Chemical
Communications

NUMBER 4/1968 21 FEBRUARY

A Proton Magnetic Resonance Co-ordination Number Study of $Mg(ClO_4)_2$ in Water–Acetone Mixtures

By ANTHONY FRATIELLO,* ROBERT E. LEE, VONE M. NISHIDA and RONALD E. SCHUSTER,
(Department of Chemistry, California State College at Los Angeles, Los Angeles, California 90032)

BY COOLING aqueous solutions of Al^{III} to − 30 to −50°, it is possible to observe separate ^1H n.m.r. signals corresponding to bulk water and water molecules in the first Al^{III} solvation shell.[1] Integration of these signals provides a direct, unambiguous value of the cation co-ordination number. This method has been applied to the study of Al^{III} solvation in aqueous solvent mixtures[2] and to the determination of co-ordination numbers of several di- and tri-valent ions, including Mg^{II}, in water when possible, and in aqueous solvent mixtures. Because of the recent controversy regarding the co-ordination number of Mg^{II} in aqueous solution,[3,4] it was felt that our results would be of interest.

In the Figure, the ^1H n.m.r. spectrum of a 0·50 M-$Mg(ClO_4)_2$ solution in a water–acetone (1 : 2) mixture is shown. Since aqueous solutions of Mg^{II} salts freeze at about −60° even when highly concentrated, the lower temperatures (−80°) needed to slow the proton exchange rate to permit the observation of the bulk and complexed water signals could be attained only by the use of solvent mixtures. As seen in the Figure, the separation of the bulk and complexed water signals is only about 80 c./sec., but they are sharp enough to permit an accurate integration and co-ordination number determination. The average of the Mg^{II} co-ordination numbers obtained from the spectrum in the Figure, and from the similar spectra observed for 0·16M- and 0·34M-$Mg(ClO_4)_2$ solutions in water–acetone (1 : 2) mixtures, and 0·63M- and 0·70M-$Mg(ClO_4)_2$ solutions in water-acetone (1 : 1) mixtures is 5·8 ± 0·2.

Some related co-ordination number results for Al^{III} and Be^{II} in water and in aqueous acetone mixtures show that Al^{III} has six water molecules in the first solvation shell in pure water,[1,5] and in a range of water–acetone mixtures.[2] Similarly, the primary solvation shell of Be^{II} contains four water molecules in pure water solution and in a wide range of aqueous acetone mixtures. In both cases, acetone acts merely as a diluent, and does not replace water in the ion solvation shell.

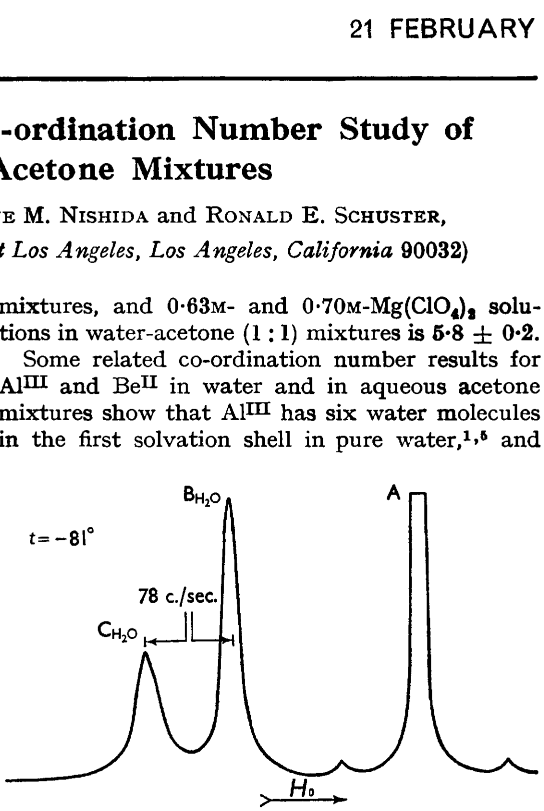

FIGURE. *The proton magnetic resonance spectra of a* 0·50M-$Mg(ClO_4)_2$ *solution in a water–acetone* (1 : 2) *mixture, recorded at* −81°, *on a Varian A*60 *NMR Spectrometer. The signals arising from bulk* (B_{H_2O}) *and complexed* (C_{H_2O}) *water are identified, as is the signal due to acetone* (A).

Thus, even though the addition of acetone changes the water structure by breaking hydrogen bonds, the primary solvation shells of Al^{III} and Be^{II} remain unaffected. Possible explanations for the lack of solvating ability of acetone in these solutions have been presented elsewhere.[2] It is significant that the co-ordination numbers of six and four, respectively, for Al^{III} and Be^{II} obtained by this ^1H n.m.r. method at about −40°, are the same values found by Jackson, Lemons, and Taube,[6] and Connick and Fiat[7] using a similar oxygen-17 technique at room temperature. Thus, the primary co-ordination shell of these ions is unchanged over a wide temperature range.

By analogy to the Al^{III} and Be^{II} results, it is reasonable to conclude that in pure water, as in the water–acetone mixtures studied here, Mg^{II} has six water molecules in the first solvation shell. This result correlates perfectly with the ^1H n.m.r, studies of methanol by Taube[8] and, more recently, by Nakamura and Meiboom,[9] and a ^1H n.m.r. study of hydrate melts.[10] However, this value is in disagreement with the co-ordination number of four obtained for Mg^{II} in water by the line width technique of Swift and Sayre.[11] Since the value of six obtained here for water–acetone mixtures is obtained by the direct observation and integration of the signals arising from bulk and complexed water molecules, and is, therefore, quite reliable, the concern recently expressed regarding the results of the line-width method may be well founded.[3] A comparison of our co-ordination number results for several ions with those obtained by the line width method will be reported soon.

The authors thank M. A. Morriss and Mr. O. R. Vanderstay for technical assistance and the Office of Saline Water, Department of the Interior, for financial assistance.

(*Received, December 7th*, 1967; *Com.* 1309.)

---

[1] R. Schuster and A. Fratiello, *J. Chem. Phys.*, 1967, **47**, 1554.
[2] A. Fratiello, R. E. Lee, V. M. Nishida, and R. E. Schuster, *J. Chem. Phys.*, in the press.
[3] S. Meiboom, *J. Chem. Phys.*, 1967, **46**, 410.
[4] T. J. Swift and W. G. Sayre, *J. Chem. Phys.*, 1967, **46**, 410.
[5] L. D. Supran and N. Sheppard, *Chem. Comm.*, 1967, 832.
[6] J. A. Jackson, J. F. Lemons, and H. Taube, *J. Chem. Phys.*, 1960, **32**, 553.
[7] R. E. Connick and D. N. Fiat, *J. Chem. Phys.*, 1963, **39**, 1349.
[8] J. H. Swinehart and H. Taube, *J. Chem. Phys.*, 1962, **37**, 1579.
[9] S. Nakamura and S. Meiboom, *J. Amer. Chem. Soc.*, 1967, **89**, 1765.
[10] C. T. Moyniham and A. Fratiello, *J. Amer. Chem. Soc.*, 1967, **89**, 5546.
[11] T. J. Swift and W. G. Sayre, *J. Chem. Phys.*, 1966, **44**, 3567.