The Formation of Al^{3+}–SO_4^{2-} Ion-pair in an Aqueous Solution of Potassium Aluminum Alum*

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In a previous paper[1] the formation constant of the Cr^{3+}–SO_4^{2-} ion-pair in an aqueous solution of violet hexaaquochromium(III) sulfate or potassium chromium alum was reported by one of the present authors. Aluminum and iron have similar properties in an aqueous solution with chromium, as is shown by the fact that these three elements belong to the same group in qualitative analysis. In order to investigate the ionic state in an aqueous solution of potassium aluminum alum, the formation constant of the Al^{3+}–SO_4^{2-} ion-pair was measured.

Experimental

Potassium aluminum alum was purified by the recrystallization of the highest grade commercial reagent. The measurement of the electrical conductivity of the solution was carried out with a Yokokawa Universal Bridge BV-Z-13A; that of the pH, with a Toa Denpa pH meter HM-8, and that of the viscosity, with an Ostwald viscosimeter.

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[1] R. Tsuchiya and A. Umayahara, This Bulletin, 36, 554 (1963).

Method of Calculation and Results

In an aqueous solution of potassium aluminum alum, the following equilibria are thought to be established:

$$[Al(H_2O)_6]^{3+} + SO_4^{2-} \xrightleftharpoons{K} [Al(H_2O)_6]SO_4^{+} \quad (1)$$

$$[Al(H_2O)_6]^{3+} \xrightleftharpoons{K_a} [Al(OH)(H_2O)_5]^{2+} + H^{+} \quad (2)$$

$$[Al(OH)(H_2O)_5]^{2+} + SO_4^{2-} \xrightleftharpoons{K} [Al(OH)(H_2O)_5]SO_4 \quad (3)$$

$$K^{+} + SO_4^{2-} \xrightleftharpoons{K'} K\text{-}SO_4^{-} \quad (4)$$

where the formation constants of reactions 1, 2 and 4 are expressed by K, K_a and K' respectively. It is reasonable to assume that the formation constant of reaction 3 is approximately equal to that of reaction 1. This assumption is justified by the two reasons described below.

By using the formation constant calculated below, we ascertained that the concentration of $[Al(OH)(H_2O)_5]SO_4$ is in the order of 10^{-6} if the initial concentration of $[Al(H_2O)_6]^{3+}$ is 10^{-4}. Aluthogh the exact value of the formation constant of Eq. 3 is not known, it is thought to be at least not larger than that of Eq. 1. Therefore, the ratio of the variation of the concentration of $[Al(OH)(H_2O)_5]SO_4$ against the concentration of $[Al(H_2O)_6]^{3+}$ with the value used as the formation constant of Eq. 3, is in the range of a few per cent. The error of the formation constant of K is very small, even where it is assumed to be equal to that of Eq. 3. The other reason, which will also be shown below, is based on the finding that the value of the acid dissociation constant, $pK_a = 4.9$, calculated by the assumption is in good agreement with the value, 5.036, in the literature.[2]

When the total concentration of aluminum contained in an aqueous solution of potassium aluminum alum is expressed by a; the concentration of sulfate ions spent for the formation of an $Al\text{–}SO_4^{+}$ ion-pair, by x, and that of sulfate ions spent for the formation of a $K\text{–}SO_4^{-}$ ion-pair, by x', and when the molecular conductivities of $[Al(H_2O)_6]^{3+}$, SO_4^{2-}, K^{+}, and hydrogen ions are expressed by Λ_1, Λ_2, Λ_5, and Λ_H respectively, we have, in a manner similar to that used in obtaining Eqs. 12 and 13 in the previous paper,[1] determined that:

$$K \fallingdotseq x/(a-x)(2a-x-x') \quad (5)$$

$$\begin{aligned}(5a\Lambda_1 + C_H\Lambda_1 + 6a\Lambda_2)x + (6a\Lambda_5 + 4a\Lambda_2)x' &= 6a^2(\Lambda_5 + \Lambda_1 + 2\Lambda_2) - 2aC_H\Lambda_1 \\ &\quad + 6aC_H\Lambda_H - 3a^2\Lambda_0\eta \quad (6)\end{aligned}$$

where Λ_0 is the observed conductivity of potassium aluminum alum in the aqueous solution and η is the specific viscosity of the solution.

The plot of the molecular conductivity of a potassium aluminum alum solution, Λ_0, measured at 25°C against the square root of the concentration, a, is shown in Fig. 1.

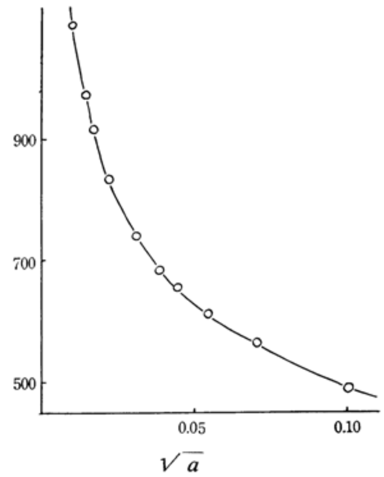

Fig. 1. The plottings of the molecular conductivities at 25°C vs. the square root of the concentrations of the potassium aluminum(III) alum solution.

By using the value of the conductivity of the potassium sulfate solution and by applying an assumption similar to that used in obtaining Eqs. 9, 13 and 15 in the previous paper[1] to Eqs. 5 and 6, the formation constant of the ion-pair, $[Al(H_2O)_6]SO_4^{+}$, and the acid dissociation constant of $[Al(H_2O)_6]^{3+}$ were computed, were $\Lambda_1 = 189$[3] was employed as the molecular conductivity of $[Al(H_2O)_6]^{3+}$ instead of that of $[Cr(H_2O)_6]^{3+}$ as in the previous paper.[1]

The values of the formation constant of the ion-pair and the corresponding ionic strength are given in Table I, as are the values of the conductivity and the pH of the potassium aluminum alum solution. The logarithm of the formation constant is plotted against the square root of the corresponding ionic strength in Fig. 2. By extrapolation of the plottings up to $\mu \to 0$, the thermodynamic formation constant of the ion-pair at 25°C was obtained as $K = 5.4 \times 10^3$.

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[2] T. Ito and N. Yui, *Sci. Rep. Tohoku Univ. Ser. I*, 37, 185 (1953).

[3] Landolt-Börnstein, "Phys. Chem. Tabellen," Ergänzungsband III, Teil III, Verlag von Julius Springer, (1936), p. 2059.

TABLE I. THE OBSERVED VALUES OF CONDUCTIVITY AND pH OF THE SOLUTION OF POTASSIUM ALUMINUM ALUM AND THE CALCULATED VALUES OF THE FORMATION CONSTANT OF ION-PAIR Al^{3+}-SO_4^{2-} AND THE ACID DISSOCIATION CONSTANT OF HEXAAQUOALUMINUM(III) ION AT THE VARIOUS IONIC STRENGTHS OF THE SOLUTION AT 25°C

a	Λ_{obs}	pH	η	$K\times10^{-3}$	$\log K$	$K_a\times10^6$	$\log K_a$	$\sqrt{\mu}$
0.0001	1093.6	4.66	1.000	4.038	3.606	6.433	$\bar{6}.8084$	0.02294
0.0002	977.11	4.47	1.000	3.872	3.588	7.434	$\bar{6}.8712$	0.03038
0.0003	923.03	4.39	1.000	3.332	3.523	7.004	$\bar{6}.8454$	0.03616
0.0005	837.15	4.26	1.000	3.430	3.535	7.586	6.8800	0.04345
0.0010	745.51	4.12	1.000	3.045	3.484	7.193	$\bar{6}.8569$	0.05665
0.0015	690.59	4.01	1.000	3.148	3.498	7.974	$\bar{6}.9017$	0.06508
0.0020	663.70	3.97	1.001	2.778	3.444	7.184	$\bar{6}.8564$	0.07346
0.0030	613.68	3.84	1.001	2.876	3.458	5.467	6.7378	0.08475
0.0050	568.71	3.75	1.003	2.786	3.445	3.524	6.5470	0.1032
0.0100	493.95	3.62	1.011	4.159	3.618	2.023	6.3060	0.1324

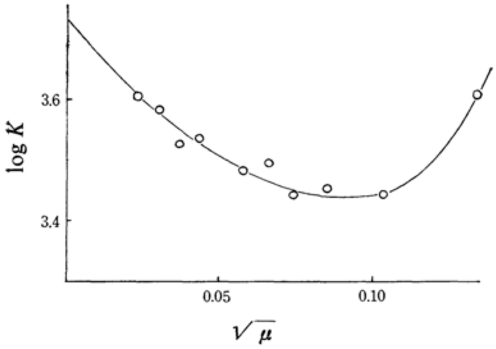

Fig. 2. The plottings of the formation constants of the ion-pair, $[Al(H_2O)_6]$-SO_4^+, in the potassium aluminum(III) alum solution vs. the square root of the ionic strength at 25°C.

In addition, the thermodynamic acid dissociation constant at 25°C was evaluated as $pK_a=4.9$ in the same manner as in the previous paper.[1)]

Discussion

The values of the formation constant of the ion-pair, $[Al(H_2O)_6]SO_4^+$, and of the acid dissociation constant of $[Al(H_2O)_6]^{3+}$ obtained in the present study are summarized in Table II, together with the corresponding values concerning $[Cr(H_2O)_6]SO_4^+$ and $[Cr(H_2O)_6]^{3+}$ obtained in the preceding paper.[1)]

TABLE II. THE FORMATION CONSTANTS OF THE ION-PAIRS, $[Cr(H_2O)_6]SO_4^+$, AND $[Al(H_2O)_6]SO_4^+$ AND THE ACID DISSOCIATION CONSTANTS OF $[Cr(H_2O)_6]^{3+}$, AND $[Al(H_2O)_6]^{3+}$ IONS AT $\mu=0$ AND 25°C

	K	pK_a
$[Cr(H_2O)_6]^{3+}$	6.3×10^4	3.95
$[Al(H_2O)_6]^{3+}$	5.4×10^3	4.9

As Table II shows, both the formation constant of the ion-pair and the acid dissociation constant are a little larger in a chromium(III) aquo complex than in an aluminum(III) aquo complex. This can be explained as follows: in a chromium(III) aquo complex, the hydrogen atom in an aquo ligand is made more positive because the stronger inductive effect of chromium attracts the electron cloud from the ligand; consequently, the acid dissociation becomes easier, and the hydrogen bonding of an aquo ligand with a sulfate ion becomes a little stronger than in an aluminum(III) aquo complex.

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