Title
THE COORDINATION NUMBERS OF BERYLLIUM AND ALUMINUM IONS IN AQUEOUS SOLUTIONS

Permalink
https://escholarship.org/uc/item/42k349k2

Authors
Connick, Robert E.
Flat, Daniel N.

Publication Date
1963-05-27
THE COORDINATION NUMBERS OF BERYLLIUM AND ALUMINUM IONS IN AQUEOUS SOLUTIONS

Berkeley, California
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
THE COORDINATION NUMBERS OF BERYLLIUM AND ALUMINUM IONS IN AQUEOUS SOLUTIONS

Robert E. Connick and Daniel N. Fiat

May 27, 1963
The Coordination Numbers of Beryllium and Aluminium Ions

in Aqueous Solutions

Robert E. Connick and Daniel N. Fiat

Department of Chemistry and
Inorganic Materials Research Division
of the Lawrence Radiation Laboratory
University of California
Berkeley, California
May 27, 1963

It has been shown by Jackson, Lemons, and Taube that if cobaltous perchlorate is added to solutions of certain diamagnetic salts it is possible to distinguish separate \( ^{17} \text{O} \) 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 \( ^{17} \text{O} \), and the side band detection technique 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.

* On leave of absence from the Weizmann Institute of Science, Isotope Department, Rehovoth, Israel.
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 2330 c.p.s. As a result of the modulation the solutions were heated from room temperature to about 39°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 Al³⁺ 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 Co²⁺ to moles of free water is 8.2 x 10⁴ p.p.m. For comparison, Swift and Connick found 7.8 x 10⁴ p.p.m. 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 Al³⁺ 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
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\textsuperscript{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\textsuperscript{2+} is therefore ca. 3 x 10\textsuperscript{-4} seconds, or somewhat greater.
References

2. Obtained from the Weizmann Institute of Science, Rehovoth, Israel.
Figure Captions

Figure 1. $^{17}$O absorption signals of water in ca. 1.5 M Al$^{3+}$ solution containing Co$^{2+}$. Solution composition in millimoles: AlCl$_3$ - 2.60; H$_2$O - 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 $^{17}$O inserted in the sample tube.

D. Derivative curve of the free and the bound water, detected by the usual method. Room temperature.

Figure 2. $^{17}$O absorption signals of water in ca. 3 M Be$^{2+}$ solution containing Co$^{2+}$. Solution composition in millimoles: BeCl$_2$ - 4.868; H$_2$O - 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.
This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission " includes any employee or contractor of the commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.