Enthalpy-Entropy Compensation of Micellization Process in Water: The Case of Ionic Liquids

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The term entropy-enthalpy compensation can be found in the literature in different categories. According to Sharp [1] extra-thermodynamic compensation is defined as a linear relationship between enthalpy and entropy of a given process. This effect is closely related to biological processes, but the phenomenon still remains a topic of discussions. Usually it is concluded is that the entropy-enthalpy compensation is the consequence of balancing repulsive and attractive interactions [2] resulting in a nearly constant Gibbs free energy that enables biological processes to respond similarly to changes in the environment independent of temperature.

Chen and coworkers [3] studied the effect of hydrophobic chain length on over 30 different nonionic, cationic, anionic and zwitterionic surfactants on entropy-enthalpy compensation, but their study was limited to few counterions only (Cl^-, Br^-, Na^+). Ionic liquids (ILs) can serve here as excellent model systems, because they exist in diverse structure and the hydrophobic part of the cation can be varied almost optional.

It this contributions, a systematic investigation of influence of alkyl chain length and of the effect of (nine) counterions on the micellization process of newly synthesised imidazolium based ILs [4] in water, carried out by isothermal titration calorimetry together with corresponding thermodynamic analysis, will be presented. Entropy-enthalpy compensation effect will be discussed in terms of "chemical" and "desolvation" part of the process and compared with this phenomenon as found in similar processes [5].

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