The method of preparation of Ag^{2+} solutions can be summarized as follows:

$$Ag(CN)_2^- \xrightarrow[20\ ^{\circ}C]{+e^-} Ag(net) \xrightarrow[\text{in recryst. } HClO_4]{-e^-(20\ ^{\circ}C)}$$

$$\underset{5M\,HClO_4}{AgClO_4 \text{ in}} \xrightarrow[\text{at} -5\ ^{\circ}C]{-e^-/Au} Ag^{2+}$$

Once a Ag^{2+} solution was obtained, e.m.f. measurements of cell (*G*) were carried out at –5 °C, after successive additions of a cold $Ce(ClO_4)_3$ in 5 *M* $HClO_4$ solution. The collected data enabled us to build a Gran diagram from which to draw the Ag^{2+} concentration at each point of the titration and, by eqn. (*1*), a set of E° values for each titration. The mean value, derived from 5 titrations at different Ag^{2+} initial concentration, Ag total concentration, and varying the $[Ag^{2+}]/[Ag^+]$ ratio over a wide range, is 1977.5 ± 1.4 mV for E°, the standard redox potential of the Ag(II, I) pair at –5 °C and in 5 *M* (6.5 *M*) $HClO_4$.

Likewise, adding to the Ag^{2+} solution, at –5 °C, successive amounts of a cold $Co(ClO_4)_2$ in 5 *M* $HClO_4$ solution, we generated Co^{3+} by the reaction: $Ag^{2+} + Co^{2+} \rightarrow Ag^+ + Co^{3+}$. After the equivalent point, the cell (*G*) becomes:

$$Au/Co^{3+}, Co^{2+}, Ag^+, H^+, ClO_4^- = 5\ M/G.E. \qquad (G')$$

for which, from $E_{R'} = E_{G'} + E_H$, holds equation (*2*):

$$E_{R'} - K \log [Co^{3+}]/[Co^{2+}] + K \log[H^+] =$$
$$E^{\circ}_{Co^{3+}/Co^{2+}} + K \log F' = E^{\circ} \qquad (2)$$

where E° is the standard redox potential of the Co(III, II) pair at –5 °C in 5 *M* (6.5 *M*) $HClO_4$. Preliminary titrations at –5 °C using cell (*G'*) gave, by eqn. (*2*), E° = 1.84 V.

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Dipolar Effects in Electrolytes

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The specific solvation of the anion by hydrogen bonding accounts for the lower reactivity in methanol. The different behaviour of the halogens with respect to the sulphonates found in the other solvents can be explained in terms of (*i*) extent of bond-breaking and bond-making in the transition state (*ii*) assistance to the leaving group by the solvent.

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Acidity Function in Organic Solvents (Acetonitrile, Phenol, Acetone and Their Mixtures)

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Acidity function (A.F.) measured by protonation equilibria of indicators of the nitroanilines family, is under investigation for H_2SO_4 (CF_3SO_3H) solution ($10^{-4} \div 10^{-1}$ *M*) in organic solvents. The chosen systems are known to be much more acidic than the aqueous ones [1, 2] but no general A.F. has been described like the well known Hammett function for the aqueous system. Some results are reported for the solvent system Phenol–Acetone with a water content variable from 0.5 to 4%. Table I shows the pK_a^S of the two indicators, *o*-nitroaniline and *p*-nitroaniline, determined by the extrapolation method in the system S (65% Phenol–35% Acetone) at variable amount of water. The reported pK_a^S values are higher than those in the water ideal state (pK_a^W), in agreement with the greater protonating ability of the system compound with the aqueous state. The variation of the pK_a values with water concentration points out that water should be considered a strong base in the Phenol–Acetone solvent system.

It is not possible to derive an acidity function using the ideal solution in water as standard state, since there are specific effects probably due to the low dielectric constant of the medium. As it is known [1, 2] it is possible to define an 'operational' acidity function H_o^S using an ideal solution in the solvent itself, as reference state. Assuming as reference state the solvent system 65% Phenol/35% Acetone with 0.5% water, it is possible to obtain consistent data of the acidity function H_o^S. Fig. 1 shows the continuous curves obtained at different water content. The

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		

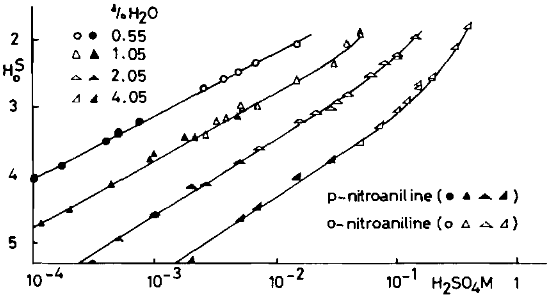

Fig. 1. Acidity function H_0^S for the system Phenol–Acetone 65/35.

variation of H_0^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_0^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_0^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 X 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-

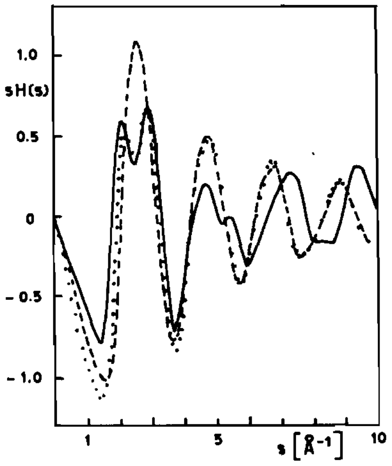

Fig. 1. Comparison of the structure function from an X-ray investigation of a 2 molal NaCl solution (dotted) [4] with the structure functions derived from MD simulations of a 2.2 molal NaCl solution with CF-water (full) and ST2 water (dashed) [3].