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Is there any sense to investigate volumetric and acoustic properties of more binary mixtures containing Ionic Liquids?

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ABSTRACT

The excess speed of sound, excess molar volume and excess molar isentropic compressibility of 52 binary mixtures containing Ionic Liquids at $T = 298.15$ K were calculated using selected literature speed of sound and density data. The second components were alcohols: methanol, or ethanol, or 1-propanol, or 2-propanol, or 1-butanol or other solvents: acetone, acetonitrile, tetrahydrofuran, dichloromethane and dimethylsulfoxide. The Balankina's relative excesses, X_{bal}, *i.e.* the ratios between excess and ideal quantities X^E/X^{id} were also determined to reduce the structural impact of pure components to absolute excesses. Analysis of quantities determined shows some patterns for concentration dependences of large groups of mixtures; thus, the scheme for influence of anion or cation of Ionic Liquids and solvent on Balankina's relative excesses was proposed. It seems that presented analysis provide the knowledge about absolute and relative excess quantities for other mixtures without doing the experimental work. It is also visible that analysis of excess molar quantities and X_{bal} parameters can support the interpretation of interactions which occur between Ionic Liquids and solvent.

1. Introduction

Acoustic and volumetric properties of pure Ionic Liquids or Room Temperature Ionic Liquids (IL or RTIL) and binary mixtures containing ILs has been investigated since 2005 [1,2]. The unique properties of ILs were at this time well recognized and described in numerous papers, *i.e.* in [3–9]. Many researchers were aware of some disadvantages of ILs which can limit their practical use almost from the beginning, like relatively high viscosity, the sensitivity to humidity or difficulties in obtaining materials of a high purity [10,11]. Tailoring of ILs, or in other words some changes in/of cation or/and anion of Ionic Liquid, may obviously reduce viscosity but at the same time it can change other properties into undesirable direction. For this reason, in some cases using binary or ternary mixtures containing ILs maybe be a good alternative to pure ILs. Their main advantage over pure ILs is low cost of samples, the more that many binary mixtures containing ILs can be cleaned repeatedly from solvent and used for preparation of new solutions.

The motivation for this work were findings presented in the previous papers of some of us [12,13]. In these articles [12,13] it has been shown that excess molar volume V^E, and excess molar isentropic compressibility K_S^E, of homologues of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ILs with some aprotic solvents, like acetonitrile, tetrahydrofuran and dimethylsulfoxide practically do not depend on the chain length of substituent attached to methylimidazolium cation of Ionic Liquid. The most popular in literature are papers where one or two ILs are investigated with different solvents including alcohols and water. Other combinations of systems are not numerous; thus, it is relatively easy to overlook the described similarity effect. The lack of significant dependence of values of V^E and K_S^E on the length of alkyl chain attached to methylimidazolium cation for some bis(trifluoromethylsulfonyl)imide ILs in solution with chosen solvents may have also important meaning. From practical point of view, it is not interesting to determine more the excess properties for similar binary systems. From the other side, the unique excess function's behavior is very interesting itself and may be interpreted through molecular interactions occurring in these systems. This can be also investigated in more detailed way.

Another parallel idea that could be used here was found in papers by Reis *et al.* [14,15], Balankina [16] and continued by one of us [17], where relative excesses, X_{bal}, *i.e.* the ratios between excess and ideal quantities X^E/X^{id} for binary systems were regarded in a place of absolute ones. Their advantage over the absolute excess functions is that they allow to reduce the impact of structural parameters on any X^E. Reis and co-workers [14,15] and later

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Przybyła *et al.* [18] regarded also the mutual dependence between excess molar volume, V^E, excess molar isentropic compressibility, K_S^E and excess speed of sound, u^E, which may be a start point for prediction of one excess function from others.

All reasons given above prompted us to carry out the detailed investigations of excess speed of sound, excess molar volumes and excess molar isentropic compressibilities of larger group of binary mixtures containing ILs and alcohols or other, molecular aprotic solvents, like acetone, acetonitrile, tetrahydrofurane (thf), dichloromethane and dimethysulfoxide (dmso). The properties of binary mixtures with alcohols were chosen due their popularity, what allowed to construct some pattern of behavior of u^E, V^E and K_S^E with variation of alcohol, or anion, or cation of Ionic Liquid. Systems with other solvents than alcohols, despite they are much more interesting for us, are difficult to investigate due to the lack of data for comparisons; thus, the only basic conclusions for this group of systems were presented here. We did not take into account the data for binary mixtures of ILs with water, because this issue deserves to be regarded in a separate paper.

While we started gathering the necessary literature data it was found immediately that they are too numerous to carry out our project in a form of short study; thus, it was necessary to find the reasonable limitation. Finally, the amount of papers containing simultaneously both quantities, the speed of sound and density of binary mixtures containing Ionic Liquid with organic solvents is limited. Since we based our investigations on comparisons, many of papers were not useful for us as presenting data for unique Ionic Liquid or solvent, or the concentration range of IL was limited in order to investigate only partial molar quantities in diluted solutions. Our selection was also dictated by necessity to find a convenient pattern for comparisons. Finally, we selected 17 articles that report the speed of sound and density data [1,12,13,19–32] for 52 systems at T = 298.15 K. Unfortunately, some data could not be used, like speed of sound and density values for [EMIm][TFO] + ethanol by Vercher and co-workers [24], since results calculated by us were far from those reported by Authors. We presume that some mistakes should be done in presentation of experimental u and d values.

In order to obtain the consistent data the excess speed of sound, excess molar volume and excess molar isentropic compressibility at T = 298.15 K were calculated in this work for 52 systems containing alcohols and other popular solvents despite such calculations were presented or not in literature. Calculated u^E, V^E, K_S^E and relative excesses X^E/X^{id} are ordered into 18 groups and are illustrated in figures in text, or in Supporting Information only if they were not previously reported in any form in the literature. If the suitable figures are available elsewhere, the appropriate citation is noted. The results for absolute excess functions are interpreted with the help of some conclusions taken from literature. Similarly, a careful analysis of relative excess properties was carried out in order to find some patterns in behavior of binary systems containing ILs. This will be also presented here in details.

2. Calculations and interpretation of absolute and relative excess functions

From the speed of sound, u, and density, d, it is possible to calculate isentropic compressibility coefficient, κ_S ($\kappa_S = -V^{-1}(\partial V/\partial p)_S \equiv d^{-1}(\partial d/\partial p)_S$, where V is the molar volume and p is pressure), using Newton–Laplace's equation:

$$\kappa_S = \frac{1}{d \cdot u^2}. \tag{1}$$

Its molar counterpart, *i.e.*, molar isentropic compressibility, K_S ($K_S = -(\partial V/\partial p)_S$) can be calculated from its relation with isentropic compressibility coefficient and molar volume:

$$K_S = V \cdot \kappa_S. \tag{2}$$

Excesses of speed of sound, u^E, or molar volume, V^E, or molar isentropic compressibility, K_S^E can be obtained from the general equation:

$$X^E = X - X^{id}, \tag{3}$$

where X denoted u, or V, or K_S. X^{id} are quantities for ideal mixtures and are defined depending on quantity; for molar volume one may found $V^{id} = \sum_{i=1}^{2} x_i \cdot V_i^o$, whereas for speed of sound in the case for two component system, u^{id} is:

$$u^{id} = \frac{V^{id}}{\left(\sqrt{(x_1 M_1 + x_2 M_2) K_S^{id}}\right)}, \tag{4}$$

where V_i° is the molar value of pure component, M is the molar mass and x is molar fraction; subscripts 1 and 2 refer to first and second component, respectively; "o" in superscripts refers to a pure state. It is necessary to mention here that term "excess" in respect of speed of sound is not very fortunate, since this quantity does not represent the excess function in the traditional thermodynamic sense. Due to the lack of more adequate name, we decided to use the term "the excess speed of sound" suggested by Douhéret at al. [33]

Molar isentropic compressibility of ideal mixture, K_S^{id}, is calculated according equation (2) using values of V^{id} and κ_S^{id} for ideal mixture. In our work κ_S^{id} was obtained from well-known relation [34]:

$$\kappa_S^{id} = \phi_1 \kappa_{S,1}^\circ + \phi_2 \kappa_{S,2}^\circ + T\left[\phi_1 \frac{V_1^\circ \left(\alpha_{p,1}^\circ\right)^2}{C_{p,1}^\circ} + \phi_2 \frac{V_2^\circ \left(\alpha_{p,2}^\circ\right)^2}{C_{p,2}^\circ} - \frac{V^{id}\left(\alpha_p^{id}\right)^2}{C_p^{id}}\right], \tag{5}$$

where the volume fractions, ϕ_i, are calculated as follows:

$$\phi_i = \frac{x_i V_i^o}{V^{id}}. \tag{6}$$

Other quantities present in equation (5), α_p is the isobaric coefficient of thermal expansion ($\alpha_p = V^{-1}(\partial V/\partial T)_p \equiv -d^{-1}(\partial d/\partial T)_p$) and C_p is the molar isobaric heat capacity. For ideal mixtures of two components C_p^{id} and α_p^{id} can be written as:

$$C_p^{id} = x_1 C_{p,1}^\circ + x_2 C_{p,2}^\circ, \tag{7}$$

$$\alpha_p^{id} = \phi_1 \alpha_{p,1}^o + \phi_2 \alpha_{p,2}^o. \tag{8}$$

It should be noticed that equation (1) thanks to relation between molar isentropic compressibility and isentropic compressibility coefficient (equation (2)) can be rewritten according to the form:

$$u^2 \cdot M \cdot K_S = V^2. \tag{9}$$

From this start point regarding equation (9) for thermodynamically ideal mixture and, in the next step, dividing all thermodynamic properties into their ideal and excess part, it is possible to obtain the final equation [14,15]:

$$\left(1 + \frac{u^E}{u^{id}}\right)^2 \cdot \left(1 + \frac{K_S^E}{K_S^{id}}\right) = \left(1 + \frac{V^E}{V^{id}}\right)^2. \tag{10}$$

The relative excess quantities, *i.e.* Balankina's excess functions (X_{bal}) were in principle invented to reduce the impact of structure parameters of compounds of binary mixture on absolute excess properties. Equation (10) can be regarded also as a convenient tool for testing the thermodynamic consistency of experimental excess