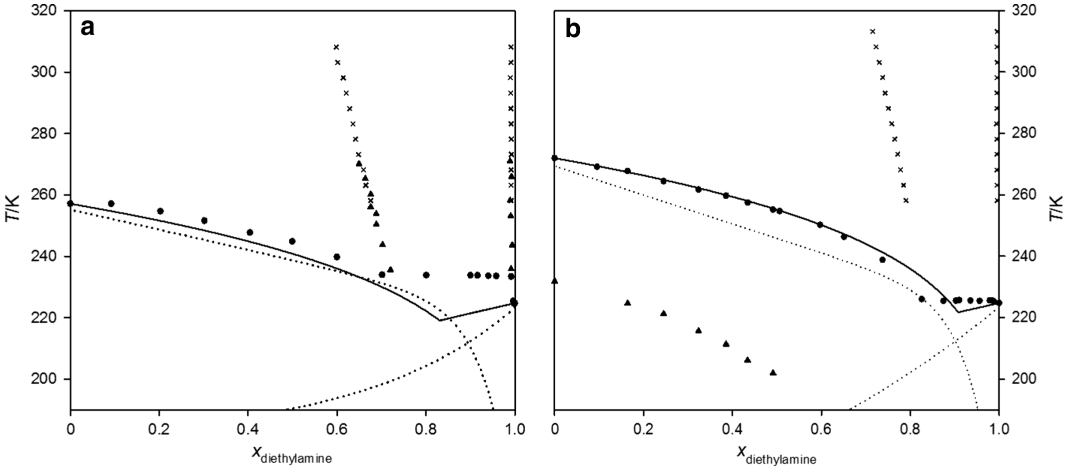

Fig. 2: (a) Diethylamine + [emim][Tf$_2$N]; • experimental SLE data, ▲ experimental LLE cloud-point data, × literature volumetric LLE data [16], solid line – ideal solubility, dotted line – smoothed COSMO-RS calculation of SLE. (b) Diethylamine + [bmim][Tf$_2$N]; • experimental SLE data, ▲ metastable SLE data, × literature volumetric LLE data [16], solid line – ideal solubility, dotted line – smoothed COSMOThermX calculations of SLE.

diethylamine melting point (more than 0.99 in mole fraction of diethylamine) and the liquid–liquid region is located in the concentration range from $x_1 = 0.70$ to 0.99 for the system with [emim][Tf$_2$N] and $x_1 = 0.82$ to 0.99 for the system with [bmim][Tf$_2$N]. The eutectic point in the [emim][Tf$_2$N]-based system lies close to pure diethylamine (x_1~0.99) at 224.57 K, whereas the temperature of fusion of the pure diethylamine is 224.73 K. In the [bmim][Tf$_2$N]-based system, the liquidus on the diethylamine side of the phase diagram is practically missing due to the overlapping liquid–liquid region. Therefore no eutectic point could be experimentally determined for this system. However, according to the experimental data (see Table S2 of the Supporting Information), the eutectic point could be expected in the composition range $0.99 < x_1 < 1$. Such differences in SLE between diethylamine + [emim][Tf$_2$N] and diethylamine + [bmim][Tf$_2$N] are reflected in the activity coefficients for the two ionic liquids in solution. The activity coefficients for [emim][Tf$_2$N] range between 1.1–1.2, whereas the activity coefficients for [bmim][Tf$_2$N] are practically equal to unity. Therefore, the experimental solubility of [bmim][Tf$_2$N] in diethylamine is in good agreement with its calculated ideal solubility. The comparison between experimental data and the calculated ideal solubility of both ionic liquids is also shown in Fig. 2. Additionally, the enthalpy of fusion of pure diethylamine was determined by DSC measurement to be 13.3 kJ·mol^{-1}. Using this value, it was then possible to calculate also the activity coefficients for diethylamine in the system with [emim][Tf$_2$N]. Because of the liquidus compositions close to pure diethylamine, these coefficients are close to unity. In the system with [bmim][Tf$_2$N] no liquidus on the diethylamine side could be measured, thus no activity coefficients for diethylamine were calculated in this system.

A significant difference between the two systems was observed in the course of cooling and heating curves. Whereas in the system with [emim][Tf$_2$N] these curves are in accordance with the theoretical expectations in compliance with the Gibbs phase rule, system with [bmim][Tf$_2$N] exhibits anomalies both in the behavior of cooling as well as heating curves. Among other, the cooling curves show abrupt changes in the slope, non-monotonous temperature-time dependence on both cooling and heating curves occurs in particular parts of concentration region. Metastable solid phase was observed in the region from mole fraction 0.5 to the pure [bmim][Tf$_2$N]. These findings are in agreement with the phase behavior of pure [bmim][Tf$_2$N] described in literature. [28] Measured temperature range and cooling mode (till 193 K) clearly enables the appearance of the supercooled liquid and metastable solid phase. Examples of anomalies on cooling and heating curves are shown in Supporting Information (Fig. 1-SI, Fig. 2-SI).

Finally, to evaluate the capability of chemical engineering software like COSMOThermX [29] to predict such complex fluid phase behavior, SLE was then calculated by COSMOThermX as a function of the diethylamine mole fraction as shown in Fig. 2a and b in the case of the diethylamine + [emim][Tf_2N] and diethylamine + [bmim][Tf_2N] mixture, respectively. From this work, it appears that eutectic composition is observed in both cases at $x_1 \approx 0.9$ and $T_{\text{eutectic}} = 213.15$ K. As expected from the similarity of the sigma profiles of each cation [30], small difference is observed from COSMOThermX calculations between the two SLE curves. A comparison between experimental data (Tables S2 and S3) with COSMOThermX calculations shows that this methodology can be only used to predict qualitatively the general SLE trend. Interestingly, by using COSMOThermX and by following the methodology proposed by Abramov et al. [31], it appears that such mixtures do not show a tendency to co-crystallize. In fact, this later result seems to prove that the experimental anomalies on cooling and heating curves, observed with the diethylamine + [bmim][Tf_2N] mixture, are not due to a co-crystalization of the system but rather to the strong tendency of the ionic liquid towards subcooling.

Liquid–liquid equilibria in the studied systems was investigated in a greater detail in a previous paper [16] in which it was shown that the mutual solubility of diethylamine with the studied ionic liquids decreased with the increasing alkyl chain length. In this work, it was possible to measure points of the binodal curve by the cloud-point method in the system diethylamine (1) + [emim][Tf_2N] at a range of temperatures lower than those from the previous work (from 270 K to the temperatures around 225 K). As shown previously by means of neutron diffraction measurements [16], the non-associating nature of diethylamine leads to a more even distribution of both ionic liquid and amine molecules on the microscopic scale. Measurements carried out in this work thus confirm not only the validity of the volumetric method data, but also the trend of the phase behavior of this system towards LCST behavior caused by this microscale arrangement. The cloud-point LLE data for the ionic-liquid rich phase were fitted by an empirical equation (6) modified from [32].

$$\ln x = A + \frac{B}{T}, \tag{6}$$

Where $A = 180.76$ and $B = -1.0935$ K, the goodness-of-fit $R^2 = 0.9729$.

For the equilibrium temperatures measured in previous work by the volumetric method [16], the composition of liquid phases was calculated and compared with the experimental value. Maximal relative deviation between these two data sets is < 1 %. The cloud-point data obtained in this work are also in good agreement with the liquid–liquid equilibrium data, measured in previous work by volumetric method.

Unfortunately, the fact that SLE and LLE largely overlap at lower temperatures in the system diethylamine (1) + [bmim][Tf_2N] made measurements of the points of the binodal curve impossible.

Conclusion

In this work solid–liquid and solid–liquid–liquid equilibria were studied in two systems of diethylamine with ionic liquid. In continuation of our previous work [16] a comprehensive picture of phase behavior was obtained that, to the best of our knowledge, was not yet presented for the studied systems in literature till now. Interesting influence of the ionic liquid structure on the properties of the studied systems found in our previous work were confirmed especially for the system diethylamine + [bmim][Tf_2N] in which the metastable crystalline phases found for the pure ionic liquid by Paulechka et al. [28] were mirrored in the strong tendency of the studied system towards subcooling and in a possible metastable solid–liquid equilibrium.

In addition to experimental data, a prediction of the solid–liquid equilibrium was carried out by the COSMO-RS methodology, showing a qualitatively good agreement between the experimental and predicted values. Excess enthalpies calculated for the studied systems using COSMO-RS showed that the systems do not possibly show a tendency towards co-crystal formation.

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