The Measurement of Solvent Isotope Effects with Cation Selective Glass Electrodes

By B. M. LOWE* and D. G. SMITH

(*Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh* EH9 3JJ)

Summary Cation selective glass electrodes can be used to measure the free energy of transfer of an ionic solute from H_2O to D_2O; the value obtained for sodium chloride is 709 ± 39 J mol^{-1}.

ALTHOUGH hydrogen selective glass electrodes (HSGE) have been used for precise measurements on protolytic equilibria in D_2O and $D_2O + H_2O$ mixtures,[1] the measurement of solvent isotope effects with cation selective glass electrodes (CSGE) has not been described. We now report results obtained with sodium chloride solutions which show that CSGE may be used to measure the free energy of transfer ΔG_t^0 $(=\Delta G_D - \Delta G_H)$ of an ionic solute between H_2O and D_2O. Values of ΔG_t^0 are small [2a] and require precise techniques for their measurement, hence despite their importance for the interpretation of kinetic solvent effects[2b] and the study of aqueous electrolyte solutions,[2a,3,4] reliable values are scarce. There are few salts for which ΔG_t^0 has been determined by more than one experimental method and for these (*e.g.* NaCl) the values[4,5,6,7] obtained by different procedures are in poor agreement.

Our procedure involves the transfer of a CSGE between a solution in ordinary water and one of similar aquamolality (*i.e.* mols of solute per 55·51 mol of solvent) in deuterium oxide, and the measurement of the e.m.f. (E_H and E_D) of cells I and II which are formed with the same CSGE and

$$\text{CSGE}\,|\,\text{NaCl } (m \text{ in } H_2O)\,|\,\text{AgCl, Ag} \qquad \text{(I)}$$

$$\text{CSGE}\,|\,\text{NaCl } (m' \text{ in } D_2O)\,|\,\text{AgCl, Ag} \qquad \text{(II)}$$

different silver–silver chloride electrodes. The difference ΔE^0 between their 'standard' e.m.f., and the corresponding value of ΔG_t^0, are calculated on an aquamolal basis with equation (1).

$$\Delta E^0 = (E_D^0 - E_H^0) = (E_D - E_H) + (2RT/F)\ln(m'\gamma'/m\gamma) = -\Delta G_t^0/F \qquad (1)$$

The measurements were carried out at 298K with E.I.L. GEA33 and GKN33 glass electrodes† using cells designed to facilitate their rapid transfer. The silver–silver chloride electrodes (electrolytic preparation) had intercomparison potentials $\leqslant 0{\cdot}03$ mV. They were kept and used under solvent saturated purified nitrogen and protected from sunlight. E.m.f. was determined with a precision of $\pm 0{\cdot}01$ mV using an E.I.L. vibron 33B electrometer backed off with a Pye precision vernier potentiometer. Selectivity constants were determined for each CSGE and their response to the low concentrations of potassium and hydrogen ions (pH = 8·1) in the solutions of purified[8] sodium chloride was found to be negligible. The D_2O was redistilled and had an isotopic purity of *ca* 99·7% (from ^{1}H n.m.r.).

The behaviour of cells (I) and (II) was investigated in a separate series of experiments in which the glass electrodes were transferred between solutions in the same solvent but with different concentrations in the range 0·1 to 1·0 aquamolal. Both the GEA33 and the GKN33 electrodes performed equally well in both solvents, e.m.f.–time drifts were slight, and the variation in e.m.f. with concentration was reproducible to within ± 0·1 mV. Analysis of the results obtained in ordinary water gave activity coefficients which agreed with literature values[9] to within $\pm 0{\cdot}003$ ($\pm 0{\cdot}2$ mV) in $\log_{10}\gamma_\pm$ over the entire concentration range. The activity coefficients $\gamma'_\pm$ obtained from the measurements in D_2O could be related to those in ordinary water by equation (2). The values obtained for the constant k

$$\log_{10}\gamma_\pm' - \log_{10}\gamma_\pm = km \qquad (2)$$

$(-0{\cdot}005_6 \pm 0{\cdot}003$ {GEA33} and $-0{\cdot}004_6 \pm 0{\cdot}003$

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† These are made from different glasses and are sold as sodium (GEA33) and potassium (GKN33) responsive electrodes.

{GKN33}) are almost within experimental error of that obtained by Van Hook and his co-workers ($-0{\cdot}0016 \pm 0{\cdot}0001$).[4]

The two values of $E_D - E_H$ obtained from the transfer of the CSGE from a solution in H_2O to one in D_2O followed by its return to the original H_2O solution agreed to within $\pm 0{\cdot}04$ mV and the mean was used to calculate ΔE^0. The values obtained with both electrodes using 0·1 and 1·0 aquamolal solutions were in good agreement and their overall mean was $-7{\cdot}3_5 \pm 0{\cdot}4$ mV. This corresponds to a free energy of transfer for sodium chloride of 709 ± 39 J mol^{-1}, in agreement with that (728 ± 125 J mol^{-1}) reported in ref. 4.

The calculation of free energies of transfer from ΔE^0 from equation (1) is only valid if the change of solvent has a negligible effect on the asymmetry potential of the CSGE. That this is so in the present case is supported by the following observations: (i) Steady e.m.f. values were established soon after each transfer and the systematic drifts found with HSGE in similar experiments[10] with hydrochloric acid were not observed. (ii) CSGE made from different glasses gave the same value for ΔE^0. (iii) When CSGE were transferred between saturated NaCl solutions $E_D - E_H$ was zero to within $\pm 0{\cdot}2$ mV.

Although reliable free energies of transfer could be obtained for other sodium salts by this method (by changing the silver–silver chloride electrode for one reversible to other anions) it may not be applicable to the salts of other cations for which CSGE are available, and further experimental work will be required to establish whether asymmetry potential effects are also negligible in these cases.

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