

The Soret effect in aqueous solutions of associating fluids. Analysis of the anomalous change of sign with varying composition

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The Soret effect is an irreversible process taking place in a mixture of two or more components in a thermal gradient. As a result of a spatial temperature gradient, changes in composition of the mixture are observed along the sample. This effect was first described by Ludwig (1856) and Soret (1880). In 1950 Prigogine *et. al* measured the Soret coefficient, defined as

$$S_T = -\frac{1}{\omega(1-\omega)} \frac{\nabla\omega}{\nabla T}, \quad (1)$$

where ω is the mass fraction of one of the components, in binary liquid mixtures. A change in the sign of the Soret coefficient for mixtures of cyclohexanol-cyclohexane was reported. Such a peculiar behaviour has been later observed in associating fluids, that is, fluids which can form hydrogen bonds.

A physical explanation, based on a microscopic description of the process, is not clear, despite several attempts to relate the Soret effect to other parameters like molecular potentials, partial molar enthalpies, and energy barriers¹⁻⁴. Furthermore, many simulations aiming at the calculation of S_T have been done in non-associating mixtures; however, the results of Molecular Dynamics simulations presented in this work are the first to quantitatively reproduce the observed change of sign in the Soret coefficient for non-ideal associating mixtures.

Effectively, we have computed the Soret coefficient through direct Non-Equilibrium Molecular Dynamics (NEMD) simulations for aqueous mixtures of methanol, ethanol (shown in the figure), dimethyl sulfoxide, and acetone. The NEMD simulations have been carried out with the constant temperature PeX (momentum exchange algorithm) scheme, improved by the authors⁵. Simulations were carried out with 800 molecules at the experimental density of the mixture, with a reaction-field methodology to account for the long-range electrostatic interactions.

In Figure 1 we present the thermal diffusion factor $\alpha \equiv TS_T$ for the water-ethanol mixture, as a function of the molar fraction of water at 298 K and 1 atm, in comparison with experimental data⁶, with a remarkable agreement. The change in the sign of the Soret take place between 80% and 90% of molar fraction of water.

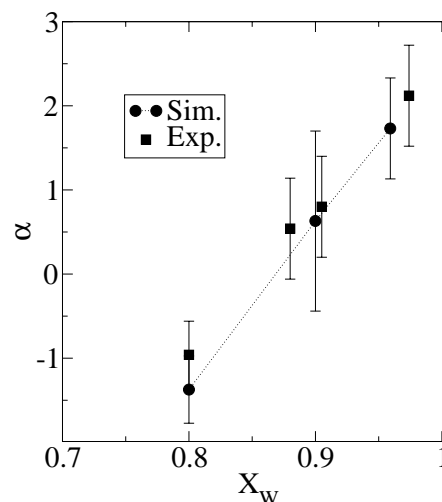


Figure 1. Comparison of the thermal diffusion factor α for the mixture water+ethanol at 298 K and 1 atm with the experimental data of⁶.

From our observations, we can infer that the behaviour of associating fluids is dominated by the strong particle-particle interactions. Thus, if the cross interaction energy (ϵ_{AB} , say) is lower than the self-interactions (ϵ_{BB} and ϵ_{AA}), then the Soret effect of the system will show a change in the sign, as it is the case in all the studied associating fluid mixtures studied. Therefore, in a dilute solution, the minority component preferably goes to the cooler side of the box. On the other hand, the composition at which the inversion takes place is proportional to the ratio of self-interactions of pure components, that is, if $\epsilon_{BB} > \epsilon_{AA}$ then the change in the sign will occur at the *B* rich concentration. We have observed such a behaviour in our simulations, in which the water-water interaction is stronger than the solute-solute interaction. A quantitative theory of this phenomenon, based in the description outlined above, is under way.

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¹ I. Prigogine, and L. De Brouckere, and R. Amand, *Physica* XVI **7**, 577 (1950).

² S. R. de Groot, and C. J. Gorter, and W. Hoogenstraaten, *Physica* **10**, 81 (1943).

³ R. Haase, and H.-W. Borgmann, and K.-H. Ducker, and W.-P. Lee, *Z. Naturforsch. A* **26**, 1224 (1971).

⁴ L. J. T. M. Kempers, *J. Chem. Phys.* **115**, 6330 (2001).

⁵ C. Nieto Draghi and J. Bonet Avalos, *Mol. Phys.* (accepted).

⁶ M. M. Bou-Ali, and O. Encenarro, and J. A. Madariaga, and C. M. Santamaria, and J. J. Valencia, *J. Phys.: Condens. Matt.* **10**, 3321 (1998).