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Thermochemistry of Mixing Imidazole-Based Ionic Liquids with Water and Organic Solvents

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Abstract—The results of the calorimetric studies of the enthalpies of mixing of some ionic liquids, 1-butyl-3-methylimidazolium chloride and acetate, with water, pentanol, dimethyl sulfoxide and dimethylformamide are presented. Protic solvents interact with the ionic liquid anion, wheras aprotic, with the cation. The mixing enthalpy depends on the dissociation degree of the ionic liquid.

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Presently, the ionic liquids are used in the production of new materials instead of many environmentally hazardous volatile solvents and as the media for the catalytic and biological reactions, gas purification, and ion separation [1–3]. The ionic liquids have the dissolving power toward many organic, inorganic, and organometallic materials. They are able to dissolve salts, fat, fiber, amino acids, mono- and polysaccharides, oils, inks, plastics, and even DNA [4]. They are highly polar, thermally stable and have very low vapor pressures. Combining the cation and anion of an ionic liquid it is possible to adjust their specific properties for the specific applications. The number of the combinations of different structures of cations and anions of ionic liquids was found to be more than 10^{18} [5]. One of the promising applications of the ionic liquids is the preparation of solutions of the natural polymers for the technological processing. For example, 1-alkyl-3-methylimidazolium halides and acetates are used to dissole the wood pulp, silk fibroin, and hair keratin [2, 6–9].

Most ionic liquids are hygroscopic and easily take up water, forming a crystal hydrate. They can be mixed with many organic solvents [4], but the binary mixtures based on the ionic liquids are still poorly studied. Meanwhile, to reduce the viscosity of the solvent and its cost seems reasonable to add a diluent into the ionic liquid. For the purposeful selection of the diluents it is necessary to know the features of their interaction with the ionic liquid, which depends not only on its physical and chemical properties (the melting point in particular), but on the solvating power of the ionic liquid. The unambiguous description of the nature of interactions in a binary system can provide the thermochemical methods, which also allow to quantify the energy of the interaction between the components of the system and to analyze the comparative data of the diluents.

The aim of this work is the calorimetric study of mixing 1-butyl-3-methylimidazolium chloride and acetate with water and protic and aprotic organic solvents.

Figures 1 and 2 show the dependence of the mixing enthalpy of the protic and aprotic diluents with 1-butyl-3-methylimidazolium chloride and acetate, respectively, from the components ratio in the system. Mixing the ionic liquids with the protic diluents and DMF in the whole composition range is accompanied by the exothermic effect. The negative values of the mixing enthalpies of the ionic liquids with the protic liquids (water and pentanol) are significantly higher than in the case of the aprotic DMF. The thermal effect of mixing 1-butyl-3-methylimidazolium acetate with dimethylsulfoxide is positive over the whole range of the compositions. The obtained values of the mixing enthalpies are integral values that include the positive enthalpy of destruction of the initial pure components and the negative enthalpies of the molecular interaction of the heterogeneous components of a binary mixture. Probably the investigated ionic liquids

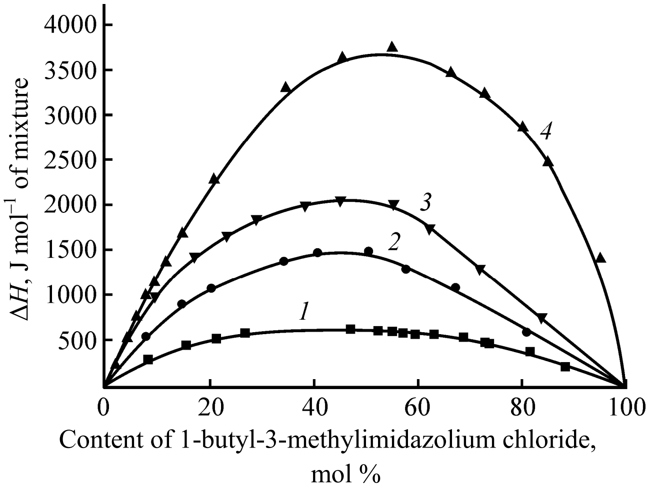

Fig. 1. Dependence of the mixing enthalpy of protic and aprotic diluents with 1-butyl-3-methylimidazolium chloride on the components ratio. (*1*) DMSO, (*2*) DMF, (*3*) pentanol, and (*4*) water.

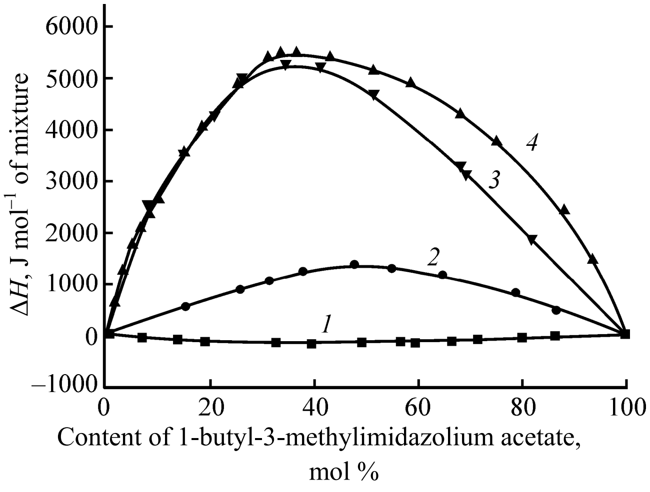

Fig. 2. Dependence of the enthalpy of mixing the protic and aprotic diluents with 1-butyl-3-methylimidazolium acetate on the components ratio. (*1*) DMSO, (*2*) DMF, (*3*) pentanol, and (*4*) water.

interact more strongly with the protic diluents water and alcohol than with the aprotic diluents. It is possible to assume that the protic diluents interact with the anions of the ionic liquids. The maximal exothermic effect of their mixing with the chloride-containing ionic liquid observed at the molar ratios of 1:1 (Fig. 1, curves *3*, *4*), and in the case of the acetate-containing ionic liquid it is shifted toward lower concentrations of the ionic liquids to the molar ratios of 1:2 (Fig. 2, curves *3*, *4*). This is explained by the structure of the acetate anion, in which the negative charge is distributed between two oxygen atoms. Accordingly, one acetate anion of 1-butyl-3-methylimidazolium acetate can simultaneously interact with two molecules of water or alcohol, while a chloride anion can interact only with one molecule of the diluent.

The aprotic diluents interact with the positively charged cations of the ionic liquids. The value of total thermal effect is much smaller. According to quantum-chemical calculations, the positive charge localized on the cation is less than on the anion, since the charge of the cation is distributed between the atoms of the imidazolium ring [11, 12]. The maximal enthalpy of the mixing with DMF and DMSO of both ionic liquids is observed at 50 mol% of the mixture. These data suggest that the thermal effect of the DMSO interaction with ionic liquids is much less than that of DMF. In the case of mixing with 1-butyl-3-methylimidazolium acetate this interaction is even weaker than the interaction of the uniform molecules of the components in the mixture, as seen from the fact that the total effect is endothermic. Although both aprotic diluents have a similar electron-donating ability (the donor numbers for DMSO and DMF are 28.9 and 26.6, respectively [13, 14]), to explain the differences in the obtained values of the mixing enthalpy it is necessary to take into account the dissociation degree of the ionic liquids in the mixture. This can be deduced by measuring the electrical conductivity of the solutions of the ionic liquids mixed with the test diluent (see the table). We can conclude that in DMSO both ionic liquids are much less dissociated and the ions are less accessible to the interaction with the diluent than in the case of dimethylformamide. As a result the positive energy of the bond breaking in the 1-butyl-3-methylimidazolium acetate exceeds the energy of the interaction of diverse components of the mixture when DMSO is added. The quantum-chemical calculations [11, 12] confirm that the interaction of a cation–anion pair in 1-butyl-3-methylimidazolium acetate is stronger than in chloride.

Electrical conductivity (μS cm^{-1}) of the ionic liquids solutions

Solvent	1-Butyl-3-methylimidazolium chloride	1-Butyl-3-methylimidazolium acetate
DMSO	176.1	152.1
DMF	539.2	282.3
Water	493.2	324.6
Pentanol	13.7	12.8

The obtained results of calorimetric studies of the enthalpies of mixing such ionic liquids as 1-butyl-3-

methylimidazolium chloride and acetate with water, pentanol, dimethyl sulfoxide and dimethylformamide makes possible the following conclusions. Protic solvents interact with the anion of ionic liquid, and aprotic, with the cation. The anions of the ionic liquids form a stronger bond with the diluents than cations where the charge is distributed between the atoms of the heterocycle. The mixing enthalpy depends on the dissociation degree of the ionic liquid. When selecting a diluent for an ionic liquid, for example, to dissolve natural polymers, DMSO can be recommended, as it interacts weakly with the ionic liquid, and therefore it does not compete for the solvated substance.

EXPERIMENTAL

The ionic liquids, 1-butyl-3-methylimidazolium chloride and acetate were purchased Aldrich, used pentanol, dimethyl sulfoxide, and dimethylformamide were of reagent grade. The solvents were dehydrated over zeolite.

The mixing enthalpies were measured at 363 K on a Calvet calorimeter (Setaram, France) using the 10 cm^3 calorimeter cells. One of the components to be mixed was placed in a glass ampule, which was broken after establishing the thermal equilibrium in the calorimeter system. The calorimeter was calibrated by the determination of the thermal effect of a KCl solution in water. The measurement error is 2.5%.

The conductivity of the ionic liquids solutions in the diluent (c 5×10^{-3} M was determined on a KL-S-1 conductometer with a glass measuring cell KL-S-1A, consisting of an air-tight measuring flask containing two parallel platinum discs (cell constant is 14.70 m^{-1}). The cell of 7 cm^3 volume was maintained at constant temperature 298 K.

REFERENCES

1. Baker, G.A., Wang, J., Fan, M., and Weatherley, L.R., *Chem. Eng. J.*, 2009, vol. 1, p. 147.
2. US Patent no. 6824599, 2002.
3. Keskin, S., Kayrak-Talay, D., Akman, U., and Hortacsu, O., *J. Supercrit. Fluids*, 2007, vol. 43, p. 150.
4. US Patent no. 20080146849 A1, 2008.
5. US Patent no. 20060189499 A1, 2006.
6. Murugesan, S. and Linhard, R.J., *Curr. Org. Synth.*, 2005, vol. 2, p. 437.
7. Phillips, D.M., Drummy, L.F., Conrady, D.G., Fox, D.M., Naik, R.R., Stone, M.O., Trulove, P.C., De Long, H.C., and Mantz, R.A., *J. Am. Chem. Soc.*, 2004, vol. 126, p. 14350.
8. Phillips, D.M., Drummy, L.F., Naik, R.R., De Long, H.C., Fox, D.M., Trulove, P.C., and Mantz, R.A., *J. Mater. Chem.*, 2005, vol. 15, no. 15, p. 4206.
9. Xie, H., Li, S., and Zhang, S., *Green Chem.*, 2005, vol. 7, p. 606.
10. Wasserscheid, P. and Keim, W., *Angew. Chem.*, 2000, vol. 112, p. 3926.
11. Novoselov, N.P., Sashina, E.S., Kuz'mina, O.G., and Troshenkova, S.V., *Khim. Volokna*, 2008, no. 3, p. 75.
12. Novoselov, N.P., Sashina, E.S., Petrenko, V.E., and Zaborskii, M., *Khim. Volokna*, 2007, no. 2, p. 153.
13. Lowry, H.T. and Richardson, K.S., *Mechanism and Theory in Organic Chemistry*, New York: Hapre & Row, 1987.
14. Moskva, V.V., *Soros. Obrazovat. Zh.*, 1999, vol. 4, p. 44.