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

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

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

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:

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

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.

### *Reference*

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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.

### *References*

1 D. Landini, A. Maia and F. Montanari, *J. Am. Chem. Soc., 100,* 2796 (1978).

2 D. Landini, A. Maia and F. Montanari, *Nouv. J. Chimie, 3,* 577 (1979).

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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