Free Energies of Transfer of Sodium Fluoride from Water to Hydrogen Peroxide–Water Mixtures using Ion-selective Electrodes

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Summary Lanthanum fluoride single crystal and sodium-responsive glass electrodes can be used in isodielectric solvent mixtures of NaF to obtain free energies of transfer which are compared with values derived from n.m.r. measurements.

THE free energy of transfer $\Delta G_t^\ominus$, the difference between the standard Gibbs function per mole of a substance in a pure solvent, usually water, and that in another solvent or solvent mixture, provides an important measure of the differences in interaction between the substance and the solvent molecules in the two media.[1-3] Lowe and Smith[4] have recently reported the use of sodium-responsive glass electrodes to obtain the free energy of transfer of sodium chloride between H_2O and H_2O–D_2O mixtures, this being the first use of cation responsive glass electrodes for this purpose. We report here the use of two ion-selective electrodes to obtain the free energy of transfer of a salt from H_2O to H_2O_2–H_2O mixtures. Apart from a classic study by Mitchell and Wynne-Jones[5] using hydrogen-responsive glass electrodes, very little electrochemical work has been reported involving hydrogen peroxide–water mixtures which are of particular interest in being isodielectric.[6]

The fluoride-responsive electrode[7] (Orion Research Inc., Cambridge, Mass.) and sodium-responsive glass electrodes (Electronic Instruments Ltd., Chertsey, Surrey, Type GEA 33) were conditioned in water, and then in 0·01 molal aqueous sodium fluoride until the potential difference between them was constant. The electrodes were transferred with suitable washing to solutions containing successively higher proportions of hydrogen peroxide but the same sodium fluoride concentration (10^{-2}) on an aquamolality scale. These techniques have been fully described for both glass and ion-selective electrodes.[8-10] The sodium-responsive glass electrode could show a mixed sodium–hydrogen ion response[11] in hydrogen peroxide solutions which are more acidic[5] than water, hence some solutions were made 10^{-2} molal in tris-hydroxymethyl-aminomethane (TRIS); this had a small effect on the measured potential at the highest peroxide concentrations studied.

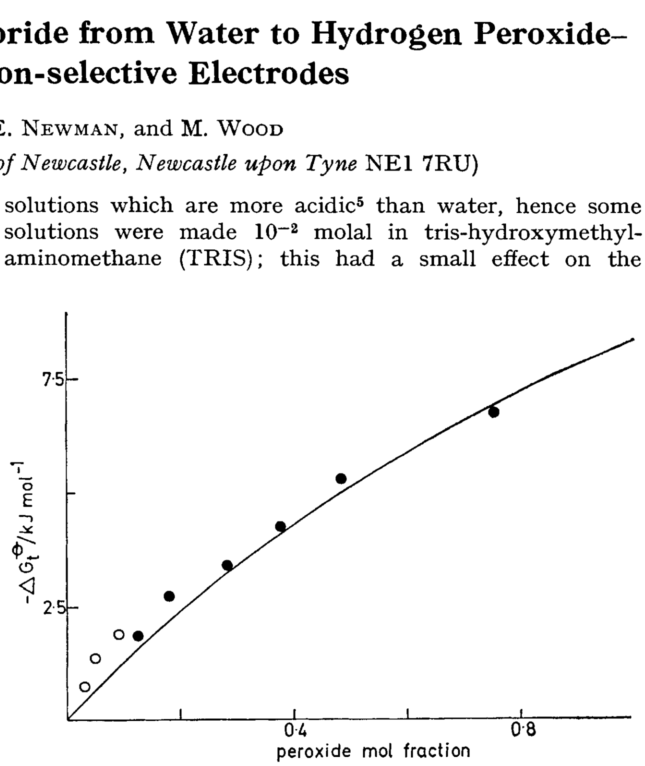

FIGURE. *Free energies of transfer* $\Delta G_t^\ominus$ *of* NaF *from water to peroxide–water mixtures.* ——— *predicted from n.m.r. chemical shifts;* ○ *e.m.f. measurements (first run);* ● *e.m.f. measurements (second run, two sodium responsive glass electrodes were used with results agreeing to better than* ±0·1 *mV).*

The difference in e.m.f. of the cells (A)

$$LaF_3 | NaF\ (0{\cdot}01),\ H_2O_2,\ H_2O | Na\ g.e. \qquad (A)$$

with two solvent mixtures, but the same sodium fluoride concentration, is given by equation (1)

$$\Delta E/\mathrm{mV} = 118{\cdot}3 \log [\gamma_1/(\gamma_2 \cdot {}_m\gamma)] \qquad (1)$$

where γ_1 is the activity coefficient of NaF in water, γ_2 that in a peroxide–water mixture referred to the aqueous standard state and $_{\rm m}\gamma$ is the medium effect activity coefficient.[1,2]

As we are dealing with isodielectric mixtures, $\gamma_1 = \gamma_2$ to a very good approximation giving equation (2).

$$F\Delta E = -\ \Delta G_{\rm t}^{\theta} = -\ RT \log {}_{\rm m}\gamma \qquad (2)$$

From the results of successsive transfers between solution of incrementally increased peroxide content, values of ΔE were obtained. By addition these were converted to differences between water and the various peroxide mixtures. This technique of making only small changes to the mixed solvent environment to which a glass electrode is subjected is preferred[8] since gross environmental changes often result in drifts in potential. Cell e.m.f.'s were steady after a few minutes and return transfers down the series back to the aqueous solution gave results in good concordance with transfers to higher peroxide content.

Our interest in free energies of transfer to hydrogen peroxide arises from alkali metal and halide n.m.r. chemical shift measurements in these solvent mixtures and their interpretation in terms of preferential solvation.[12] Results for $^{19}F^-$ indicate preferential solvation by peroxide and for $^{23}Na^+$ slight preferential solvation by water. Analysis of these gives a free energy of preferential solvation $\Delta G_{\rm ps}^{\theta}$ for NaF, relating to the process,

$$NaF(H_2O)_n + nH_2O_2 \longrightarrow NaF(H_2O_2)_n + nH_2O$$

where n is the sum of the solvation numbers each assumed equal to 4. This can be shown to be identical *for isodielectric solvent mixtures only* with the free energy of transfer of ions from water to the second pure solvent. The n.m.r. data can be used to predict the free energy of transfer from water to the *mixed* solvents by consideration of the detailed thermodynamics of preferential solvation.[13] The comparison is shown in the Figure. The deviation of the e.m.f.-derived points from the predicted curve amounts to a maximum of 0·8 kJ or about five times the experimental uncertainty in the e.m.f. measurements.

The n.m.r.-derived values of $\Delta G_{\rm ps}^{\theta}$ relate to single ions being obtained from infinite dilution chemical shifts of the ionic nuclei which are measures of the immediate environment of the ion when it is free of interactions with neighbouring ions.[12] Comparison of these spectroscopically-derived single ion quantities for other mixed solvent systems with e.m.f.-derived values split by extra-thermodynamic assumptions is a line of research which we are actively pursuing.

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[1] O. Popovych, *Crit. Revs. in Analyt. Chem.*, 1970, **1**, 73.
[2] R. G. Bates, 'Determination of pH,' Wiley, New York, 1964, pp. 189—194.
[3] D. Feakins and P. J. Voice, *J.C.S., Faraday I*, 1972, **68**, 1390 and earlier papers in this series.
[4] B. M. Lowe and D. G. Smith, *J.C.S. Chem. Comm.*, 1972, 989.
[5] A. G. Mitchell and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, 1955, **51**, 1690; 1956, **52**, 824.
[6] W. C. Schumb, C. N. Satterfield, and R. L. Wentworth, 'Hydrogen Peroxide,' Reinhold, New York, 1955, p. 262.
[7] M. S. Frant and J. W. Ross, *Science*, 1966, **154**, 1553.
[8] W. H. Beck, J. Caudle, A. K. Covington, and W. F. K. Wynne-Jones, *Proc. Chem. Soc.*, **1963**, 110.
[9] A. K. Covington and J. Caudle, *J. Chem. Educ.*, 1972, **49**, 552.
[10] A. K. Covington and J. M. Thain, *J. Chem. Educ.*, 1972, **49**, 554.
[11] G. Eisenman in 'The Glass Electrode,' Wiley Reprint, New York, 1965, pp. 233—238.
[12] A. K. Covington, T. H. Lilley, K. E. Newman, and G. Porthouse, in preparation.
[13] A. K. Covington, T. H. Lilley, and K. E. Newman, in preparation.