Solvation of the Sodium Ion in Mixtures of Methanol and Dimethyl Sulfoxide

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Sodium NMR has been used to study the solvation of the sodium ion in solutions of sodium methoxide in methanol and in mixtures of methanol and dimethyl sulfoxide. The results obtained are compatible with a solvation model without any strong tendency for preferential solvation of the sodium ion by methanol or dimethyl sulfoxide.

The solvation of ionic species in different solvents plays an important role in chemical reactions and chemical equilibria. The increasing interest in the detailed knowledge of solvent – solute interactions has lead to a large amount of recent work on solvation phenomena. Refs. 1 and 2 could be consulted for references to such work.

Many different experimental methods have been used in studying the solvation of ions. The development of modern nuclear magnetic resonance instruments has made direct studies of solvation of many different ions possible. Special interest has been paid to alkali metal cations.[3] The solvation of these ions in both aqueous and non-aqueous solvents is of great importance in organic chemistry as they act as counter-ions in many reactions.

In our studies of solvent isotope effects and the fractionation factor for sodium methoxide in mixtures of methanol and dimethyl sulfoxide (DMSO)[4] we found it necessary to get to know the solvation of the sodium ion in these systems in closer detail. As nothing seems to have been done on the solvation of the sodium ion in this solvent system we

decided to undertake such a study and to use ^{23}Na NMR for this purpose.

EXPERIMENTAL

The ^{23}Na NMR measurements were made using a modified Varian XL 100 spectrometer operating at 26.45 MHz at 27 °C. Stoppered 12 mm NMR tubes were used in which 5 mm sealed NMR tubes with the reference solution had been inserted. The inner tube was fixed in a concentric way be means of teflon rings.

The solvents of listed quality were obtained from the following manufacturers and used without further purification: *Methanol*, anhydrous, H_2O <0.01% w/w, May & Baker. *Methanol-O-d*, 99.9 atom %, CIBA-GEIGY. *Dimethyl sulfoxide*, H_2O <0.01%, Riedel de Haën AG.

Sodium methoxide solutions were made by dissolving sodium in methanol under nitrogen. The concentration of the sodium methoxide was determined by titration against potassium phthalate using phenolphthalein as indicator. All handling of the solutions and filling of the tubes was made under nitrogen.

The reference solution, 0.05 M NaCl, was made up using distilled water. In cases (at high concentrations of DMSO) when the reference signal was masked by the sample signal, the reference was replaced by a secondary reference solution of sodium methoxide in methanol, *i.e.*, the solution which was used as sample solution for measurements in pure methanol. In the experiments concerning the salt and isotope effects 0.05 M $NaClO_4$ in methanol was used. Some of the samples were then measured against both sodium chloride in water and sodium methoxide in methanol. This made independent evaluations of the chemical shift difference between sodium chloride in water and

sodium methoxide in methanol possible. In no case did these differences deviate by more than 1 ppm from the mean value.

The difference in chemical shift between the sample and the reference signal was evaluated by fitting two Lorentz curves to the experimental spectrum.

A positive shift from the reference is downfield.

The reported chemical shifts have been corrected for differences in bulk magnetic susceptibility between the sample and reference according to eqn. (1),[5] where δ_{obs} is the observed chemical shift and χ_v^{ref} and χ_v are the volume magnetic susceptibilities of reference and sample solutions, respectively. For mixtures of methanol and DMSO the volume susceptibility (χ_v^{mix}) was calculated according to eqn. (2),[6] where V denotes volume of component added to the mixture. The contribution of the salt to the susceptibility has been assumed to be negligible.

$$\delta_{corr} = \delta_{obs} + \frac{2\pi}{3}(\chi_v^{ref} - \chi_v) \qquad (1)$$

$$\chi_v^{mix} = \frac{V^{MeOH}}{V^{MeOH} + V^{DMSO}} \chi_v^{MeOH} +$$

$$\frac{V^{DMSO}}{V^{MeOH} + V^{DMSO}} \chi_v^{DMSO} \qquad (2)$$

RESULTS AND DISCUSSION

The results of the present investigation are presented in Fig. 1 where the measured chemical shift of 0.03 M sodium methoxide relative to 0.05 M NaCl is plotted against the mol fraction of DMSO.

The salt effects have been investigated at three different solvent compositions, 0, 50 and 95 mol % DMSO. In the first two mixtures no salt effects were found, i.e., the extrapolated chemical shift at infinite dilution did not deviate beyond the experimental error from that at the concentrations used in this investigation although at 50 mol % the scatter in shift values was somewhat more pronounced than in methanol. This may reflect the larger uncertainty in shift determination in DMSO mixtures as compared to methanol because of line broadening. In 95 mol % DMSO the salt effect had to be corrected for. The magnitude of the correction is demonstrated in Fig. 1. Since the correction at the higher mol fraction is significant whereas that at intermediate is negligible, we simply assume a change in effect that is linear in the mol fraction of DMSO above 50 mol % and zero at lower DMSO content. In spite of lack of physical
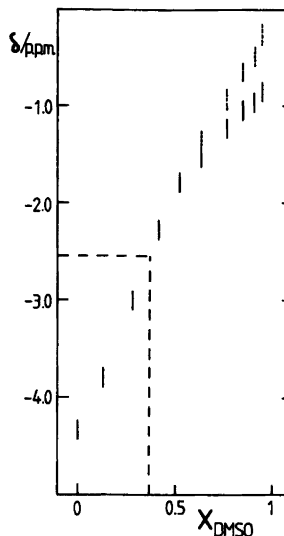

Fig. 1. Chemical shift of Na$^+$ in MeOH – DMSO, counter-ion MeO$^-$, relative to Na$^+$ in H$_2$O (0.05 M), counter-ion Cl$^-$. Corrections for difference in magnetic susceptibility have been applied. Corrections for salt effects are indicated in the figure. Dotted lines are uncorrected shifts. Dashed line gives "iso-solvation point". The shift in pure DMSO was obtained from extrapolation. Error limits are estimated to ±0.1 ppm (See experimental) and are indicated in the figure.

argument behind this crude assumption it is unlikely to cause any serious errors in the discussion below.

It can be seen that there is a smooth change in the chemical-shift value when the fraction of DMSO is increased in the solution. The overall change in chemical shift from pure methanol to pure DMSO is rather small but there appears, however, to be a definite curvature in the plot.

Plots of the type presented in Fig. 1 have been used in order to investigate preferential solvation of ions in mixtures of solvents.[3,7] The most straightforward but least quantitative way to analyze the results is to determine the isosolvation point.[8] This is the point at which the chemical shift is midway between the values of the pure solvents. The shift in pure DMSO was estimated from extrapolation. The ion is thought to be preferentially solvated by the solvent which has the lower mol fraction at that point. In the present case that would correspond to a slight preferential solvation by DMSO as indicated by the dotted line in Fig. 1.

As pointed out above, this treatment is rather qualitative and a more quantitative approach could be made according to Covington.[9-12] This treatment assumes that the exchange of solvent molecules in the solvation shell of an ion proceeds *via* successive exchange equilibria where a solvent molecule of one kind replaces a solvent molecule of another kind. In the simplest form of the theory the equilibrium constants for these exchange equilibria are assumed to be related solely by statistics. Another assumption is that the chemical shift varies linearly with the composition of the first solvation shell.

$$\frac{1}{\delta} = \frac{1}{\delta_p}\left(1 + \frac{Y}{K^{m/n}}\right) \tag{3}$$

The equation which is used in the treatment of data is, for the present case, eqn. (3), where δ is the observed chemical shift relative to the one in pure methanol. The symbol δ_p denotes the chemical shift difference between DMSO and methanol. K is the equilibrium constant for the overall equilibrium (4),

$$Na^+(MeOH)_n + \frac{n}{m}DMSO \rightleftharpoons$$
$$Na^+(DMSO)_{n/m} + nMeOH \tag{4}$$
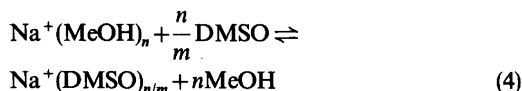
$Y = a_{MeOH}^m / a_{DMSO}$, a indicating activity. In a plot of $1/\delta$ vs. Y, δ_p is obtained from the intercept and then $K^{m/n}$ can be calculated from the slope. The result of the analysis could be seen from Fig. 2.*

In the case $m=1$, *i.e.*, the number of solvating methanol molecules is the same as the number of solvating DMSO molecules, the plot is obviously not linear. If, however, $m=3/4$, *i.e.*, the number of DMSO molecules solvating Na^+ is somewhat larger than the number of methanol molecules, a good straight line ($r=0.9996$) is obtained from which $K^{3/4n} = 1.52$ M$^{-4/3}$ could be calculated.

The free-energy change accompanying the overall exchange of solvent molecules is according to eqn. (5), where ΔG_{ps}° is called the free energy of

$$\Delta G_{ps}^\circ = -RT\ln K \tag{5}$$

preferential solvation. In the present case one can determine $3/4n\, \Delta G_{ps}^\circ = -1.04$ KJ mol^{-1} at 300 K. It should be noted that our use of activities instead of

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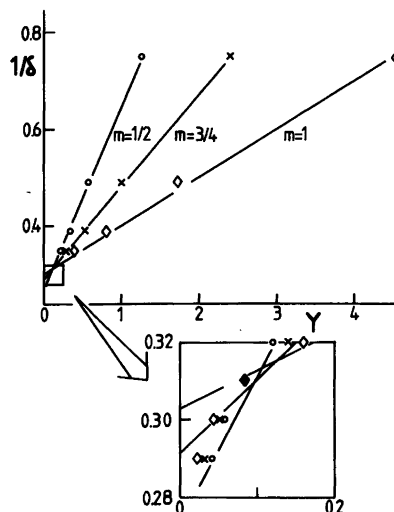* Due to the small accuracy (± 0.1 ppm) the point at $x_{DMSO} = 0.13$ has been excluded.

Fig. 2. Plots of $1/\delta$ against Y, where δ is taken relative to the shift in pure MeOH and $Y = a_{MeOH}^m / a_{DMSO}$, a being the activities of MeOH and DMSO in the binary mixture according to Ref. 13. The point at $x_{DMSO} = 0.13$ is omitted in this context due to the small accuracy. The lines were obtained from a least-squares analysis and the correlation coefficients were for $m=1/2$, 0.9995; $m=3/4$, 0.9996 and for $m=1$, 0.998.

mol fractions is an improvement that is possible only in a limited number of solvent systems due to the lack of activity data. Although activity coefficients of methanol in DMSO and of DMSO in methanol are appreciably different from unity due to strong molecular interactions the effect on ΔG_{ps}° is not dramatic.

If, $m=1/2$, is used, *i.e.*, the number of DMSO molecules solvating Na^+ is twice the number of methanol molecules, a good fit is obtained too, but in this case ΔG_{ps}° becomes slightly positive. This is just to show that under different sets of assumptions the calculated numbers of solvating molecules may change and also the free energy of preferential solvation but over a rather narrow range. The significance of "stoichiometric" coefficients should thus not be over-estimated. From the data in the present investigation it seems unsafe to pinpoint any particular model of solvation but the conclusion that the difference in preference between methanol and DMSO in the solvation shell of the sodium ion is small may safely be drawn.

A similar conclusion was reached for Li$^+$ in

mixtures of water and DMSO where a slight preferential solvation by water was found.[11] Preferential solvation of H^+, Ag^+ and Cu^{2+} by water in mixtures of DMSO and water has also been suggested.[14]

By studying the effect of substitution of H_2O by D_2O on the nuclear magnetic relaxation of the sodium ion, Holz[15] found a slight preferential solvation of the sodium ion by water in mixtures of water and DMSO. In view of the assumptions made the author states that a small change in parameters used would change the result into "non-preferential solvation" of the sodium ion in water–DMSO mixtures. We have found the solvent isotope effect in methanol on the chemical shift of the sodium ion to be negligible making such an approach impracticable in the present case.

The result obtained in the present investigation thus seems rather plausible. It is further possible that the result is a manifestation of the known ability of DMSO to accept hydrogen bonds and thus the forces between methanol and DMSO are strong enough not to be broken by the interaction with the sodium ion. This is evident from a comparison of the Gutmann Donor Numbers[16] of the pure solvents. DMSO exhibits a much stronger electron-pair donating (EPD) ability than methanol. In addition, evidence has been given[2] that on breaking the DMSO structure by adding a cosolvent its EPD characteristics are enhanced. The present results should thus not be looked upon as evidence in favour of the idea that methanol is comparable to DMSO as a cation solvating medium.

REFERENCES

1. Coetzee, J. F. and Ritchie, C. D., Eds., *Solute-Solvent Interactions*, Dekker, New York, Basel 1969.
2. Coetzee, J. F. and Ritchie, C. D., Eds., *Solute-Solvent Interactions*, Dekker, New York, Basel 1976, Vol. 2.
3. Chapter 13 in Ref. 2.
4. Baltzer, L. and Bergman, N.-Å. *To be published.*
5. Live, D. H. and Chan, S. I. *Anal. Chem. 42* (1970) 791.
6. Greenberg, M. S. and Popov, A. I. *Spectrochim. Acta A 31* (1975) 697.
7. Laszlo, P. *Angew, Chem. 90* (1978) 271.
8. Frankel, L. S., Stengle, T. R. and Langford, C. H. *Chem. Commun.* (1965) 393.
9. Covington, A. K., Lilley, T. H., Newmann, K. E. and Porthouse, G. A. *J. Chem. Soc. Faraday Trans. 1, 69* (1973) 963.
10. Covington, A. K., Newmann, K. E. and Lilley, T. H. *J. Chem. Soc. Faraday Trans. 1, 69* (1973) 973.
11. Covington, A. K., Lantzke, I. R. and Thain, J. M. *J. Chem. Soc. Faraday Trans. 1, 70* (1974) 1869.
12. Covington, A. K. and Thain, J. M. *J. Chem. Soc. Faraday Trans. 1, 70* (1974) 1879.
13. Quitzsch, K., Ulbrecht, H. and Geischer, G. *Z. Phys. Chem. Leipzig 234* (1967) 33.
14. Cox, B. G., Parker, A. J. and Waghorne, W. E. *J. Phys. Chem. 78* (1974) 1731.
15. Holz, M. *J. Chem. Soc. Faraday Trans. 1, 74* (1978) 644.
16. Reichardt, C. *Solvent Effects in Organic Chemistry*, Verlag Chem., Weinheim, New York 1979, p. 17.