

# Molecular Versus Ionic liquids: Development of a Thermodynamic Framework for Predicting Vaporization Thermodynamics

Sergey P. Verevkin, Ralf Ludwig

University of Rostock, Albert-Einstein Str. 27, Rostock, Germany

sergey.verevkin@uni-rostock.de

Ionic liquids based on the pyridinium cations show good result in desulfurization of fuels. The knowledge of their vaporisation thermodynamics is of practical importance. The standard molar enthalpies of vaporization of pyridinium based ionic liquids were derived from the vapor pressure temperature dependences measured by the quartz-crystal microbalance method. We have collected available primary experimental results on vapour pressures, and enthalpies of phase transitions (solid-solid, crystal-gas, and liquid-gas) of analogous molecular species – substituted pyridines. These data were evaluated using the structure-property correlations. The consistent sets of evaluated thermodynamic data on the *molecular* and *ionic* liquids were used to develop the “centerpiece” based group-additivity method for predicting enthalpies of vaporization of *molecular* and *ionic* compounds.

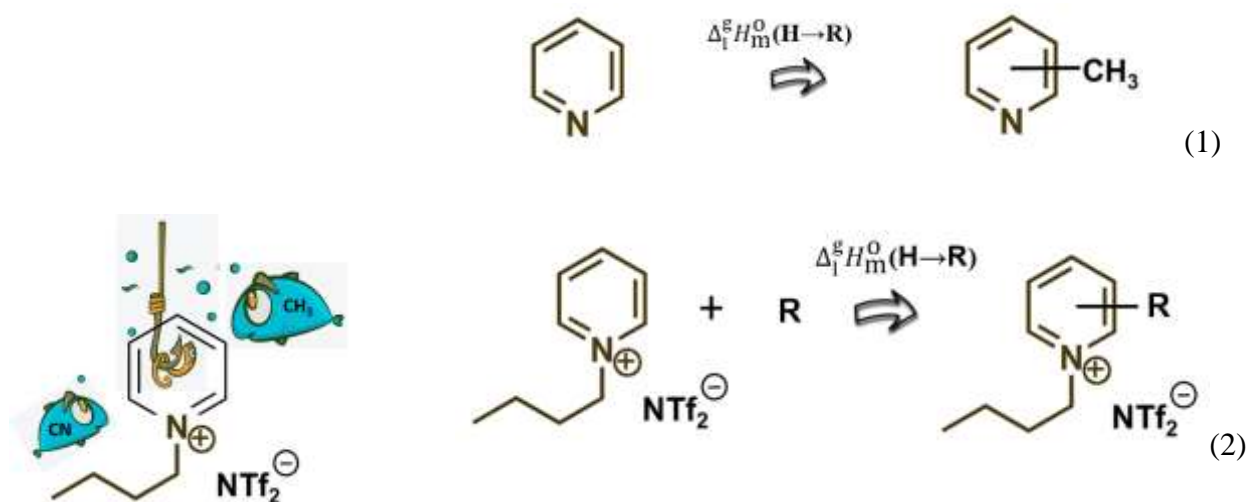
The main idea of this work is demonstrated in Fig. 1. The general transferability of the contributions to the enthalpy of vaporization from the *molecular* liquids to the *ionic* liquid has been established [1]. Indeed, the vaporization enthalpies of *e.g.* of pyridine derivatives can be reliably predicted with the help of a simple contribution,  $\Delta_1^{\text{g}}H_m^{\text{o}}(\text{H}\rightarrow\text{R})$ , representing the replacement of a H-atom in pyridine with any substituents (see Eq. 1). It has been found, that for pyridinium based ionic liquids the same numerical values for the contributions  $\Delta_1^{\text{g}}H_m^{\text{o}}(\text{H}\rightarrow\text{R})$  can be used to estimate their vaporization enthalpies  $\Delta_1^{\text{g}}H_m^{\text{o}}(298.15\text{ K})$  as given by Eq. (2).

The “centerpiece” approach is closely related to the broadly used group-additivity (GA) methods. In conventional GA methods, the energetics of a molecule of interest is gathered from a possibly small groups (based on the idea of a “LEGO® bricks”) with well-defined contributions. In contrast, the idea of the “centerpiece” approach is to select a potentially large “core” molecule that can mimic the structure of the molecule of interest, but the selected “core” molecule is supposed to possess well-established thermodynamic properties. For example, the  $[\text{C}_4\text{-Py}][\text{NTf}_2]$  can be considered as one of the potential “centerpiece” molecules (see Fig. 1, Eq.2), which is related to prediction of ILs vaporization enthalpies using the  $\Delta_1^{\text{g}}H_m^{\text{o}}(\text{H}\rightarrow\text{R})$  contributions evaluated in this work. Different substituents can be attached to this “centerpiece” in various positions. The visualization of the “centerpiece” approach for R-substituted  $[\text{C}_4\text{-Py}][\text{NTf}_2]$  ionic liquid is given in Fig. 1. A small, but not negligible correction term was supposed to reconcile estimated results with experiment. The corrected “centerpiece” approach was recommended to predict vaporization enthalpies of ILs [2].

## REFERENCES

- [1] Verevkin, S.P.; Zherikova, K.V.; Martynenko, E.A., J. Mol. Liq. 350 (2022) 118576.
- [2] Verevkin, S.P., Zaitsau, D.H., Ludwig R., Molecules 27 (2022) 2321.

FIGURES



**Figure 1:** Assessment the enthalpy of vaporization,  $\Delta_1^g H_m^o(298.15 \text{ K})$  in *molecular* (Eq. 1) and in *ionic* liquids (Eq. 2), and visualization of the “centerpiece” approach for the substituted the [C4-Py][NTf<sub>2</sub>] (left). Estimation of  $\Delta_1^g H_m^o(298.15 \text{ K})$ -values for [R-1-C<sub>4</sub>-Py][NTf<sub>2</sub>] ionic liquids (right).