

Behaviour of Hydrogen and Silver–Silver Chloride Electrodes in Acetonitrile Solutions

By H. P. BENNETTO* and JAN J. SPITZER
(Queen Elizabeth College, London W.8)

Summary Under suitable conditions, silver–silver chloride and hydrogen electrodes operate reversibly in acetonitrile–methanol mixtures; the free energy of transfer of H^+Cl^- from methanol to acetonitrile–methanol (40:60) has been determined from the results of cell measurements.

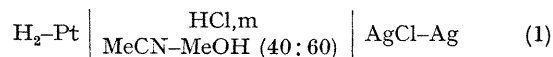
STUDIES of ionic solvation in solvents containing acetonitrile have formerly been hampered by experimental difficulties. Thus the silver–silver chloride¹ and hydrogen² electrodes reportedly give unstable potentials in pure acetonitrile. Since these electrodes function satisfactorily in methanol,³ however, we have investigated their behaviour in acetonitrile–methanol mixtures, and have obtained precise thermodynamic data relating to hydrogen and chloride ions in these media from e.m.f. work.

Silver–silver chloride electrodes of the thermal-electrolytic type¹ perform reversibly in mixtures containing up to 80 wt % acetonitrile. In practice the solutions must be pre-saturated with silver chloride before an electrode is immersed, to minimise the dissolution of the electrode surface to give complex chloride species.^{1,4} Cell e.m.f.s

constant to ± 0.01 mV are then achieved, and duplicate electrodes agree to within < 0.05 mV.

In mixtures containing up to 50 wt % of acetonitrile, hydrogen electrodes prepared in the normal manner² show large fluctuations of potential. Very lightly platinised electrodes, however, reach within 1 h a steady potential (± 0.05 mV) which varies only slightly with hydrogen pressure, but rises by about 0.2 mV per hour, owing to poisoning by the solvent or by trace impurities. Unplatinised polished electrodes⁵ are more effective; their potential agrees with that of a lightly platinised electrode, and moreover it remains constant to ± 0.01 mV and is unaffected by the rate of hydrogen bubbling. It is therefore taken to be a true equilibrium value. The agreement between several of these electrodes is 0–0.2 mV, regardless of their size.

Measurements have been made on the cell (1) at 25° with



semi-micro apparatus.⁶ In the preparation and manipulation of solutions, care was taken to eliminate moisture, and

by our estimates the water content (*ca.* 10^{-3} mol dm $^{-3}$) gives only small errors of 0.05 mV or less. The Figure

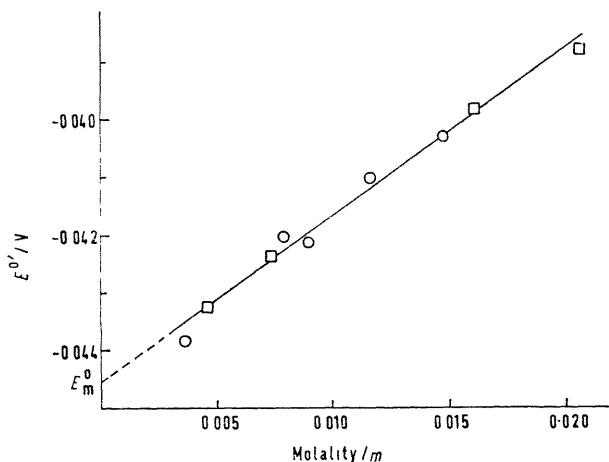


FIGURE. Concentration dependence of E° .

shows the concentration dependence of E° , the measured e.m.f. corrected in the conventional way for molality and Debye-Hückel terms. The two sets of points are from independent series of experiments which required different batches of solvent, and thereby establish the reproducibility of the results. The computed value of E_m° , the standard potential of the silver-silver chloride electrode on the molal scale, is $-0.0445_6 \pm 0.0001_3$ V. This is probably reliable to 0.2–0.3 mV in view of the uncertainties of the hydrogen electrodes.

From the corresponding E_m° value for methanol³ (-0.0101 V) we calculate $\Delta G_i^{\circ}(\text{HCl})$, the molar free energy of transfer of hydrogen and chloride ions from methanol to the 40% mixture, to be 3400 ± 30 J. The positive sign is not predicted by simple electrostatic theories, and probably reflects the poor anion-solvating ability of acetonitrile.⁷ Future work with the other halogen acids is designed to test this hypothesis, to establish the relative sizes of the ionic contributions to ΔG_i° , and to examine their dependence on the structural properties of the solvents.

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