ENTALPIES OF 1-ETHYL- AND 1-BUTHYL-3-METHYLIMIDAZOLIUM ACETATES FORMATION AND VAPOURIZATION

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Ionic liquids have several distinguished properties superior to those of traditional organic solvents such as low vapor pressure, nonflammability, large liquidus range, high solvating capacity. Among all kinds of ionic liquids, acetic acid ionic liquids with the characteristics of strong solubility and good catalytic property have attracted considerable attention from both academic community and industry. They can be used for enzyme-friendly co-solvent for resolution of amino acids, cellulose dissolution and so on. The objects of the present study are two ionic liquids 1-ethyl-3-methylimidazolium acetate $[C_2MIm][OAc]$ and 1-butyl-3-methylimidazolium acetate $[C_4MIm][OAc]$.

In literature information on thermochemical properties of $[C_2MIm][OAc]$ and $[C_4MIm][OAc]$ are fragmentary presented. It is known that these substances do not crystallize upon cooling, but have a glass transition about 200 K [1]. The authors [1, 2] studied the heat capacity of the compounds in the glass and liquid states. Data on the enthalpies of $[C_2MIm][OAc]$ and $[C_4MIm][OAc]$ formation and vaporization could not be found in the literature. The aim of the present work is determination of thermochemical properties of these ionic liquids: standard enthalpies of formation in the liquid and gaseous state and enthalpies of vaporization at 298.15 K.

In the present study commercial reagents of ionic liquids manufactured by «Sigma-Aldrich» with initial purity 98.3 weight % and 97.6 weight % for $[C_2MIm][OAc]$ and $[C_4MIm][OAc]$ correspondingly, were investigated. Before experiments samples were dried under vacuum for constant weight. The purity of the ionic liquids was confirmed by elemental (C, H, N, O, Br) and 1H NMR analysis.The enthalpy of solution of ionic liquids were measured in water at 298.15 K by calorimeter 6755 Parr Instrument Company. The enthalpies of $[C_2MIm][OAc]$ and $[C_4MIm][OAc]$ formation in the liquid state at 298.15 K were determined by Hess law on the basis of the experimental data and $[C_2MIm]^+$, $[C_4MIm]^+$(aq) [3] and $][OAc]^-$(aq) [4] enthalpies of formation. The gas phase enthalpies of formation of $[C_2MIm][OAc]$ and $[C_4MIm][OAc]$ were calculated assuming the existence of these ionic liquids in the vapor in the form of ion pairs. The conformational analysis was performed by considering the possible structures of the $[C_2MIm]^+$ and $[C_4MIm]^+$ cations and taking into account the different arrangement of the $[OAc]^-$ anion around them. The B3LYP-D3(BJ)/def2-TZVPP method was used to optimize the geometry and calculate the oscillation frequencies. Based on the calculated vibration frequencies, the correction for zero vibrations and the thermal correction were estimated. The energy of the most stable conformers [C2MIm][OAc] and [C4MIm][OAc] was calculated by the DLPNO-CCSD(T1)/CBS method. The theoretical values of the gas phase enthalpies of formation of [C2MIm][OAc] and [C4MIm][OAc and the experimental values for liquid compounds were used to estimate their enthalpies of vaporization.

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