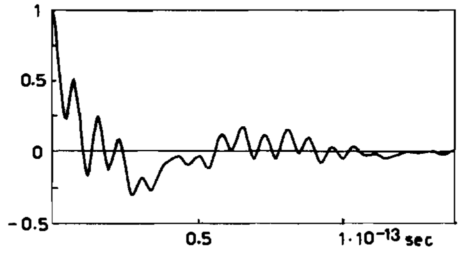

Fig. 2. Normalized velocity autocorrelation function for all hydrogens in a 2.2 molal NaCl solution from a simulation with CF water.

mental structure function obtained from X-ray diffraction [4] is now better reproduced (Fig. 1). In the region of $s > 5$ Å^{-1} the agreement is less good due to an inappropriate ion–oxygen pair potential.

From the velocity autocorrelation function of the hydrogens (Fig. 2) hindered translational, librational and vibrational frequencies are derived and differences in these frequencies between the hydration water of the ions and bulk water are discussed.

References

1 F. H. Stillinger and A. Rhaman, *J. Chem. Phys.*, *68*, 666 (1978).
2 H. Kistenmacher, H. Popkie and E. Clementi, *J. Chem. Phys.*, *58*, 5627 (1973); *59*, 5842 (1973).
3 P. C. Vogel and K. Heinzinger, *Z. Naturforsch.*, *31a*, 463 (1976).
G. Pálinkás, W. O. Riede and K. Heinzinger, *Z. Naturforsch.*, *32a*, 1137 (1977).
4 G. Pálinkás, T. Radnai and F. Hajdu, *Z. Naturforsch.*, in press.

Calorimetric Study of the Enthalpies of Solvation in Cyclohexane and in Water for Homologous Aliphatic Ketones and Esters

G. DELLA GATTA, L. STRADELLA

Instituto di Chimica Generale ed Inorganica, Facoltà di Farmacia, Università di Torino, via P. Giuria, 9, 10125 Turin, Italy

and P. VENTURELLO

Istituto di Chimica Organica, Facoltà di Scienze, Università di Torino, via G. Bidone 36, 10125 Turin, Italy

The standard enthalpies of solution at infinite dilution were determined for homologous aliphatic ketones and esters in water and in cyclohexane at 298.15 K, using a rotating Calvet calorimeter and solutions concentrations about 5×10^{-4} mole fraction. Vaporization enthalpies, obtained for each compound with an effusion calorimetric cell, were added to calculate the solvation enthalpies.

For the n-substituted compounds the solvation enthalpies are linearly dependent on the number (N) of carbon atoms for $N > 2$, giving the following values for the solvation of the methylene group.

Comp./Solv.	Ketones	Esters
Water	−3.11	−3.46
Cyclohex.	−4.41	−4.88

$\Delta H^\circ_{\text{solv}}(\text{–CH}_2\text{–})/\text{kJ mol}^{-1}$

Extrapolation to $N = 0$ should give values related to the solvation enthalpies of the functional groups, but this is complicated because of the deviation from the linearity of the curves for $N < 2$. The observed deviations, greater for water, are connected with the 'structural effect' produced in the solvent by the functional groups.

Comparisons are made between solvation enthalpies of n-ketones and n-esters with the corresponding values of branched or cyclic substitutes. In both solvents, all branched chain compounds show enthalpies of solvation that are less exothermic than for the normal isomers. On the other hand all the symmetrically substituted ketones show heavily increased solvation enthalpies in comparison with the corresponding methyl substituted compounds.

Isotopic Tracer Self-Diffusion. A Method of Studying the Structure of Liquid Solutions

EWA HAWLICKA and WŁADYSŁAW REIMSCHÜSSEL

Institut of Applied Radiation Chemistry, Technical University of Łódź, Wróblewskiego 15, 93-540 Łódź, Poland

The self-diffusion for both components in binary solutions: benzene–toluene (1), benzene–nitrobenzene (2), benzene–aniline (3), benzene–hexane (4) and benzene–cyclohexane (5) has been carried out. In Fig. 1a the benzene self-diffusion coefficients D_B in the aforegoing solutions as a function of benzene mole fraction x_B are presented. In Fig. 1b the self-diffusion coefficients of the others are presented.

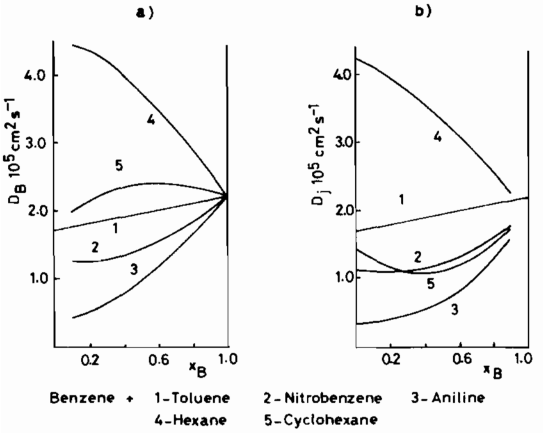

Fig. 1.

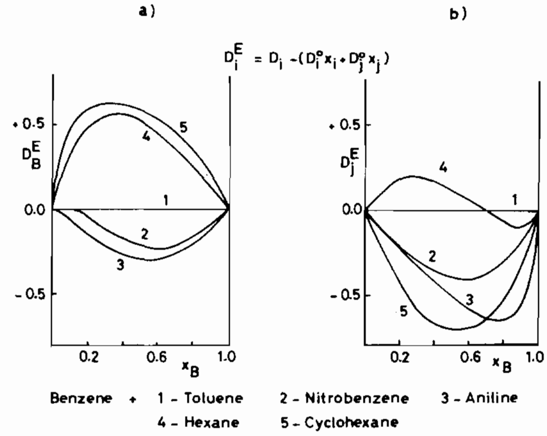

Fig. 2.

In order to describe these solutions it is proposed a new function called the excess self-diffusion coefficient D_i^E defined as:

$$D_i^E = D_i - (D_i^o x_i + D_j^o x_j)$$

where D_i denotes experimentally obtained self-diffusion coefficient for the given mole fraction x_i and D_i^o, D_j^o are self-diffusion coefficients of pure components i and j respectively.

The values of the excess self-diffusion coefficients for benzene D_B^E are presented in Fig. 2a and for other components in Fig. 2b.

The studied solutions can be thus divided in three categories:

i) $D_i^E = 0$, $D_j^E = 0$, the solutions are ideal *e.g.* benzene–toluene;

ii) $D_i^E < 0$, $D_j^E < 0$, the solutions exhibiting specific interactions between molecules of both components leading to the formation of a common structure *e.g.* benzene–nitrobenzene and benzene–aniline;

iii) $D_i^E < 0$, $D_j^E > 0$, the solutions without a common structure due to stronger interactions between i–i and j–j than i–j molecules.

It seems that the new function introduced here *i.e.* the excess self-diffusion coefficient may be conveniently used to characterize the solutions investigated as it enables to determine explicitly the variation in mutual relations between molecules of all the components in solutions in respect to the interactions in pure liquids.