Solvation Spectra. Part XLIX.[1] The Solvation of d^{10} Cations by Water and Methanol studied by Proton Magnetic Resonance Spectroscopy

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Molal shifts induced in the resonance of hydroxyl protons of water and methanol by the d^{10} cations Ag^+, Zn^{2+}, Cd^{2+}, and Hg^{2+} (methanol only) are systematically down-field of the shifts induced by corresponding alkali and alkaline earth cations. The cause of this effect is thought to be primarily an increased covalency in the metal–solvent bonding. Since Zn^{2+} is known to be octahedrally co-ordinated in methanol, a suggestion that the enhanced down-field shift is caused by an asymmetric solvation for Ag^+ is questioned.

FOLLOWING the observation of a separate hydroxyl proton resonance in the n.m.r. spectrum of magnesium perchlorate in methanol at low temperatures,[2] we have established molal shifts for individual ions in methanol,[3] water,[4] ethanol, glycol, and ammonia,[5] which, it is argued, are close to the absolute values. This approach seems to be accepted [6-8] and will be used herein.

When a separate resonance can be detected, the solvation number for the cation is directly forthcoming, being about six for Mg^{2+} in methanol [2] and water,[9] and also for Zn^{2+} in methanol.[3,10] However, for the majority of cations, separate resonances from bonded solvent molecules cannot be detected and it is not possible to obtain solvation numbers from the molal shifts for such ions by any direct method.

The particular case of shifts induced by aqueous silver(I) cations has been studied recently by Akitt.[11] He found an anomalous low-field shift for Ag^+ when compared with those for Na^+ or K^+, which have comparable surface charge-densities. He used the method developed by Malinowski and his co-workers [12-14] to estimate a solvation number of *ca.* 0.6 for aqueous Ag^+, and then used the concept of an asymmetric solvent shell to explain the extra down-field shift.[11] We felt that such a low solvation number was improbable for an ion with a d^{10} configuration, and have therefore extended this study to other cations of this electronic structure in the hope of shedding further light on the phenomenon.

EXPERIMENTAL

Water was doubly distilled from alkaline permanganate. Methanol (Hopkin and Williams, Carl-Fischer Reagent Grade) was dried over calcium hydride. Salts were all perchlorates of the highest available grade. They were dried in a vacuum oven at *ca.* 40 °C, and any residual water was estimated by standard procedures. For methanol studies, salts were recrystallised from methanol solutions that had been dried over a molecular sieve. In some cases a trace of perchloric acid was added to stabilise the solutions. Mercuric perchlorate was not sufficiently soluble in water to give reliable shifts. Salt concentrations were checked using EDTA and suitable indicators.

N.m.r. spectra were measured on a Jeol 100 MHz spectrometer. For aqueous solutions, tetramethylammonium perchlorate and sodium 3-trimethylsilylpropanesulphonate were used as internal markers, and the good agreement obtained for these was taken as evidence that they were not seriously perturbing the solvents. The C–H proton peak was used as a reference for methanolic solutions. Measured shifts are all related to the value for the hydroxyl resonance of the pure solvent under identical conditions in the Table and Figure, down-field shifts being taken as negative.

Shifts were studied in the concentration range zero to *ca.* 1M, and 4—5 measurements were made in this range for each system. The shifts were all closely linear and the data given in the Table were obtained from the best straight lines through the origin and the data points.

Solutions of cadmium perchlorate in methanol were studied just above the melting point in the hope of resolving a separate peak for the cation solvent shell, but to no avail. Similarly, aqueous solutions containing various aprotic solvents such as acetone were studied close to their solidification temperatures but, again, no separate resonance could be detected.

RESULTS AND DISCUSSION

Solvation Numbers.—Only in the case of the zinc cation can the n.m.r. spectra be used to give a direct measure of the solvation number. In our view, the method used by Akitt [11] for Ag^+, based upon the procedure of Malinowski [12-14] is unsound. This method, which involves a comparison of the temperature-induced shifts for pure solvent and salt solutions, rests entirely upon the assumption that the shifts for the solvent molecules directly associated with the ions are temperature independent. On the electrostatic model frequently used, this may be expected but, on the hydrogen-bond model that we have proposed,[3-5] it cannot be true.

In this model we have attempted to explain curves such as those in Figure 1 in terms of the strengths of the hydrogen bonds involved, the shifts being assigned to

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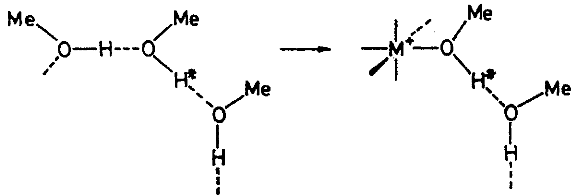
the changes involved on going from structures such as (I) and (II), for cations.



(I) (II)

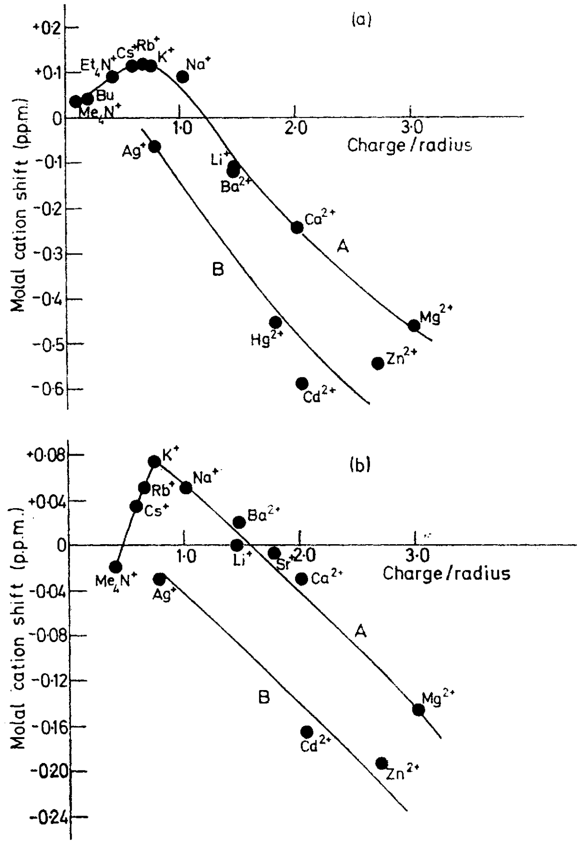
We consider that a major effect of the cation is to modify the strength of the H* · · · O hydrogen bonds, which may, of course, be stronger or weaker than that in (I). In our view, any calculation of the effect of cations must include this hydrogen bonding as a major factor. Thus, we would predict shifts of magnitudes comparable with those for pure solvents for the solvent shells of weakly bonded ions.

It can be argued that the results for ions such as Mg^{2+}, for which primary solvent shells give rise to resolved resonances, support the claim that these resonances are, indeed, relatively insensitive to temperature changes. They are certainly less temperature sensitive than the hydroxyl resonance of the pure solvent,[1] but this reflects, in our view, the fact that the hydrogen bonding linking primary and secondary solvent molecules is stronger than that in bulk solvent and, indeed, this has been used as one argument in favour of strong secondary solvation for such ions.[1]

Thus, in our view, the solvation number of *ca.* 0.6 reported for Ag^+ has no significance. However, others have derived low solvation numbers for Ag^+ by rather indirect methods,[15-17] and, as has been stressed by Akitt,[11] Ag^+ often prefers a co-ordination number of two, and it seems that this is probably the value he favours. We stress that solvent molecules are in large excess, and that silver(I) often exhibits a co-ordination number of four for simple σ-bonding ligands. It seems to us unlikely that water and methanol would not further solvate two-co-ordinated cations.

The explanation [11] for the down-field shift shown by solvent co-ordinated to silver ions relative to the alkali-metal cations hinges strongly on the concept that this solvation is not centrosymmetric. So far as we can understand the argument,[11] it seems that the effect of the secondary solvent molecules can be ignored for spherically symmetric systems, but not if they are asymmetric. Our view, outlined above and elsewhere,[3-5] requires that secondary solvent molecules exert a major control on the measured shifts, irrespective of the nature of the ion and the symmetry of the primary solvent shell.

In any case, as is shown by curve B of the Figure, all the ions of d^{10} configuration are ' anomalous ' relative to those of s^2p^6 configuration (curve A). The results for Zn^{2+} are noteworthy since this ion, having a solvation number of six (in methanol), is probably solvated symmetrically. (There is no electronic reason for any distortion, and if the solvation were grossly asymmetric more than one n.m.r. peak would be expected.)



Molal ion shifts as a function of charge/radius for a range of cations in (a) methanol at 313 K and (b) water at 273 K

In our view, the reason why curve B is displaced downfield from curve A stems from the degree of charge-transfer or covalency in the cation–solvent σ bonds.

Molal ion n.m.r. shifts in p.p.m. for water and methanol hydroxyl protons for a range of metal perchlorates

Cation	In H_2O		In MeOH	
	at 273 K	at 298 K	at 204 K	at 313 K
Cd^{2+}	−0.165	−0.178	−0.250	−0.562
Ag^+	−0.030	−0.013	−0.040	−0.066
Zn^{2+}	−0.192	−0.175	−0.316 [b]	−0.537
Hg^{2+}			−0.26 [a]	−0.45 [a]
Ca^{2+}	−0.030 [c]	−0.062 [c]	−0.144	−0.245
Ba^{2+}	+0.020 [c]	−0.015 [c]	−0.120	−0.117

[a] Large error because of dehydration difficulties and broad bands. [b] Ref. R. N. Butler and M. C. R. Symons, *Trans. Faraday Soc.*, 1969, **65**, 945. [c] Data from ref. 4.

Covalent contributions are undoubtedly small for ions such as Na^+, but are appreciable for Ag^+, even when octahedrally co-ordinated by chloride ions.[18] This will have the effect of increasing the acidity of the protons of

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ligand solvent molecules and, hence, will give rise to an extra down-field shift.

It may be noteworthy that the curve linking Ag^+, Hg^{2+}, and Cd^{2+} in Figure 1a does not pass through the point for Zn^{2+}, which falls between the two curves. If our covalency concept is correct, this is to be expected, since Zn^{2+} shows a smaller tendency to form covalent bonds than the remaining three d^{10} cations.

We conclude that there is no n.m.r. evidence in favour of an abnormally low solvation number for Ag^+, and that this is probably not less than four on average in water and methanol. The extra down-field shifts exhibited by $\cdots d^{10}$ ions is ascribed to covalency effects rather than to asymmetric solvation.

We thank the S.R.C. for a C.A.S.E. award to R. D. B. and Dr. Farnell of Kodak Limited, Harrow, for helpful advice and assistance.

[5/1375 *Received*, 11*th July*, 1975]