The Fractionation of Hydrogen and Deuterium Isotopes in Solutions of Sodium Methoxide

By R. A. MORE O'FERRALL†

(*Physical Chemistry Laboratory, South Parks Road, Oxford*)

ADDITION of sodium methoxide to methanol causes a pronounced downfield shift in the n.m.r. absorption of the hydroxylic protons[1] and, for the same concentration of base, the shift is increased by the presence of CH_3OD. This indicates that the lighter isotope of hydrogen has a greater tendency to concentrate in the exchangeable proton positions associated with the sodium and methoxide ions than in the bulk solvent. By measuring the dependence of the chemical shift on the concentration of base in solutions of different isotopic composition, the D:H ratios in the solvation shells of the ions and in the free solvent can be compared.

The experimental procedure and the analysis of the results followed closely those of previous studies on aqueous solutions[2] and on acidic solutions of methanol,[3] in particular, the work of Gold.[2b,3] Measurements were made at $25 \pm 2°$ with a Varian A-60A n.m.r. spectrometer with dioxan ($< 1\%$) as an internal standard. In the Figure, the chemical shifts of the OH signal relative to its position in

pure methanol are shown plotted against the mole fraction of sodium methoxide for solutions containing zero and $90·3\%$ CH_3OD. Provided the concentration of the sodium methoxide is sufficiently low for the number of molecules bound in its ionic solvation shells to be neglected in comparison with the number in the bulk solvent, and provided, also, that only a single set of ν equivalent hydrogens associated with each pair of solute ions differs in isotopic composition from that of the solvent, the ratio of the limiting slopes of the plots shown in the Figure may be written, $(S_x - \delta_0)/(S_H - \delta_0) = (1 - x + x\phi)^{-1}$, where x is the atom fraction of deuterium; S_H and S_x are the limiting slopes (as $[NaOCH_3] \to 0$) for solutions of deuterium fractions zero and x respectively; and the fractionation factor, ϕ, measures the D:H ratio in the ν sites associated with the solute relative to the D:H ratio in the solvent. The evaluation of ϕ requires knowledge of the term δ_0 which represents contributions to the chemical shift from exchangeable hydrogens not subject to fractionation. An

† Present address: Department of Chemistry, Rice University, Houston, Texas, 77001.

estimate of δ_0 was obtained by a method similar to that used by Gold in allowing for the effect of chloride ion in fractionation studies of methanolic solutions of hydrochloric acid.[3] It was supposed that in sodium methoxide fractionation is confined to the solvation shell of the methoxide ion and that contributions to δ_0 arise only from the sodium ion. Recent measurements of the molal chemical shifts in methanol of sodium perchlorate,[3] $\delta(NaClO_4) = 0\cdot251$ p.p.m., and of the perchlorate ion,[4] $\delta(ClO_4^-) = ca.\ 0\cdot070$ p.p.m., allow derivation of the molal chemical shift of the sodium ion, $\delta(Na^+) = \delta(NaClO_4) - \delta(ClO_4^-) = 0\cdot181$ p.p.m., and conversion to c./sec. and concentration units of mole fraction permits identification of $\delta(Na^+)$ with δ_0. Combining $\delta_0 = 0\cdot34 \times 10^3$ c./sec., $S_H = -1\cdot39_3 \times 10^3$ c./sec., $S_x = -1\cdot86_3 \times 10^3$ c./sec., and $x = 0\cdot90_3$ leads to the value‡ of $\phi = 0\cdot76$.

This results for sodium methoxide may be compared with similar measurements of the fractionation factors for the hydronium ion[2] $(0\cdot69)$ and for the hydroxide ion [2a] $(ca.\ 0\cdot8)$ in aqueous solution. By combining data from n.m.r. and a variety of equilibrium studies, evidence has been obtained that the fractionation of these ions may be interpreted solely in terms of exchange of the hydrogens covalently bonded to the ions.[5] The present measurement is of interest in demonstrating that a strong base can lead to fractionation effects of comparable importance arising only from the contributions of molecules bound in its ionic solvation shells.

If, indeed, the assumptions made are correct, the equilibrium constant for complete exchange of the fractionating hydrogens is $\phi^{-\nu}$ and, in the absence of effects other than fractionation, the corresponding free energy difference is that for transfer of the methoxide ion between CH_3OH and CH_3OD.[6]

$$CH_3O^-[CH_3OD]_\nu + \nu CH_3OH \rightleftharpoons$$
$$CH_3O^-[CH_3OH]_\nu + CH_3OD$$
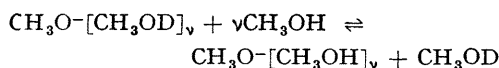
Furthermore, the value of $\phi^{-\nu}$, and hence of ν, is of importance for the interpretation of solvent isotope-effects in methanolic solutions; and for reactions in which the dominant fractionation effect arises from the presence of a methoxide ion in the reactants, $\phi^{-\nu}$ sets a rough upper limit to the solvent isotope effect that can be expected. Solvent isotope-effects $[k(CH_3OD)/k(CH_3OH)]$ have been measured for the rates of base-catalysed β-elimination and hydrogen exchange of fluoren-9-ylmethanol[7] $(2\cdot1$ and $2\cdot6$ respectively), for the hydrogen exchange of pentafluorobenzene[3] $(2\cdot3)$ and for the equilibrium addition of methoxide ion to 2,4-dinitroanisole to form a Meisenheimer complex[9] $(2\cdot6)$. The values are sufficiently large to suggest that ν must be greater than unity; and since the methoxide ion

has three lone pairs available for hydrogen bonding, an obvious interpretation would suggest the same number for ν.

The presumption that fractionation with the solvent is effectively confined to a single set of equivalent hydrogens associated with the methoxide ion is not without foundation. There are indications[10] that the free energy for transfer of the sodium ion between H_2O and D_2O is close to
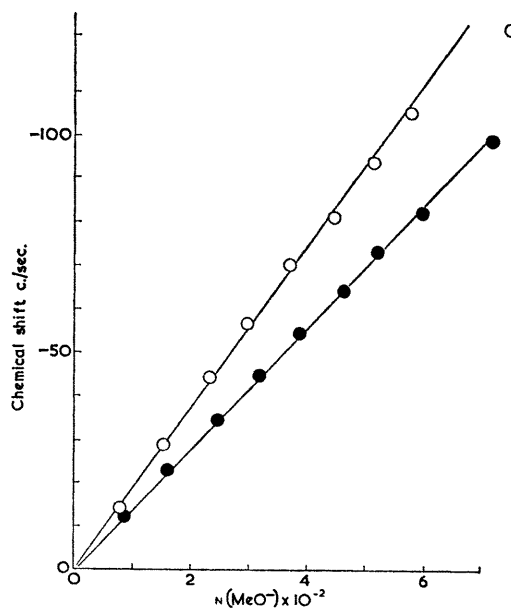

FIGURE. *The chemical shift of the OH group, relative to that of pure methanol, plotted against the mole fraction of added base for methanolic solutions of sodium methoxide.* ○ *Deuterium fraction,* $x = 0\cdot903$; ● *deuterium fraction,* $x = 0$.

zero, and it seems unlikely that in this respect its behaviour in methanol differs significantly. Moreover, in view of the evidence[2,5] that, in aqueous solution, fractionation associated with the hydrogen ion is confined to the unit H_3O^+, it is improbable that important fractionation effects for the methoxide ion could persist beyond its primary solvation shell. Possibly the least tenable assumption is that hydrogens beyond the primary solvation shell do not contribute significantly to the chemical shift. Experiments are planned to investigate this point and also to measure and verify the uniqueness of ν.

‡ Uncorrected for δ_0, $\phi = 0\cdot72$. The molal chemical-shift of sodium methoxide, $\delta(NaOCH_3) = -0\cdot74_4$ p.p.m. The value of $\delta(CH_3O^-) = \delta(NaOCH_3) - \delta(Na^+) = -0\cdot92_5$ p.p.m. may be compared with $\delta(H^+) = -0\cdot827$ p.p.m. (ref. 3).

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