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Fig. 1. EPR line from an aqueous solution of $VOCl_2$

Figure 1: Fig. 1. EPR line from an aqueous solution of $VOCl_2$

Abstract

Full Text

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DESTRUCTION OF THE HYDRATION SHELLS OF VANADYL IONS UNDER THE ACTION OF THE ELECTROSTATIC FIELD OF DIAMAGNETIC IONS. AN EPR STUDY

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It was shown in (1) that exchange interactions of the electron spins of VO^{2+} in aqueous solutions of vanadyl salts (2) are greatly enhanced when the acidity of the solutions is increased. Continuing the investigation, we found that no less substantial an increase in exchange interactions can be obtained if, instead of acid, some diamagnetic salt is added to vanadyl solutions, the cations of which create a strong electrostatic field in their surroundings (possess a high value of the hydration energy). As an example, Fig. 1 gives a recording

Fig. 1. EPR line from an aqueous solution of $VOCl_2$, $N \sim 3$ mol/liter, additionally containing: 0 (*a*); 0.75 (*b*); 1.5 (*v*); 3 (*g*) mol/liter of the diamagnetic salt $BeCl_2$. Frequency of the oscillating magnetic field $\nu_0 = 9330$ MHz; $T \sim 290°$K.

of the electron paramagnetic resonance line from an aqueous solution of vanadyl chloride (the frequency of the oscillating magnetic field here and in all other experiments was 9330 MHz). The concentration of $VOCl_2$ was kept constant and equal to ~ 3 mol/liter. As the content of the diamagnetic salt $BeCl_2$ in the solution is increased, the EPR line narrows sharply (Fig. 1*b*–1*g*), which also indicates an increase in exchange interactions.

Analysis of the measurement results makes it possible to indicate unambiguously the main cause of the observed effect. In aqueous solutions of vanadyl, hydration of the vanadyl ions hinders close approach (collisions) of VO^{2+} ions and, consequently, exchange between the electron spins of VO^{2+}. Under the influence of the electrostatic field of diamagnetic ions, partial destruction of the hydration shells of VO^{2+} occurs, since the activation energy required for water molecules to leave the first coordination sphere of VO^{2+} ions is lowered (4). As a result, the probability of direct contacts between VO^{2+} ions increases, which leads to an increase in exchange interactions (narrowing of the EPR line).

schematic structure of associated vanadyl hydrate complexes

Figure 2: schematic structure of associated vanadyl hydrate complexes

graph showing dependence of EPR line width on additions of diamagnetic salts or acid

Figure 3: graph showing dependence of EPR line width on additions of diamagnetic salts or acid

It should be noted that, in order for exchange of spin states between a pair of approaching ions $\mathrm{VO}^{2+} \ldots \mathrm{VO}^{2+}$ to become possible, it is sufficient for only one water molecule to leave the first coordination sphere of one of the partners. It is quite probable that under the action of the majority of diamagnetic ions (an exception may be such strongly hyd-

ions (such as Al^{3+}), only the water molecule in the trans position to the vanadyl oxygen is, in the main, removed (this molecule is coordinated least strongly), so that exchange takes place in associates.

As a result of thermal motion the associates are destroyed and formed again. However, only those pairs participate in exchange whose lifetime τ exceeds the reciprocal value of the exchange frequency: $\tau > 1/\omega_e \sim 10^{-10}$ sec ($\omega_e \sim 10^{10}$ sec^{-1} (^{3})).

Thus, by measuring the width of the EPR line of VO^{2+} ions as a function of the content of a diamagnetic salt in the solution, one can obtain direct information on the destruction of the hydrate shells of VO^{2+} under the action of diamagnetic ions.

Having this in mind, we studied the influence of many diamagnetic ions on the EPR line width of vanadyl ions. A 2.6-molar aqueous solution of $VOCl_2$ was chosen as the object of study. The necessity of working with comparatively concentrated vanadyl solutions was due to the fact that, as the solutions are diluted, the probability of collisions of vanadyl ions with one another decreases (exchange interactions are removed), and, in accordance with the molecular mechanism described, diamagnetic ions gradually cease to affect the EPR line width. The measurement results are presented in Figs. 2–4: the line width, ΔH, of a 2.6-molar $VOCl_2$ solution is plotted as a function of the content of a diamagnetic salt or acid in the solution. For a purely aqueous solution (concentration of diamagnetic additions $N = 0$), the width ΔH is conventionally taken as equal to unity. From the course of the curves in Fig. 2 it follows that the effectiveness of the dehydrating action of diamagnetic cations increases in the series:

Fig. 2. Dependence of the EPR line width of a 2.6-molar aqueous $VOCl_2$ solution on additions to the solution of diamagnetic salts (acid). ΔH is the line width in arbitrary units; N is the molar concentration of the added diamagnetic

salt or acid. $\nu_0 = 9300$ MHz; $T \sim 290^\circ$K.

$$\mathrm{Cs}^+ < \mathrm{Rb}^+ < \mathrm{NH}_4^+ < \mathrm{K}^+ < \mathrm{Na}^+ < \mathrm{Li}^+ < \mathrm{H}^+ < \mathrm{Sr}^{2+} < \\ < (\mathrm{Ca}^{2+},\ \mathrm{Mg}^{2+},\ \mathrm{Be}^{2+}) < \mathrm{Al}^{3+}. \quad (1)$$

Table 1 gives the values of the crystallochemical radii r (^{5}) and hydration heats $-\Delta H_i$ (^{6}) of the diamagnetic ions.

Comparing the data of Table 1 with the obtained series of cation effectivenesses (equation 1), we come to the conclusion that the dehydrating action of cations is the greater, the smaller their radius and the larger their electric charge; i.e., the dehydrating action of cations increases with increasing heat of their own hydration.

Let us dwell on the existing exceptions. The most important and interesting exception is the strong dehydrating action of the proton. In its dehydrating action the proton stands above all the monovalent cations studied by us (equation 1), even the Li^+ cation, which has the smallest radius: $r_{\mathrm{Li}^+} = 0.68$ Å (Table 1). If the dehydrating action of the proton were reducible to the action of the oxonium ion H_3O^+, it would be close to that of a monovalent molecular- of the ion NH4+, since the radii of the molecular ions H3O+ and NH4+ are approximately equal. In reality, however, the dehydrating action of the proton proves to be much greater (see Fig. 2). This circumstance is undoubtedly connected with the special molecular nature of the hydrogen ion and its high

Table 1

	Cs+	Rb+	NH4+	K+	Na+	Li+	Sr2+	Ca2+	Mg2+
r (Å)	1.65	1.49	1.43	1.33	0.98	0.68	1.20	1.04	0.74
$-\Delta H$ (kcal/g-ion)	67	43	78	81	101	127	353	386	467

(continued)

	Be2+	Al3+	Cd2+	Zn2+	In3+	Br−	Cl−	F−
r (Å)	0.34	0.57	0.99	0.83	0.92	1.96	1.81	1.33
$-\Delta H$ (kcal/g-ion)	601	1125	439	496	994	76	84	116

Fig. 3 and Fig. 4: plots of ΔH versus N for various salts

Figure 4: Fig. 3 and Fig. 4: plots of ΔH versus N for various salts

mobility (penetrating ability). In aqueous acid solutions, excess protons are not fixed to particular water molecules, but make activated jumps from one molecule to another (7). The potential barrier overcome by the protons in doing so is very small. It follows that hydrogen ions in aqueous acid solutions may be regarded as a kind of "proton gas" distributed over the poles of water molecules (8). Apparently, in aqueous solutions closer approaches occur between VO2+ and H+ ions than between VO2+ ions and any other diamagnetic cations,[*] which accounts for the high efficiency of hydrogen ions (Fig. 2, equation 1).

Fig. 3. The same as in Fig. 2

Fig. 4. The same as in Figs. 2 and 3

The hypothesis of the strong dehydrating action of hydrogen ions was used by O. Ya. Samoilov as the basis for explaining the anomalous values of the heats of dissolution of mineral salts in acid solutions (8). However, the validity of this point of view did not appear indisputable ((6), p. 283). Our results quite unambiguously demonstrate the correctness of the fundamental premise of O. Ya. Samoilov' s concept (8).

Another exception to the regularity under consideration (the dehydrating action of cations is the greater, the larger the heats of their own hydration) is the indistinct difference in the dehydrating capacity of the cations Ca2+, Mg2+, Be2+, whereas, judging from the data of Table 1, the dehydrating capacity of these cations should increase in the sequence Ca2+ < Mg2+ < Be2+. The following reasons are possible. According to

[*] At present it can no longer be assumed that excess protons can enter directly into the hydration shells of the cations of dissolved salts (8). Measurements by the proton magnetic resonance method have shown that the hydration shells of cations practically do not participate in reactions with acids (9).

According to Samoilov[8], Ca^{2+} ions (as well as ions whose hydration energy is less than that of Ca^{2+}) undergo Brownian translation in solutions—activated jumps from one temporary equilibrium position to another—mainly without water molecules of the hydrate shells, whereas Mg^{2+}, Be^{2+} ions (and, of course, Al^{3+} ions, whose hydration energy is still greater) move chiefly in the form of hydrate complexes. This effect probably leads to some increase in the distances of the closest possible approaches of the VO^{2+} ion to Mg^{2+}, Be^{2+}, and Al^{3+} ions and, consequently, to some extent diminishes the dehydrating action of the latter.

On the other hand, it is necessary to take into account the possible role of the formation of chloride complexes. Complex formation with chlorine ions is practically absent in the case of cations of all alkali metals and of Be^{2+} cations, but binding into chloride complexes of such cations as Mg^{2+} and Sr^{2+} may be appreciable. The formation of chloride complexes, by lowering the effective positive charge of diamagnetic particles, should be accompanied by a decrease in their dehydrating action.

The role of complex formation with Cl^- anions is illustrated especially clearly by the example of the cations Zn^{2+}, Cd^{2+}, and In^{3+} (Fig. 3). The listed cations form fairly strong chloride complexes. In accordance with this, Zn^{2+} and Cd^{2+} ions exhibit a very weak dehydrating action, while the trivalent In^{3+} ion, in its dehydrating action, is inferior to the divalent and larger Ca^{2-} ion (the ionic radii of In^{3+} and Ca^{2+} are 0.92 and 1.04 Å, respectively; see Table 1).

Figure 4 gives curves for vanadyl solutions containing additions of CsCl, CsF, NaCl, and NaBr. It is usually assumed that the dehydrating action of anions is negligibly small, since the sizes of anions are large. However, we see that replacing CsCl by CsF increases the effectiveness of the diamagnetic additive, whereas replacing NaCl by NaBr, on the contrary, decreases it. Evidently, we are dealing with the dehydrating action of the anions Cl^-, F^-, and Br^-, and this action increases in the sequence
$Br^- < Cl^- < F^-$, which corresponds to an increase in the hydration energies of the anions. The considerable dehydrating action of anions most likely indicates a high probability of associations of the type $VO^{2+} \cdot H_2O \cdot A$, where A is the salt anion.

The experimental data of Figs. 3 and 4 may be summarized as follows. The solution contains cations K_1, K_2 and anions A. The influence of cations K_2 and anions A on the hydration of cations K_1 is studied. If cations K_1 have a greater affinity for the anions, then the anions intensify the dehydrating action of cations K_2 (a specific example is Fig. 4). If, on the contrary, the anions are grouped predominantly with cations K_2, then a weakening of the dehydrating action of cations K_2 occurs (a specific example is Fig. 3).

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Note: Figure translations are in progress. See original paper for figures.