TABLE I. pK_a of *o*- and *p*-Nitroaniline.

pK_a^S Solvent: Phenol–Acetone (65–35)			pK_a^W Solvent: Water	
% water	*p*-nitroaniline	*o*-nitroaniline	*p*-nitroaniline	*o*-nitroaniline
0.55	4.27	2.50	1.00	–0.29
1.05	3.55	1.80		
2.05	2.77	1.07		
4.05	1.91	0.23		

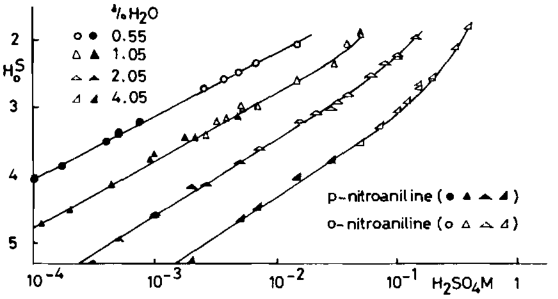

Fig. 1. Acidity function H_o^S for the system Phenol–Acetone 65/35.

variation of H_o^S with the log of sulphuric acid concentration is a linear function with the expected slope –1 at low acid concentration. The variation of H_o^S with solvent composition from 40% to 85% Phenol in Acetone with water concentration from 0.5 to 4%, can be expressed by an empirical relation. The relationship points out that the acidity grows with the content of phenol and decreases with the content of water and acetone. The H_o^S parameter has been correlated with the kinetic constant of some scission reaction related to the synthesis of phenol from cumenehydroperoxide.

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A Molecular Dynamics Study of an Aqueous NaCl-Solution

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In this molecular dynamics study on an aqueous NaCl solution a central force model for water was employed. The pair potentials between oxygen–oxygen, oxygen–hydrogen and hydrogen–hydrogen were taken from the latest version of the central force water model given by Stillinger and Rahman [1]. The ion–oxygen and ion–hydrogen pair potentials were adjusted to *ab initio* calculations of Kistenmacher, Popkie and Clementi [2].

The basic periodic box with a sidelength of 18.42 Å contained 200 oxygen atoms, 400 hydrogen atoms, 8 sodium and 8 chloride ions equivalent to a 2.2 molal solution. The simulation was extended over 3500 time steps of 4×10^{-16} seconds to a total time of 1.4 picoseconds.

Structural properties are obtained and discussed, *e.g.* the different radial distribution functions, the orientation of the water molecules in the hydration shell of the ions and the influence of the ions on water geometry.

These properties are compared to those of an earlier simulation of an aqueous NaCl solution with the rigid ST2-water model. Especially the double peak in the range of the first maximum of the experi-

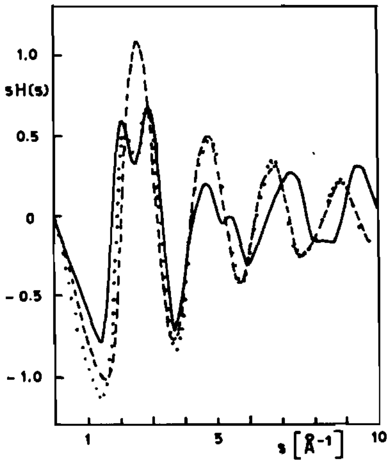

Fig. 1. Comparison of the structure function from an X-ray investigation of a 2 molal NaCl solution (dotted) [4] with the structure functions derived from MD simulations of a 2.2 molal NaCl solution with CF-water (full) and ST2 water (dashed) [3].

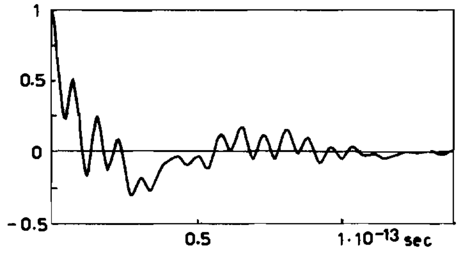

Fig. 2. Normalized velocity autocorrelation function for all hydrogens in a 2.2 molal NaCl solution from a simulation with CF water.

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.

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

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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

$\Delta H^{\circ}_{\mathrm{solv}}(\text{–}CH_2\text{–})/\mathrm{kJ\ mol^{-1}}$

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

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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.