

# Thermodynamics of vaporization of ionic liquids with hexafluorophosphate anion.

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Ionic liquids (ILs) have been considered as a new green chemical wave which excited both the academia and the chemical industry. The “second generation” of ILs started with the “neutral” weakly coordinating anions such as hexafluorophosphate ( $\text{PF}_6^-$ ) and tetrafluoroborate ( $\text{BF}_4^-$ ) and has awakened a broad interest to these neoteric materials. However, from the very beginning ILs with these two anions have been claimed to be thermally non-stable and the experimental vapor pressure studies on these ILs have been considered as impossible. This contribution contradicts this common opinion with reliable measurements of vaporization enthalpies of ILs series  $[\text{C}_n\text{mim}][\text{PF}_6]$  with ( $n = 2..18$ ) using the Quartz Crystal Microbalance (QCM) techniques. The QCM method has been developed for studies of vaporization thermodynamics for extremely low volatile compounds with the possibility to separate the vaporization and decomposition processes. The experimental values of vapor pressures and the vaporization enthalpies of  $[\text{C}_n\text{mim}][\text{PF}_6]$  were tested with the available entropy and enthalpy of formation of liquid and gas phases.

Determination of the liquid phase enthalpies of formation of ILs with  $\text{PF}_6^-$  anion is a challenging task. As a rule, enthalpies of formation are determined by using the combustion calorimetry. However, this method is not developed for compounds with combination of P and F elements yet. Alternatively, the solution calorimetry opens the bypass way for determination of liquid phase enthalpies of formation for ILs. Combination of the experimental results from the solution calorimetry and the high-level quantum-chemical methods was applied to test consistency of the experimental enthalpies of vaporization measured with the QCM. Analysis of the chain length dependence of the enthalpy of vaporization has revealed an unexpected change in the trend of for alkyl chain longer than  $\text{C}_{10}$ . Such type of dependence was never observed for the molecular compounds and seem to be an evidence competition of intermolecular interaction in ILs with changing preferences from the Coulomb to the dispersion interactions with the increasing the alkyl chain length.