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Imidazolium based ionic liquids containing methanesulfonate anion: comprehensive thermodynamic study

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ABSTRACT

New experimental vapor pressures and vaporization enthalpies of the ionic liquids $[C_n\text{mim}][\text{CH}_3\text{SO}_3]$ (with the alkyl chain length $n=2, 3$ and 4) have been measured by the QCM and TGA methods. Energies of combustion of $[C_2\text{mim}][\text{CH}_3\text{SO}_3]$ and $[C_4\text{mim}][\text{CH}_3\text{SO}_3]$ were measured in a high-precision rotating-bomb combustion calorimeter and used for calculation the aqueous enthalpy of formation of the $\Delta_f H_m^0(\text{CH}_3\text{SO}_3\text{aq}^-)$ anion. The solubility parameters of ILs under study have been derived from experimental $\Delta_1^E H_m^0(298.15\text{K})$ and used for estimation of miscibility of some common solutes in $[C_n\text{mim}][\text{CH}_3\text{SO}_3]$. This comprehensive thermodynamic study will facilitate chemical engineering calculations of processes involving ionic liquids.

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1. Introduction

Ionic Liquids (ILs) have been considered as a neoteric solvents for different types of catalyzed and non-catalyzed chemical reactions. They could be a practical alternative to the traditional phase separation due to a possibility to remove the reaction products from the solvent by the thermal means, because of the negligibly low vapor pressure of ILs even at elevated temperatures. Thus, the solvent and catalyst can be retained quantitatively during the synthesis or distillation processes and the more volatile reaction products can be easily separated. Moreover, ILs are also claimed to be useful as heat-transfer fluids in solar heating and absorption refrigerating systems (Van Valkenburg et al., 2005). One of a most attractive feature of ILs is the possibility to adjust their physical-chemical properties according to the task, due to the countless number of available cations and anions. Nevertheless, a very restricted number of ILs are nowadays commercially available on the large-scale. Two of them: the 1-ethyl-3-methylimidazolium methanesulfonate $[C_2\text{mim}][\text{CH}_3\text{SO}_3]$ and

1-butyl-3-methylimidazolium methanesulfonate $[C_4\text{mim}][\text{CH}_3\text{SO}_3]$ are actually produced by BASF on the kilogram scale under the trade names of Basonics™ ST 35 and Basonics™ ST 78 (with a general assay of purity of 95%, containing 0.5% water, and 2% of chloride anion). The $[C_2\text{mim}][\text{CH}_3\text{SO}_3]$ was successfully used for the separation of, ethyl-tetra-butyl ether and ethanol (Arce et al., 2006). The high selectivity of extraction of aromatic hydrocarbons from aliphatic hydrocarbons and especially of thiophene from heptane by the $[C_2\text{mim}][\text{CH}_3\text{SO}_3]$ was shown by Blahut et al. (2010). Continuous gas drying with the $[C_2\text{mim}][\text{CH}_3\text{SO}_3]$ has been shown as a very promising alternative drying agent to the conventional absorbent triethylene glycol (Krannich et al., 2016a). It has turned out that the drying capacity of the IL system is about two times higher compared to triethylene glycol. Hence, a simple plant design comparable to that of industrial adsorption plants might be applied (Krannich et al., 2016b). The $[C_2\text{mim}][\text{CH}_3\text{SO}_3]$ is also on the list of the perspective ionic liquids able to dissolve biomass (Freire et al., 2011). The $[C_4\text{mim}][\text{CH}_3\text{SO}_3]$ was reported to be successful for the dissolution and delignification of lignocellulosic materials

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(Myllymäki and Aksela, 2005), dissolution of silk fibroin (Phillips et al., 2004), and electrodeposition of metals (Endres et al., 2003).

An extensive search about the thermochemical and thermophysical properties of $[C_n\text{mim}][\text{CH}_3\text{SO}_3]$ using the ILThermo Database ('Ionic Liquids Database – ILThermo', n.d.), as well as in the current literature has revealed very scarce for amount of the thermophysical properties (density, viscosity and heat capacity), as well as on thermochemical properties (enthalpies of formation, solution, vaporization, etc.).

For the effective utilization of ILs, a precise thermodynamic property data of solvents and working fluids are required. The absence of the thermodynamic data is hindering both a more fundamental understanding of the structure-property relationships of ILs as well as their successful and large-scale application. Last decade our research group have performed comprehensive studies of different ILs containing the imidazolium cation (Verevkin et al., 2013; Zaitsau et al., 2016) with the aim of reliable prediction of thermodynamic properties of ILs. This work represents a continuation of these previous studies and provides reliable data for the energetics of vaporization and formation of a selected set of pure ILs. The objects of the investigation were now three imidazolium-based ILs with the alkyl-imidazolium cations $[C_n\text{mim}]$ (with the chain length $n=2, 3$, and 4), combined with the methanesulfonate anion $[\text{CH}_3\text{SO}_3]$. The comprehensive thermodynamic investigation has included: vapor pressure measurements by using quartz-crystal microbalance (QCM) and thermogravimetry (TGA), high-precision combustion and solution calorimetry, as well as differential scanning calorimetry (DSC) measurements. From this experimental data, the vapor pressures for ILs at 373 K and 473 K have been derived. The latter values are important for the practical applications of the methanesulfonate containing ILs for the cellulose dissolution (Freire et al., 2011), heat absorption pumps (Heym et al., 2010), or for the Solid Catalysts with Ionic Liquid Layer (SCILL) (Heym et al., 2015). From the vapor pressure-temperature dependencies the vaporization enthalpies of $[C_n\text{mim}][\text{CH}_3\text{SO}_3]$ were derived and used for estimation of Hildebrandt solubility parameters of ILs. A combination of results from the combustion and solution calorimetry have been used to derive the energetics of the aqueous anion $[\text{CH}_3\text{SO}_3]$, which is required for prediction of the feasibility of electrochemical processes in the presence of ILs.

2. Experimental section

2.1. Materials

The sample of 1-ethyl-3-methylimidazolium methanesulfonate $[C_2\text{mim}][\text{CH}_3\text{SO}_3]$ (CAS # 145022-45-3, Product # 4.90286.0100) used in this work was purchased from Merck with the purity assay of 99% mass from the NMR according to specification. The sample of 1-propyl-3-methylimidazolium methanesulfonate $[C_3\text{mim}][\text{CH}_3\text{SO}_3]$ (CAS # 216299-72-8, Product # 4.90286.0100) was commercially available from Sigma-Aldrich with the purity of $\geq 98\%$ mass (determined by NMR) according to specification. The sample of 1-butyl-3-methylimidazolium methanesulfonate $[C_4\text{mim}][\text{CH}_3\text{SO}_3]$ (CAS 342789-81-5, Product # Im0422cR199) was commercially available from Solvonic with the purity of 99% mass according to specification. Prior to the experiments, samples were subjected to vacuum evaporation at 333 K and 10^{-2} mbar for more than 24 h to reduce possible traces of solvents and moisture. Samples used in vaporization studies were additionally conditioned inside of the vacuum chamber at the highest temperature of experiment within 12 h. This additional purification allowed for removing of residual traces of water and volatile impurities as well as for collecting the amount of the vaporized IL required for the FTIR analysis. The residual water content at the level of 20–40 ppm in both $[C_n\text{mim}][\text{CH}_3\text{SO}_3]$ samples prepared for combustion calorimetry was determined using the Karl Fischer titration (a DL35

Mettler Toledo with the HydranalTM Reagent). The appropriate corrections to the combustion energies have been applied.

2.2. Determination of the molar vaporization enthalpy

2.2.1. Quartz-crystal microbalance (QCM) method

The vapor pressures and the standard molar enthalpies of vaporization of $[C_n\text{mim}][\text{CH}_3\text{SO}_3]$ series were determined by using the QCM method (Verevkin et al., 2011a, 2011b). The vaporization enthalpies were derived from the temperature dependences of the experimentally measured change in the vibrational frequency of the quartz crystal. In our method a sample of an IL is placed in an open cavity (Langmuir evaporation) inside of the thermostat block and it is exposed to vacuum (10^{-5} Pa) with the whole open surface of the loaded compound. The QCM is placed directly above the measuring cavity containing the sample. During the vaporization into a vacuum, a certain amount of sample is deposited on the quartz crystal. The change of the vibrational frequency Δf was directly related to the mass deposition Δm on the crystal according to the Sauerbrey equation (Sauerbrey, 1959):

$$\Delta f = -Cf^2 \Delta m S_C^{-1} \quad (1)$$

where f is the fundamental frequency of the crystal (6 MHz in this case) with $\Delta f \ll f$, S_C is the surface of the crystal, and C is a constant (Zaitsau et al., 2016). The measured frequency change rates (df/dt) can be used for calculation of absolute vapor pressures p_s according to the equation:

$$p_s = K' \frac{df}{dt} \sqrt{\frac{T}{M}} \quad (2)$$

where the $K' = (9.5 \pm 1.1) 10^{-6} \text{ Pa s kg}^{1/2} \text{ Hz}^{-1} \text{ K}^{-1/2} \text{ mol}^{-1/2}$ is the empirical constant containing all parameters of the Sauerbrey equation as well as parameters specific for the geometry of the experimental setup (Zaitsau et al., 2016). The K' -value for our apparatus was evaluated with the help of reliable vapor pressure data on imidazolium and pyridinium-based ILs compiled in references (Zaitsau et al., 2016). Using the frequency change rate df/dt measured by the QCM the molar enthalpy of vaporization, $\Delta_1^{\text{g}}H_m^{\text{o}}(T)$ at experimental temperatures is obtained by:

$$\ln\left(\frac{df}{dt} \sqrt{T}\right) = A' - \frac{\Delta_1^{\text{g}}H_m^{\text{o}}(T_0) - \Delta_1^{\text{g}}C_{p,m}^{\text{o}}T_0}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right) + \frac{\Delta_1^{\text{g}}C_{p,m}^{\text{o}}}{R} \ln\left(\frac{T}{T_0}\right) \quad (3)$$

where A' is the empirical constant; T_0 appearing in Eq. (3) is an arbitrarily chosen reference temperature, which we have set to 298.15 K in this study. The value $\Delta_1^{\text{g}}C_{p,m}^{\text{o}} = C_{p,m}^{\text{o}}(\text{g}) - C_{p,m}^{\text{o}}(\text{liq})$ is the difference between the molar heat capacities of the gaseous, $C_{p,m}^{\text{o}}(\text{g})$, and the liquid phase, $C_{p,m}^{\text{o}}(\text{liq})$, respectively. The vaporization enthalpy $\Delta_1^{\text{g}}H_m^{\text{o}}(298.15 \text{ K})$ at the reference temperature is calculated according to the Kirchhoff's equation:

$$\Delta_1^{\text{g}}H_m^{\text{o}}(298.15 \text{ K}) = \Delta_1^{\text{g}}H_m^{\text{o}}(T_{\text{av}}) + \Delta_1^{\text{g}}C_{p,m}^{\text{o}}(298.15 - T_{\text{av}}) \quad (4)$$

where T_{av} is the average temperature of the temperature range of the QCM study. In order to detect and avoid any possible effect of impurities on the measured frequency loss rate

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