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Prediction of the enthalpies of vaporization for room-temperature ionic liquids: Correlations and a substitution-based additive scheme

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ABSTRACT

The literature data on the enthalpies of vaporization for aprotic ionic liquids (ILs) published by the end of May 2014 were analyzed and the most reliable $\Delta_l^g H_m$ values were derived for 68 ILs. The selected enthalpies of vaporization were correlated with density and surface tension using symbolic regression and a number of effective correlation equations were proposed. The substitution-based incremental scheme for prediction of the enthalpies of vaporization of imidazolium, pyridinium and pyrrolidinium ILs was developed. The standard error of the regression for the developed scheme is significantly lower than that for the atom-based group-contribution schemes proposed earlier.

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1. Introduction

Significant scientific and practical potential of ionic liquids (ILs) as solvents, reaction media, catalytic systems, and reference compounds for calculation of thermodynamic and transport properties of liquid systems with strong Coulombic interactions cannot be implemented without reliable data on their thermodynamic properties. Further improvement of the existing industrial processes involving ILs and development of new production schemes requires detailed data on thermodynamic properties of ILs such as heat capacities, enthalpies of vaporization, saturation vapor pressures, enthalpies of combustion, etc.

The enthalpy of vaporization $\Delta_l^g H_m$ is one of key quantities for compounds involved in chemical production. For ILs, which are well-known for their very low saturated vapor pressure over the temperature range of their thermal stability, the experimental determination of this quantity is a complicated task. However, for technical application of these compounds at least estimated values of the enthalpy of vaporization and the saturated vapor pressure are essential. It should also be noted that the modern methods of computational chemistry allow evaluating various thermodynamic and transport properties of compounds over wide temperature and pressure ranges based on the thermodynamic parameters of vaporization process for the studied system obtained from experiment.

The complete review of the experimental and theoretical techniques used in $\Delta_l^g H_m$ determination for ILs can be found in Ref. [1]. Normally, $\Delta_l^g H_m$ for ILs is determined from the temperature dependence of the rate of mass loss or proportional to it quantities obtained during effusion of the saturated vapor into vacuum through a small orifice or during direct vaporization of liquid into vacuum [2,3,4,5,6]. The enthalpy of vaporization can also be evaluated from the temperature-dependent intensities of the specific bands in the gas-phase UV spectra [7]. In the transpiration method [8], the stream of inert gas is saturated with IL and the concentration of the latter is determined by weighing.

In contrast to the techniques mentioned above, where solid theoretical background describing the vaporization process is available, the TGA method [9] is not so obvious in application. As a matter of fact, the TGA technique is similar to the transpiration method but saturation of the gas stream does not occur. Recently, Verevkin et al. [10] reviewed the available literature on determination of $\Delta_l^g H_m$ with this method. According to the review, Price and Hawkins [11] were first who proposed using the Langmuir equation [12] to describe sublimation of crystal in a gas stream in a TGA apparatus. This equation is often used for description of IL vaporization in TGA [9,10], particularly for high flow rates of the inert purge gas. According to the Langmuir equation, p is proportional to $dm/dt\sqrt{T}$. However, this equation was derived for evaporation in vacuum and, to our best knowledge, theoretical

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