Hydrogen Isotope Fractionation between the Solvent and Hydrogen Ions in Methanol Solution

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THE parameter l, expressing the deuterium fractionation between the aqueous hydrogen ion and water [$l \equiv (\mathrm{D:H})_{\mathrm{L_3O}}/(\mathrm{D:H})_{\mathrm{L_2O}}$, where L = D or H], is the key quantity in the formulation of expressions for rate and equilibrium constants in H_2O–D_2O systems. Its direct measurement has been carried out by n.m.r. methods[1] but these results are subject to some reservations, the chief of which concerns the uncertain magnitude of the chemical shift due to the anions which are inevitably present together with the hydrogen ion in an aqueous solution of a strong mineral acid.

Analogous measurements have now been carried out with hydrochloric acid in dry methanol, and in methan[^{2}H]ol, containing 2·6 mole percent MeOH (Figure). In this solvent it is possible to evaluate anion shifts separately[2] and, accordingly, the solution of the problems can be carried a little further. From published data,[2] the molal shift of the perchlorate ion is *ca.* + 0·070 p.p.m. This value is stated[2] to be independent of temperature in the range −65° to −30° and we therefore assume that no serious error is introduced by taking it to apply also at +33°. From our own measurements of the molal shifts for sodium chloride (+0·074 p.p.m.), sodium perchlorate (+0·251 p.p.m.), and hydrochloric acid (−0·934 p.p.m.), we accordingly evaluate the molal shift of the methanolic hydrogen ion to be

$$\delta_{\mathrm{H^+}} = \delta_{\mathrm{HCl}} - \delta_{\mathrm{ClO_4}} + \delta_{\mathrm{NaClO_4}} - \delta_{\mathrm{NaCl}} \\ = -0{\cdot}827 \text{ p.p.m.}$$

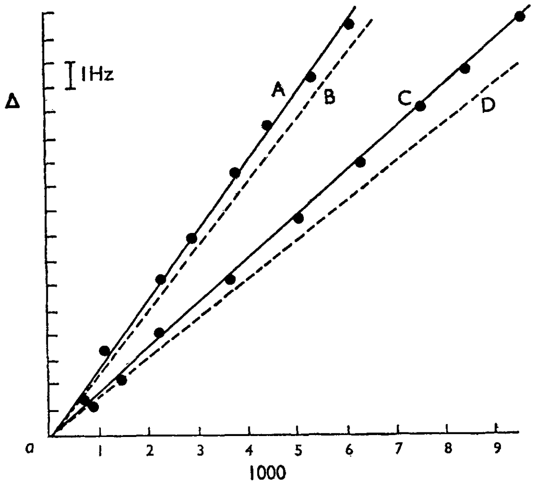

FIGURE. *Chemical shift* (Δ) *of* HCl *in methanol solution at* 60 *MHz* (33°).

A, Experimental points for MeOD–MeOH (97·4% D); B, corresponding slope for hydrogen ion, corrected for anion shift; C, experimental points for MeOH; D, corresponding slope for hydrogen ion, corrected for anion shift. (a = mole fraction of acid).

All shifts are measured relative to the methyl resonance. In the absence of corresponding measurements of anion and salt shifts in methan[^{2}H]ol solvent we assume, as an interim measure, that these shifts will be only slightly changed by the isotopic change of the solvent, on the fairly well founded assumption that exchange isotope effects involving chemically bound hydrogen nuclei are more pronounced than other solvent isotope effects. Inasmuch as the salt shifts constitute a correction amounting in total to less than 15% of the measured shift, the degree of correctness of the assumption (which we intend to test) is in any event of only minor importance. Applying these corrections to the lines of the Figure (after conversion to a units, to eliminate the spurious isotope effect due to concentration changes on the molality scale resulting from the density difference between isotopic solvents) we obtain the two broken lines which represent the shifts due to protons in hydrogen ions at the acid concentrations defined by the mole fraction a. The ratio of their slopes (1·641) is, at low concentrations, equal to $(1-n+nl)^{-1}$ whence $l[\equiv (\mathrm{D:H})_{\mathrm{MeOL_2^+}}/(\mathrm{D:H})_{\mathrm{MeOL}}]$ is evaluated to be 0·60. The ratio of the uncorrected slopes is 1·567 and would lead to a value of 0·63. The fractionation is greater than in the case of the aqueous hydrogen ion, which is perhaps a reflection of the more acidic character of the methanolic hydrogen ion.

Our procedure involves the assumption that hydrogen chloride in methanol solution is ionised (though not necessarily fully dissociated), which we propose to justify more fully later.

We have applied our result to a preliminary analysis of kinetic measurements of hydrogen ion catalysis in methanol (at concentrations below

2×10^{-3} M) and find that our value of l for methanol is sensible. These measurements will be reported later.

The discrepancy between the values obtained with and without explicit consideration of anion shifts is thought to reflect the approximate size of the correction to which the value of l for aqueous solution is liable and which we hope to be able to evaluate on the basis of the considerations given.

Some of the assumptions inherent in the approach outlined remain to be tested. To the ones already mentioned we must add the need for a demonstration that "anion shifts" evaluated in this manner are independent of the nature of the cation employed, *i.e.* that they do not contain a component due to cation effects beyond the first solvation shell.

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[1] V. Gold, *Proc. Chem. Soc.*, **1963**, **141**; A. J. Kresge and A. L. Allred, *J. Amer. Chem. Soc.*, **1963**, **85**, **1541**.

[2] R. N. Butler, E. A. Phillpott, and M. C. R. Symons, *Chem. Comm.*, **1968**, **371**.