ENTHALPIES OF VAPORIZATION OF IONIC LIQUIDS

V.N. Emelyanenko[1]*, Dz.H. Zaitsau[1], S.P. Verevkin[1], C. Schick[2]

[1] Department of Physical Chemistry, University of Rostock,

Dr-Lorenz-Weg 1, 18059 Rostock, Germany

[2] Department of Physics, University of Rostock, Rostock,

Wissmarsche Str. 43-45, 18057 Rostock German

* Corresponding author: vladzimir.yemelyanenko@uni-rostock.de

Keywords: Ionic liquids, Enthalpy of vaporization, Thermogravimetry.

Introduction: Experimental measurements of vapor pressures in the range < 1 Pa is a challenging task. Ionic liquids (ILs) as a neoteric solvents and environmentally friendly solvents have extremely low vapor pressures (~ 10^{-10} Pa at 298 K). This fact significantly decreases the number of possible experimental methods suitable for the determination their enthalpies of vaporization. Development of two new experimental methods Quartz Crystal Microbalance (QCM) and Thermogravimetry (TGA) have been performed in our laboratory.

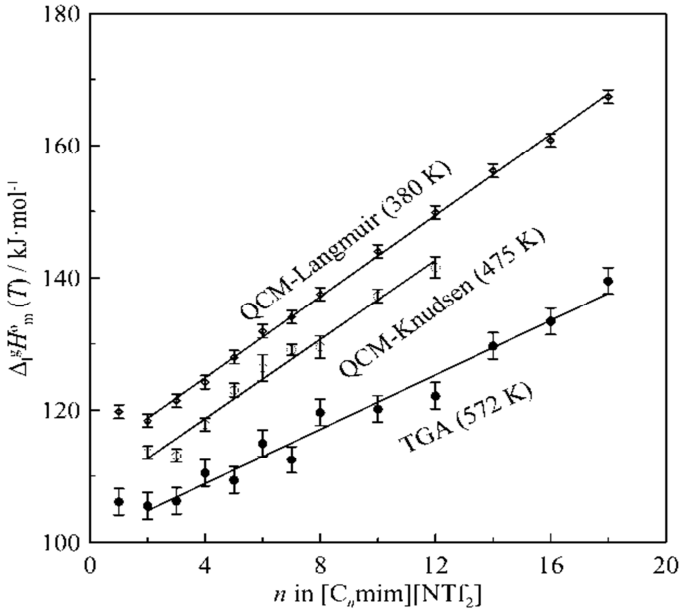

Figure1. Dependence of the enthalpy of vaporization, $\Delta_l^g H_m^o$(T), for 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imides on the length of the cation alkyl chain (n).

Results and discussion: The comprehensive investigation of the enthalpy of vaporization for the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imides was carried out using Langmuir equation for the vaporization from the open surface. The reliability of Langmuir method coupled with the quartz microbalance mass uptake determination was proved by the experiments with the data for $[C_2mim][NTf_2]$, where reliable results are available from the traditional Knudsen method. TGA method was extensively tested with the low-volatile molecular compounds.

Conclusions: It was found that the enthalpy of vaporization for $[C_nmim][NTf_2]$ homologues series additively increases from $[C_2mim][NTf_2]$ to $[C_{18}mim][NTf_2]$ with the increment value of 3.2 kJ·mol^{-1} for CH_2 group at 380 K. This value is 0.5 to 1.0 kJ·mol^{-1} lower than that those found for the molecular compounds: n-alkyl benzenes, n-alkyl nitriles, and n-alkanols. Our new experimental results based on the concurring results from QCM and TGA methods have revealed in contrast with the available literature data the definite linear dependence of the vaporization enthalpies on the chain length. Ambiguity of the $\Delta_l^g C_{p\,m}^o$-values required for temperature adjustments of vaporization enthalpies was resolved and simple method based on the experimental liquid heat capacities has been suggested. We have shown that enthalpies of vaporization generally obey group additivity; however the values of the additivity parameters for ionic liquids are different from those for molecular compounds.