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Berkeley, California

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THE COORDINATION NUMBERS OF BERYLLIUM AND
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May 27, 1963

The Coordination Numbers of Beryllium and Aluminium Ions
in Aqueous Solutions

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May 27, 1963

It has been shown by Jackson, Lemons, and Taube¹ that if cobaltous perchlorate is added to solutions of certain diamagnetic salts it is possible to distinguish separate O^{17} n.m.r. signals arising from the waters in the first coordination sphere of the diamagnetic ions and the free water, respectively. The paramagnetic salt shifts the free water signal to lower field, whereas, the signal of the bound water is not shifted appreciably. These authors pointed out that the coordination numbers of the ions could be obtained from the observed resonance for the bound water, but unfavorable signal to noise ratio prevented any such determination.

In the present work the signal to noise ratio was increased by using water enriched to 11.48 % in O^{17} , and the side band detection technique^{3,4} was employed instead of the usual derivative method. Thus only a single integration of the signal, rather than a double integration, was required to yield relative populations. Furthermore, the side band method eliminated the possibility of broadening through high modulation.

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As the width of the lines exceeded the highest modulation frequency, 400 c.p.s., of the Varian sweep unit, the Varian integrator was used for modulating the magnetic field at a frequency of 2)88 c.p.s. As a result of the modulation the solutions were heated from room temperature to about 35°C, except where indicated. The rf frequency was 5.415 m.c.

With aluminium the absorption curves were Lorentzian within experimental error (Fig. 1), thereby facilitating the resolution of the overlapping portions of the absorption signals (Fig. 1B). The true width of the lines as well as the relative populations in the two environments were calculated from the products of the widths times the heights of the resolved curves. The hydration number of Al^{3+} was found to be 6.07, 5.95, 5.86, and 5.82 from four separate measurements.

From Fig. 1 the full width at half height is 650 and 580 c.p.s. for the bound and free water respectively. The resonance of the free water is shifted, relative to the bound to lower field by 2330 c.p.s. (430 p.p.m.). The shift divided by the ratio of moles of Co^{2+} to moles of free water is 8.2×10^4 p.p.m. For comparison, Swift and Connick found 7.8×10^4 p.p.m.⁴ in a 0.01 M cobaltous sulfate solution containing 0.1 M perchloric acid at 27°C. An inversion of this calculation to give the hydration number of Al^{3+} as proposed by Jackson, Lemons, and Taube,¹ must await a redetermination of the latter value under conditions appropriate to the aluminium experiment.

A paramagnetic shift of the bound water of 60 c.p.s., relative to pure water was observed (Fig. 1C).

The beryllium curves (Fig. 2) were not perfectly symmetrical, apparently as a result of chemical exchange, as shown by the temperature dependence of the width of the bound water curve in Fig. 2C. Making an approximate correction for the asymmetry, hydration numbers of 3.95, 4.18 (Fig. 2A), 4.24, and 4.30

-3-

were found.

Figure 2C shows that the width of the resonance of the free water decreases with increasing temperature while the width of the water bound to the Be^{2+} increases, presumably as a result of increase in the rate of exchange of coordinated water molecules with the bulk water molecules. The lifetime of the water molecules in the first coordination sphere at room temperature on Be^{2+} is therefore ca. 3×10^{-4} seconds, or somewhat greater.

References

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Figure Captions

Figure 1. O^{17} absorption signals of water in ca. 1.5 M Al^{3+} solution containing Co^{2+} . Solution composition in millimoles: $AlCl_3$ - 2.60; H_2O - 91.0; $HClO_4$ - 0.812; $Co(ClO_4)_2$ - 0.396.

- A. Complete spectrum showing first side bands of free and bound water, each separated by twice the modulation frequency.
- B. Resolution of the overlapping portions of the absorption signals, with curve (a) the tail of the free water signal and curve (b) the bound water signal.
- C. Paramagnetic shift of the bound water relative to pure water. The sharp signal on the right is from a reference capillary of water containing O^{17} inserted in the sample tube.
- D. Derivative curve of the free and the bound water, detected by the usual method. Room temperature.

Figure 2. O^{17} absorption signals of water in ca. 3 M Be^{2+} solution containing Co^{2+} . Solution composition in millimoles: $BeCl_2$ - 4.868; H_2O - 86.47; $HClO_4$ - 1.72; $Co(ClO_4)_2$ - 0.520.

- A. Absorption curves using the side band technique. Resolved curve for bound water shown on right.
- B. Derivative curve of the absorption signals of the free and bound water. Room temperature.
- C. Temperature dependence of the bound water signal.

Fig. 1.

Fig. 2.

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