

Aqueous Solutions of Nonelectrolytes: Thermodynamic Investigations

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This contribution is based on experimental work published recently and not so recently [1-4], and on material presented in lectures delivered at various occasions, such as at the PhandTA 6 (2002) in Ascona, Switzerland, at the 57th Calorimetry Conference (*Hugh M. Huffman Memorial Award Lecture 2002*) in New Brunswick, NJ, USA, and at this year's mega event THERMO International in Boulder, CO, USA [5]. Its rationale can be simply stated. Water is the most abundant substance on the surface of our *blue planet* and it is the principal constituent of all living organisms known to us. For instance, the human body consists of about 70% water by weight (though this percentage depends somewhat on age). Thus it is not surprising that fairly simple aqueous solutions of nonelectrolytes occupy a pivotal position in biophysical chemistry. They serve as model systems for studying *hydrophobic effects* [6,7] which are thought to play a central role in many biochemical processes, such as conformational changes of biopolymers, the binding of a substrate to an enzyme, the aggregation of lipids in biomembranes, *etc.* Apart from biology, hydrophobic effects are also important in surface aggregation, mineral flotation, coagulation and so forth, that is to say in areas of interest for the chemical engineer.

Perhaps the simplest and most thoroughly studied hydrophobic effects are connected with the poor solubility of gases in liquid water at ordinary conditions (compared to the solubility in other solvents), and associated partial molar enthalpy changes and partial molar heat capacity changes on solution at infinite dilution, respectively [1,8,9]. Thus, in this contribution I shall first review the underlying thermodynamic formalism, and then present a few results on selected aqueous systems, such as $\{\text{H}_2\text{O} + n\text{-C}_l\text{H}_{2l+2}\}$.

References

- [1] E. Wilhelm, R. Battino and R.J. Wilcock, *Chem. Rev.* **1977**, 77, 219.
- [2] T.R. Rettich, Y.P. Handa, R. Battino and E. Wilhelm, *J. Phys. Chem.* **1981**, 85, 3230.
- [3] T.R. Rettich, R. Battino and E. Wilhelm, *J. Solution Chem.* **1992**, 21, 987.
- [4] T.R. Rettich, R. Battino and E. Wilhelm, *J. Chem. Thermodyn.* **2000**, 32, 1145.
- [5] E. Wilhelm, T.R. Rettich and R. Battino, *The Solubility of Propane in Water: A High-Precision Study*. THERMO International 2006, Boulder, Colorado, USA, July 30 – August 4, 2006; Book of Abstracts, p. 47.
- [6] C. Tanford, *The Hydrophobic Effect*, 2nd edition, Wiley, New York, **1980**.
- [7] A. Ben-Naim, *Hydrophobic Interactions*, Plenum, New York, **1980**.
- [8] E. Wilhelm, *Thermochim. Acta*, **1997**, 300, 159.
- [9] E. Wilhelm, *Low-Pressure Solubility of Gases in Liquids*, in *Experimental Thermodynamics, Vol. VII: Measurement of the Thermodynamic Properties of Multiple Phases*, Eds.: R.D. Weir and Th.W. de Loos. Elsevier, Amsterdam, The Netherlands, **2005**, pp.137-176.