Thermodynamics of imidazolium based ionic liquids with cyano containing anions

CrossMark

Dzmitry H. Zaitsau [a], Kaija Pohako-Esko [b], Sören Arlt [c], Vladimir N. Emel'yanenko [a], Peter S. Schulz [b], Peter Wasserscheid [b], Axel Schulz [c], Sergey P. Verevkin [a,d,*]

[a] Department of Physical Chemistry, Department of "Science and Technology of Life, Light and Matter", University of Rostock, Dr-Lorenz-Weg 2, 18059 Rostock, Germany
[b] Lehrstuhl für Chemische Reaktionstechnik der Universität Erlangen Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany
[c] Department of Inorganic Chemistry, University of Rostock, Albert-Einstein Str. 3a, 18059 Rostock, Germany
[d] Department of Physical Chemistry, Kazan Federal University, Kremlevskaya str. 18, 420008 Kazan, Russia

ARTICLE INFO

ABSTRACT

Thermochemical investigation of the series of 1-alkyl-3-methylimidazolium ionic liquids with $B(CN)_4$ and $PF_2(CN)_4$ anions is presented. Absolute vapor pressures and vaporization enthalpies have been measured by using quartz-crystal microbalance. Gas-phase enthalpies of formation of ILs were calculated by using the high-level quantum-chemical method G3MP2. From a combination of experimental and theoretical results, the enthalpy of formation of aqueous $B(CN)_4$ ion was derived for the first time.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Imidazolium based ionic liquids containing the $[B(CN)_4]^-$ anion provide a unique combination of highly interesting properties for practical applications in dye-sensitized solar cells such as a very low viscosity, wide electrochemical window, and hydrolytic stability [1,2]. Furthermore, these ILs demonstrated the highest separation selectivity for CO_2/N_2 [3] and the highest solubility for CO_2 [4] among the imidazolium based ionic liquids combined with anions also containing the nitrile groups such as $[N(CN)_2]^-$ or $[C(CN)_3]^-$.

Studies of the physico-chemical properties of ILs and especially thermodynamic properties are important for optimization of processes of their synthesis, purification, and for prediction of their solubility in different solvents. A combination of solution calorimetry with quantum-chemical calculations can be successfully used for a quick appraisal of the liquid phase standard enthalpies of formation $\Delta_f H_m^o(l)$ of ILs. The idea is that energetics of the dissolution of an IL in water can be used to derive energetics of aqueous cation and anion. The standard enthalpy of formation of an ion in aqueous solution, $\Delta_f H_m^o(ion_{aq})$, is referenced to the formation of the hydrated ion. They are obtained by arbitrarily assigning a value of zero to H^+ ion; that is, $\Delta_f H_m^o(ion_{aq}) = 0$. Then the enthalpies of formation of all other aqueous ions can be determined relative to the heat of formation of the $H^+(aq)$ ion by using the experimentally measured enthalpy of solution $\Delta_{sol} H_m^\infty(salt)$ at infinite dilution. The enthalpy of formation of a salt or an IL in aqueous solution, $\Delta_f H_m^o(IL_{aq})$, can be considered as a sum of appropriate contributions from the aqueous cation and the anion constituting the IL:

$$\Delta_f H_m^o(IL_{aq}) = \Delta_f H_m^o\left(cation_{aq}^+\right) + \Delta_f H_m^o\left(anion_{aq}^-\right) \quad (1)$$

The enthalpy of reaction 1 is defined as the standard molar enthalpy of solution of an IL at infinite dilution $\Delta_{sol} H_m^\infty(IL)$, under assumption of full dissociation of IL in water (at conditions of the infinite dilution). $\Delta_{sol} H_m^\infty(IL)$-values are precisely measured with help of the solution calorimetry. Standard molar enthalpies of formation of aqueous cations and anions specific for typical salts are well known from the literature [5]. Experimental enthalpies of formation of aqueous cations and anions specific for the ionic liquids are in progress now [6,7]. Thus, for many ILs the $\Delta_f H_m^o(IL_{aq})$-value can be principally obtained from summation of $\Delta_f H_m^o(cation_{aq}^+)$ and $\Delta_f H_m^o(anion_{aq}^-)$ contributions according to Eq. (1). Combining the aqueous enthalpy of formation of an IL with the calorimetrically measured enthalpy of solution of IL in water, the liquid phase enthalpy of formation of an IL can be derived:

$$\Delta_f H_m^o(IL_l) = \Delta_f H_m^o(IL_{aq}) - \Delta_{sol} H_m^\infty(IL) \quad (2)$$

* Corresponding author at: Department of Physical Chemistry, Department of "Science and Technology of Life, Light and Matter", University of Rostock, Dr-Lorenz-Weg 2, 18059 Rostock, Germany.
E-mail address: sergey.verevkin@uni-rostock.de (S.P. Verevkin).