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Alkyl-imidazolium tetrafluoroborates: Vapor pressure, thermodynamics of vaporization, and enthalpies of formation

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ABSTRACT

The absolute vapor pressures for the series of $[C_nmim][BF_4]$ ionic liquids with (n = 2, 4, 6, 8, and 10) were measured over the temperature range 404–457 K by using the quartz-crystal microbalance. An absence of possible thermal decomposition was monitored by the ATR-IR spectroscopy. The molar enthalpies of vaporization of ionic liquids under study were derived from vapor pressure temperature dependences and adjusted to the reference temperature 298.15 K. The liquid phase molar enthalpy of formation of $[C_2mim][BF_4]$ was derived from the solution calorimetry and combined with its molar vaporization enthalpy to get the first experimental gas-phase molar enthalpy of formation of the $[BF_4]^-$ containing ionic liquid. A computational approach based on the DLPNO-CCSD(T) method was used to calculate the theoretical gas-phase molar enthalpy of formation of $[C_2mim][BF_4]$. The theoretical and experimental results were found to be in agreement within the combined uncertainties, providing the mutual validation of experimental and computational procedures used in the current study.

1. Introduction

Exploitation of renewable energy sources based on wind power or on solar collector technology requires the development of advanced heat transfer fluids [1] which are thermally stable and can be produced on the large scale from low-cost precursors. The ionic liquids (ILs) containing tetrafluoroborate $[BF_4]^-$ or hexafluorophosphate $[PF_6]^-$ have sufficient thermal stability at ambient temperatures but at elevated temperatures, they can release highly corrosive HF. Nevertheless, the experimental studies of thermal stability, vapor pressures and vaporization thermodynamics of these comparatively low-cost ILs are of academic interest leading to understanding the structure –property relationships in ILS. In our recent papers, we studied the thermodynamics of the $[C_nmim][PF_6]$ series [2] and pyridinium-based ILs with $[BF_4]^-$ anion [3]. In focus of this current work we used experimental and theoretical methods to obtain a consistent set of thermodynamic data for the $[C_nmim][BF_4]$ series of ILs (see Fig. 1), including vapor pressures, vaporization enthalpies, solution enthalpies, liquid and gas-phase enthalpies of formation. Accurate vapor pressures and enthalpies of vaporizations for these ILs are important in the development of the theory regarding their liquid state, validation of force field models applied in molecular dynamics and Monte Carlo simulations.

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2. Materials and methods

2.1. Materials

Ionic liquids of the $[C_nmim][BF_4]$ family (see Table 1) were of commercial origin (IoLiTec GmbH) with initial purity higher than 98–99%. The content of halogen anions in the samples under study was <100 ppm according to the specification given by the manufacturer.

Prior to the vaporization experiments, ionic liquids were exposed to vacuum inside of the experimental chamber at 444–456 K (highest temperatures of vapor pressure study, see Table 2) for at least 12 h. During this pre-conditioning procedure, the traces of possible volatile impurities were removed and a certain amount of vaporized IL sample was collected on the cold quartz sensor in order to perform ATR-FTIR analysis and detect a possible decomposition of the IL under study.

2.2. Quartz crystal microbalance. Vapor pressure and vaporization enthalpy determination

Vapor pressures and vaporization enthalpies of ionic liquids from the $[C_nmim][BF_4]$ family were measured with the quartz crystal microbalance (QCM) technique combined with the evaporation from an open surface described by the Langmuir equation. The detailed description of the applied QCM-Langmuir technique can be found elsewhere [4]. The absolute vapor pressures of ILs under study were derived from

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