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The Dissociation Constant of the Cobalt(III) Hexammine–Sulfate Ion Pair from Spectrophotometry

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RECEIVED MAY 9, 1958

The dissociation constant of the ion pair formed by the association of $Co(NH_3)_6{}^{+++}$ and $SO_4{}^{=}$ has been estimated to be 0.0013 ± 3.5% in water at 25° from changes in the optical density of the cobaltic ion in the presence of sulfate. This value s compared with previous answers. The effect of ion-pair size is examined.

Shifts in the absorption bands of Co(III) complex ions which are produced by certain anions can be attributed to ion association. Posey and Taube[1] have used these effects to obtain the corresponding equilibrium constants and for the system

$$Co(NH_3)_6{}^{+++} + SO_4{}^{=} = Co(NH_3)_6SO_4{}^{+}$$

they derived a value of $K = 4.76 \times 10^{-4}$ (where K is the dissociation constant) at zero ionic strength in water at 24.5°. This corresponds reasonably well with 3.0×10^{-4} which Davies[2] calculated from the solubility of some sparingly soluble cobalt hexammine salts in dilute K_2SO_4 and with 2.77×10^{-4} which Jenkins and Monk[3] obtained by application of Onsager's limiting equation to conductance measurements of the sulfate salt of the cobaltic ion. However, a much higher value, namely, $11.3 \pm 0.3 \times 10^{-4}$, was obtained by Bale, Davies and Monk[4] using spectrophotometric methods, and in view of the large discrepancies, especially between the two optical studies, we have made further measurements. These are now given.

Experimental

A Hilger Uvispek, model H700.307 Spectrophotometer fitted with a water-jacketed cell holder which could be kept at 25 ± 0.1° and 1 cm. quartz cells were used. These were carefully cleaned and intercompared by filling with the same solutions before measuring absorption shifts. To avoid handling the cells after placing them in the cell holder, they were filled by pipet and emptied by a suction jet four times before the final filling. This technique was introduced by Prue and Davies.[5] Measurements were taken until the readings were constant for at least 15 min. To eliminate possible errors in our previous work, fresh samples of $Co(NH_3)_6(ClO_4)_3$, Na_2SO_4 and $NaClO_4$ were prepared. Over the concentration range studied, the last two showed no absorption at the wave length used (235 mμ).

Discussion and Results

If D_1 is the optical density of a solution containing a molar $Co(NH_3)_6(ClO_4)_3$, b molar Na_2SO_4 and c molar $NaClO_4$, while D_2 is the optical density of a solution containing only the first of these, then

$$D_1 - D_2 = \epsilon_2 - \epsilon_1 \qquad (1)$$

where ϵ_2 and ϵ_1 are the molar extinction coefficients of the ion pair of concentration x, and of the cobaltic ion. Also

$$K = (a - x)(b - x - y)f_1f_2/xf_3 \qquad (2)$$

where y = $NaSO_4{}^-$ ion-pair concentration, and f represents activity coefficients.[6] Combination gives

$$K/(\epsilon_2 - \epsilon_1) = a(b - x - y)f_1f_2/(D_1 - D_2)f_3 - (b - x - y)f_1f_2/(\epsilon_2 - \epsilon_1)f_3 \qquad (3)$$
$$= \alpha f_1f_2/f_3(D_2 - D_1) - \beta f_1f_2/f_3$$

Various values of $D_1 - D_2$ were obtained by varying b, keeping a fixed. In the first set $NaClO_4$ was added to keep the ionic strength I constant, whence by plotting $ab/(D_2 - D_1)$ against b, a first value of $1/(\epsilon_2 - \epsilon_1)$ was obtained. First values of x were then calculated by equation 1, and first values of y using $K(NaSO_4{}^-) = 0.19$ and a generalized activity coefficient expression.[7] A plot of $\alpha/(D_2 - D_1)$ against β gave a second value of $1/(\epsilon_2 - \epsilon_1)$. The process was repeated until this term did not change. In all about a 5% change occurred between the first and last series.

A second set of solutions in which $NaClO_4$ was omitted gave the data from which K values were calculated from equation 2, deriving each value of x from equation 1 and the activity coefficients from

$$-\log f_i = 0.5z_i{}^2(I^{1/2}/(1 + BaI^{1/2}) - CI) \qquad (4)$$
$$I = 6a + 3b - 6x - 2y$$

Two values of the mean ion radius $\mathring{a}$ were tried. The first is based on the assumption that the cation and anion touch to form an ion pair, and the empirical method of Robinson and Stokes[8] was used to calculate this distance. The required ion mobilities are[3,6] 99.2 and 80.0, giving $\mathring{a}$ = 3.8 Å. B is $50.29/(DT)^{1/2}$ and the empirical constant C was adjusted until K showed no significant trend over the concentrations investigated. For the second value of $\mathring{a}$, Bjerrum's equations[9] were used, taking the average K from the first set of results. Our data are given in Tables I and II.

TABLE I

MEASUREMENTS AT CONSTANT IONIC STRENGTH

10^4a = 5.073; 235 mμ

10^2b	3.00	2.50	2.00	1.50	1.00
10^2c	..	1.49	3.01	4.50	5.99
$D_1 - D_2$	0.190	0.181	0.1655	0.1455	0.1175
10^3y	3.05	2.75	2.35	1.85	1.30
$10^5\alpha$	7.08	6.14	5.32	4.48	3.65
$10^2\beta$	2.66	2.19	1.735	1.285	0.845

The average value of $1/(\epsilon_2 - \epsilon_1)$ was derived by the method of least squares. The average values

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TABLE II

DISSOCIATION CONSTANT OF $Co(NH_3)_6SO_4^+$

$10^4a = 10.15$, $K(a)$, $\mathring{a} = 3.8$ Å., $C = 0.70$; $K(b)$, $\mathring{a} = 6.2$ Å., $C = 0.39$, $1/(\epsilon_2 - \epsilon_1)$

10^2b	1.00	1.50	2.00	2.50	3.00	3.50
$D_1 - D_2$	0.304	0.332	0.354	0.3685	0.384	0.394
10^2y	0.52	1.1	1.85	2.7	3.75	4.95
10^2I	3.16	4.53	5.89	7.15	8.44	9.68
$10^3K(a)$	1.26	1.275	1.25	1.265	1.245	1.265
$10^2K(b)$	1.35	1.375	1.345	1.36	1.31	1.32

of K in Table II are (a) 0.00126 and (b) 0.001345. The 6.5% difference between these stresses the need to obtain measurements at very low ionic strengths for in these regions the $B\mathring{a}$ factor becomes less important and K can be found with greater precision. Our present answer is a little higher than our previous one.[4] This is chiefly due to the fact that for the latter $B\mathring{a}$ was taken as 1.0; if this were used for our present measurements, K would be 0.00120, *i.e.*, within 6% of the previous result. Accordingly the new measurements confirm the earlier ones, which were obtained at 248 and 250 mμ. It is difficult to indicate why we differ from Posey and Taube[1] since they have not given experimental details. Their method requires a straight line extrapolation and, judging by their Fig. 1, this was not too successful. These authors differ from us in that they used solutions containing 0.0001 *M* $HClO_4$. We repeated our measurements in the presence of 0.001 *M* acid, but this did not have any effect.

Another feature which also awaits an explanation is the large discrepancy between the conductance[3] and spectrophotometric values. It is possible that the new Fuoss–Onsager conductance treatment[10] may eventually provide an answer. Preliminary calculations with 1:1-valent salts show that this gives higher dissociation constants than do the older methods based on the limiting Onsager equation. This is in contrast to what happens when modifications are applied to the original Onsager treatment so that the effect of ion size can be examined. Davies, Otter and Prue[11] illustrate this in a discussion of the dissociation of cupric sulfate. The limiting law value of the dissociation constant in water at 25° is 0.0049, whereas for an ion-pair distance of 10 Å. it is 0.0040. The same type of trend was found by these authors by an analysis of cryoscopic and spectrophotometric data when increasing ion-pair distances are used. By the last of these methods they calculate K to be 0.0080 for an ion-pair distance of 4.3 Å. and with 10 Å., $K = 0.0040$. This is a much wider variation than we obtain with the present results on trying different ion sizes and is partly due to differences of experimental procedure. Davies, Otter and Prue balanced the optical densities of cupric sulfate against those of cupric perchlorate, and since they did not use constant ionic strengths, their interpretation involved using molar extinction coefficients which vary with the chosen ion-pair distance. Prue[12] can see no justification for taking a unique value of ϵ_2, although this contradicts the arguments leading to equation 3 unless the factor f_1f_2/f_3 does not remain constant at constant ionic strength. One way of examining this would be to obtain data leading to Table I with non-associating salts other than $NaClO_4$. An indirect test is to repeat the procedure at different constant ionic strengths. Judging by our work with the ion pair UO_2Cl^+, $\epsilon_2 - \epsilon_1$ does remain constant up to an ionic strength of about one but can change considerably in more concentrated media.

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[CONTRIBUTION FROM THE BIOLOGICAL LABORATORIES, HARVARD UNIVERSITY]

The Combination of Manganous and Cobaltous Ions with Imidazole[1]

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RECEIVED MAY 15, 1958

Imidazole forms weak complexes with manganous ion, $\log k_1 = 1.65$, $\log k_2 = 1.25$ and with cobaltous ion, $\log k_1 = 2.42$, $\log k_2 = 1.95$, $\log k_3 = 1.58$, $\log k_4 = 1.2$ at 25° and ionic strength 0.16. The weakness of the binding does not permit a determination of the higher association constants at this ionic strength. A correlation between the binding of a series of metal ions with ammonia and with imidazole is described.

Imidazole has been shown to be a useful model compound for the metal ion combining capacity of the histidyl group in proteins.[2] The study of its combination with metallic ions is here extended to the biologically important manganous ion and cobaltous ion.

Experimental

The imidazole was the same as that used previously,[3] cobaltous nitrate was Fisher Certified Reagent and manganous nitrate was Fisher Certified Reagent assayed solution. All solutions were CO_2 and O_2 free, prepared from distilled water which was passed through a mixed bed ion-exchange column and through which nitrogen was bubbled.

Standardized sodium hydroxide solution was added from a Gilmont ultramicroburet of 1.00-ml. capacity. The *p*H

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(1) This work was supported by grants from the National Science Foundation (G-3230) and from the United States Public Health Service (H-3169).

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