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Formation Constants of Aluminum(III)-Maleate Complexes Determined by Potentiometric Titration

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Complex formation constants for the complexation of Al^{3+} with maleate ion have been determined by potentiometric titration. Limiting values of $(3 \pm 1) \times 10^5$ and $(2 \pm 1) \times 10^3$ are obtained for K_1 and K_2, respectively, at a temperature of 25 °C. Maleate behaves as a bidentate ligand, which is consistent with its behavior toward other metal(III) ions.

Introduction

There is considerable interest in the effect of carboxylic acids on aluminum speciation in soils and aquatic media. Complex formation constants for Al^{3+} with many carboxylic acids which function as monodentate ligands can be found in the literature (*1-4*). For the dicarboxylic acids, which potentially function as bidentate ligands, only the complex formation constants for oxalic acid have been published (*5*, *6*). By contrast, complex formation constants have been determined for several diphenols and hydroxybenzoic acids (*7-9*). In this paper, complex formation constants, determined by potentiometric titration, are reported for Al^{3+}-maleate.

Experimental Section

Stock solutions were prepared using distilled, CO_2-free water as follows: sodium hydroxide (Fischer, 98.3% by mass, certified ACS), ~1 M; perchloric acid (Fischer, 70% by mass, reagent ACS), 1.00 M; aluminum perchlorate nonahydrate (Aldrich, 98% by mass), 0.100 M; and maleic acid (Aldrich, 99% by mass), 0.100 M. Potassium hydrogen phthalate (Fisher, 99.95-100.05% by mass, certified ACS) was used to standardize the sodium hydroxide. On the basis of three replicate measurements, the concentration was found to be 0.938 ± 0.005 mol L^{-1}. Using distilled, CO_2-free water, 12 solutions, each with a volume of 50.0 mL, were prepared from the stock solutions (Table I). Each solution was titrated with 0.0999 ± 0.0007 mol L^{-1} sodium hydroxide, prepared from stock sodium hydroxide and standardized with potassium hydrogen phthalate, potentiometrically by means of a Fisher Accumet 750 ion analyzer (relative accuracy, ±0.001 pH, ±0.2 °C; stability, ±0.0025 pH/24 h, ±0.2 °C/24 h), equipped with an automatic temperature compensator, a pH electrode, and a double junction calomel reference electrode. The electrodes were calibrated using buffer solutions of pH 4.00 ± 0.02, 7.00 ± 0.02, and 10.00 ± 0.02 (Fisher certified).

Table I. Compositions of Titrated Solutions

soln	perchloric acid concn (mol L)	aluminum(III) concn (mol L)	maleic acid concn (mol L)
1	1.00×10^{-2}		
2	1.00×10^{-2}	5.00×10^{-3}	
3	1.00×10^{-2}		1.00×10^{-3}
4	1.00×10^{-2}	5.00×10^{-3}	1.00×10^{-3}
5	1.00×10^{-2}		2.50×10^{-3}
6	1.00×10^{-2}	5.00×10^{-3}	2.50×10^{-3}
7	1.00×10^{-2}		5.00×10^{-3}
8	1.00×10^{-2}	5.00×10^{-3}	5.00×10^{-3}
9	1.00×10^{-2}		0.0125
10	1.00×10^{-2}	5.00×10^{-3}	0.0125
11	1.00×10^{-2}		0.0250
12	1.00×10^{-2}	5.00×10^{-3}	0.0250

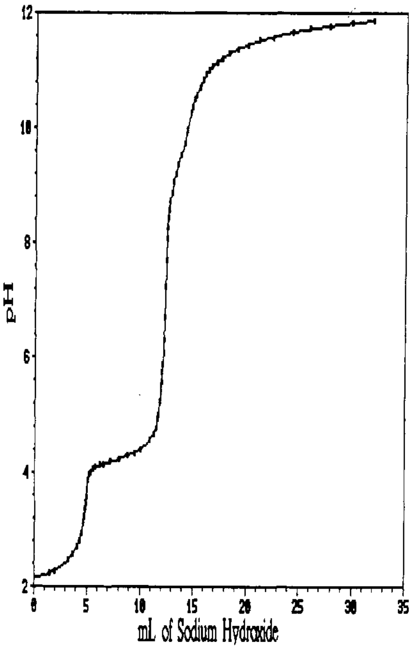

Figure 1. Potentiometric titration curve for solution 2 of Table I.

Results and Discussion

The titration curve for the mixture of perchloric acid and aluminum(III) is shown in Figure 1. In order to obtain the experimental points in the pH range from 4 to 9, it was necessary to wait for as long as 5 to even 15 min after the addition of each increment of sodium hydroxide, until the meter reading stabilized. The buffer region in the pH range of 4-5 corresponds to the sequential addition of one, two, and three hydroxide ions to each Al^{3+} ion. The cloudy solution which forms in this region shows that colloidal aluminum trihydroxide is being formed. The kinetics is slow, because the mechanism of formation involves several intermediate

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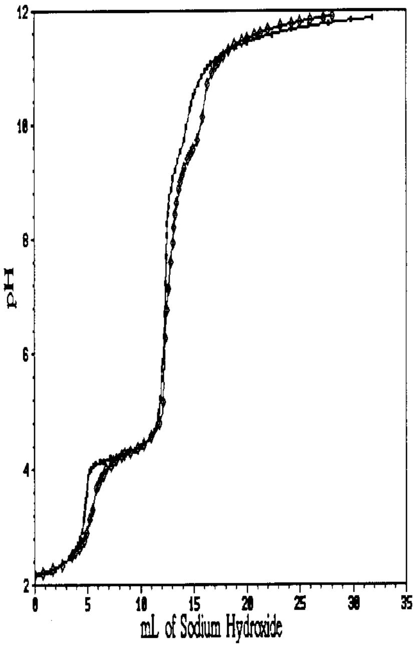

Figure 2. Overlaid potentiometric titration curves for solutions 2 and 4 of Table I.

species (*6*). As the pH increases beyond 5, trihydroxide is converted to $Al(OH)_4^-$.

If a ligand forms only weak complexes with Al^{3+}, then the presence of the organic ligand simply shifts the above titration curve along the volume axis (*6*). If a ligand forms strong complexes with Al^{3+}, the above titration curve will be strongly perturbed (*6*). In the latter case, complex formation constants may be determined easily using the Calvin–Bjerrum method. Analogous to the procedure followed in ref 6, solutions with total ligand to total metal ratios of 0.2, 0.5, 1, 2.5, and 5 were titrated with 0.0999 ± 0.0007 mol L^{-1} sodium hydroxide. It is observed that the titration curve for Al^{3+} is significantly perturbed even at the smallest ratio (Figure 2). This figure shows that there are two regions of perturbation, one in the pH range 2.4–6.0 and the other in the pH range 6.8–11.6.

In principle, the first formation constant can be obtained by analyzing the solution pairs 7–8, 9–10, and 11–12, and the second formation constant can be obtained by analyzing the solution pairs 9–10 and 11–12. The digital titration data for these six solutions are tabulated in Table II. Potentially, maleic acid can be either a monodentate ligand or a bidentate ligand. If it is monodentate, then protonized complexes will form in solution. The complex formation equilibria which can occur are the following:

$$Al(H_2O)_{7-x}(LH)_{x-1}{}^{4-x} + H_2L \rightleftarrows Al(H_2O)_{6-x}(LH)_x{}^{3-x} + H_3O^+ \quad (1)$$

$$Al(H_2O)_{7-x}(LH)_{x-1}{}^{4-x} + HL^- \rightleftarrows Al(H_2O)_{6-x}(LH)_x{}^{3-x} + H_2O \quad (2)$$

The mean number of protons split off, z, is given by

$$z = \frac{\sum_1^x ax[Al(H_2O)_{6-x}(LH)_x{}^{3-x}]}{[Al(H_2O)_6{}^{3+}] + \sum_1^x [Al(H_2O)_{6-x}(LH)_x{}^{3-x}]} = \frac{\Delta_{OH}}{C_{Al}} \quad (3)$$

If maleic acid is bidentate, then the following complex formation equilibria can occur:

$$Al(H_2O)_{8-2x}L_{x-1}{}^{5-2x} + H_2L \rightleftarrows Al(H_2O)_{6-2x}L_x{}^{3-2x} + 2H_3O^+ \quad (4)$$

$$Al(H_2O)_{8-2x}L_{x-1}{}^{(5-2x)} + HL^- \rightleftarrows Al(H_2O)_{6-2x}L_x{}^{(3-2x)} + H_3O^+ + H_2O \quad (5)$$

Now the mean number of protons split off, z, is given by

$$z = \frac{\sum_1^x ax[AlL(H_2O)_{6-x}L_x{}^{3-2x}]}{[Al(H_2O)_6{}^{3+}] + \sum_1^x [Al(H_2O)_{6-x}L_x{}^{3-2x}]} = \frac{\Delta_{OH}}{C_{Al}} \quad (6)$$

In both eqs 3 and 6, Δ_{OH} is the difference of the concentration of the added sodium hydroxide to obtain equal pH values of the solution with ligand and perchloric acid and the solution with all three reagents and C_{Al} is the total aluminum concentration. If the complex formation equilibria can be described exclusively by eq 4, then $a = 2$. If the complex formation equilibria can be described exclusively by either eq 1 or eq 5, then $a = 1$. If the complex formation equilibria can be described exclusively by eq 2, then $a = 0$. Because K_{a1} for maleic acid is large, pK_{a1} = 1.910 (*10*); either eqs 1 and 2 or eqs 4 and 5 must be considered. If maleic acid is monodentate, then "*a*" will be a constant between 0 and 1 for the first stepwise formation process. If maleic acid is bidentate, then "*a*" will be a constant between 1 and 2 for the first stepwise formation process. In either case, "*a*" must be determined experimentally. At each pH value, z is calculated using the following equation:

$$z = \frac{\Delta_{OH}}{C_{Al}} = \frac{(V'''-V'')M}{V_0 C_{Al}} \quad (7)$$

where M is the concentration of the titrant (0.0999 mol L^{-1}), V_0 is the initial volume of the titrand (50.0 mL), V'' is the volume of titrant needed to reach the pH value when the solution containing perchloric acid and the ligand is titrated, and V''' is the volume of titrant needed to reach the pH value when the solution containing all three reagents is titrated. Formation curves for the complexes are obtained by plotting z versus pH. These curves are shown in Figures 3–5 for ligand concentrations of 5.00 × 10^{-3}, 0.0125, and 0.0250 M, respectively.

The formation curve obtained when a ligand concentration of 0.0250 M is used shows two breaks, one at z = 1.34 and the second at z = 2.67. The first break corresponds to a solution in which the aluminum exists almost entirely in the form AlL^+. Thus, "*a*" in eq 6 has a value of 1.34. The seocnd break corresponds to a solution in which the aluminum exists almost entirely in the form AlL_2^-. In this case, z should be equal to $2a$. The observed value, 2.67, is in good agreement with $2a$.

The first formation constant can be calculated from the following equation:

$$K_1 = \frac{[AlL^+]}{[Al^{+3}]C_L\alpha_{L^{2-}}}\frac{f_{AlL^+}}{f_{Al^{+3}}f_{L^{2-}}} \quad (8)$$

where C_L is the total concentration of free ligand, $\alpha_{L^{2-}}$ is the fraction of unprotonated ligand, and the f's are activity coefficients. The value should be calculated for conditions where both AlL^+ and Al^{3+} are present in analytic amounts; thus, K_1 should preferentially be calculated at z = 0.670. The

Table II. Titration Data for Solutions 7–12 (V_7–V_{12} Are the Volumes (mL) for Solutions 7–12)

pH	V_7	V_8	V_9	V_{10}	V_{11}	V_{12}
2.30	3.62	1.13	5.52	3.31	10.04	6.58
2.35	4.08	2.50	6.32	4.43	11.00	7.98
2.40	4.59	3.15	6.90	5.50	11.87	90.22
2.45	5.00	3.89	7.42	6.33	12.41	10.16
2.50	5.26	4.41	7.84	7.02	13.04	11.26
2.55	5.55	4.91	8.24	7.64	13.52	12.16
2.60	5.75	5.32	8.58	8.24	13.97	12.79
2.65	5.95	5.68	8.86	8.69	14.41	13.52
2.70	6.16	6.00	9.12	9.09	14.60	14.07
2.80	6.40	6.47	9.51	90.73	15.14	15.09
2.90	6.61	6.82	9.87	10.26	15.52	15.81
3.00	6.80	7.12	10.12	10.71	15.94	16.49
3.10	6.91	7.36	10.33	11.08	16.23	17.09
3.20	7.00	7.64	10.48	11.41	16.44	17.56
3.30	7.12	7.80	10.58	11.75	16.61	17.98
3.40	7.13	8.02	10.70	12.05	16.78	18.32
3.50	7.19	8.26	10.80	12.32	16.90	18.52
3.60	7.24	8.51	10.84	12.55	17.03	18.91
3.70	7.30	8.79	10.89	12.83	17.07	19.22
3.80	7.32	9.09	10.93	13.06	17.15	19.47
3.90	7.34	9.41	10.97	13.31	17.20	19.72
4.00	7.36	9.76	11.02	13.54	17.24	19.89
4.10	7.38	10.09	11.04	13.81	17.28	20.11
4.20	7.40	10.46	11.11	14.04	17.40	20.41
4.30	7.41	10.83	11.16	14.29	17.49	20.57
4.40	7.43	11.27	11.19	14.54	17.57	20.92
4.50	7.47	11.78	11.24	14.82	17.65	21.00
4.60	7.51	12.38	11.28	15.18	17.74	21.42
4.70	7.55	12.96	11.31	15.64	17.90	21.83
4.80	7.62	13.37	11.47	16.19	18.07	22.25
4.90	7.66	13.70	11.55	16.88	18.28	22.84
5.00	7.70	13.87	11.67	17.24	18.49	23.37
5.10	7.74	14.04	11.73	17.65	18.79	23.90
5.20	7.81	14.16	11.99	18.06	19.18	24.61
5.30	7.89	14.27	12.15	18.34	19.55	25.26
5.40	7.97	14.39	12.38	18.64	20.04	25.86
5.50	8.12	14.50	12.64	18.97	20.66	26.57
5.60	8.25	14.61	12.96	19.26	21.21	27.22
5.70	8.37	14.73	13.28	19.60	21.82	28.05
5.80	8.50	14.84	13.61	19.98	22.50	28.76
5.90	8.65	14.98	13.93	20.29	23.24	29.24
6.00	8.80	15.10	14.32	20.67	23.85	30.19
6.10	8.95	15.21	14.67	21.04	24.65	31.72
6.20	9.07	15.33	15.00	21.36	25.33	32.32
6.30	9.18	15.44	15.38	21.70	25.82	33.50
6.40	9.31	15.59	15.67	22.04	26.44	34.04
6.50	9.43	15.70	15.93	22.28	26.99	34.45
6.60	9.52	15.81	16.14	22.57	27.36	34.81
6.70	9.58	15.96	16.40	22.77	27.79	35.16
6.80	9.69	16.07	16.59	22.94	28.15	35.40
6.90	9.47	16.13	16.74	23.14	28.46	35.64
7.00	9.78	16.24	16.85	23.29	28.65	35.87
7.10	9.80	16.33	16.93	23.43	28.83	36.05
7.20	9.80	16.41	17.04	23.58	29.01	36.28
7.20	9.80	16.41	17.04	23.58	29.01	36.28
7.40	9.83	16.58	17.19	23.86	29.26	36.47
7.50	9.85	16.70	17.23	23.95	29.39	36.64
7.60	9.85	16.75	17.26	24.07	29.51	36.77
7.70	9.87	16.81	17.30	24.15	29.57	36.88
7.80	9.87	16.87	17.30	24.24	29.63	36.99
7.90	9.90	16.93	17.34	24.33	29.63	36.99
8.00	9.90	17.01	17.34	24.43	29.63	36.99
8.10	9.92	17.07	17.34	24.46	29.63	37.06
8.20	9.92	17.13	17.34	24.55	29.69	37.17
8.30	9.94	17.21	17.34	24.63	29.69	37.25
8.40	9.96	17.32	17.38	24.69	29.69	37.33
8.50	9.96	17.36	17.38	24.80	29.75	37.40
8.60	9.96	17.43	17.38	24.88	29.75	37.48
8.70	9.99	17.51	17.38	24.98	29.75	37.62
8.80	9.99	17.62	17.38	25.04	29.75	37.70
8.90	9.99	17.73	17.42	25.18	29.75	37.85
9.00	10.01	17.91	17.42	25.30	29.75	38.00
9.10	10.01	18.05	17.42	25.51	29.80	38.19
9.20	10.03	18.23	17.45	25.64	29.80	38.31
9.30	10.03	18.45	17.45	25.98	29.80	38.56
9.40	10.05	18.70	17.45	26.16	29.87	38.86
9.50	10.05	18.99	17.49	26.38	29.87	39.12
9.60	10.07	19.28	17.49	26.68	29.93	39.43
9.70	10.09	19.54	17.49	26.95	29.93	39.68
9.80	10.09	19.75	17.52	27.18	29.93	39.86
9.90	10.12	20.01	17.56	27.34	30.00	40.08
10.00	10.2	20.12	17.60	27.55	30.00	40.24
10.10	10.14	20.19	17.60	27.63	30.06	40.36
10.20	10.18	20.30	17.64	27.77	30.13	40.49
10.30	10.21	20.37	17.68	27.92	30.19	40.61
10.40	10.25	20.51	17.72	28.04	30.26	40.78
10.50	10.34	20.62	17.84	28.17	30.32	40.93
10.60	10.43	20.77	17.89	28.34	30.46	41.11
10.70	10.52	20.91	17.96	28.52	30.59	41.36

concentrations of $\mathrm{AlL^+}$ and $\mathrm{Al^{3+}}$ are calculated using eq 6 with $x = 1$ and material balance for aluminum. C_L is calculated using material balance for the ligand. The fraction of L^{2-} is calculated using the pH value at the chosen z and the acid dissociation constants of maleic acid (*8*). Notice that the calculation assumes that the amount of uncomplexed aluminum in the form of dimers, the $\mathrm{Al_{13}}$ polycation, or $\mathrm{Al_{13}}$ aggregates is negligible. All the published determinations of this type have involved the same assumption. As for those results, the complex formation constants will be only approximate. This same assumption allows the concentrations of all ions in the solution to be determined, and thus the ionic strength of the solution can be calculated. The activity coefficients are determined by interpolation from the values reported in Table 6-1 of ref *9*.

The second formation constant can be calculated from the equation

$$K_2 = \frac{[\mathrm{AlL_2}^-]}{[\mathrm{AlL^+}]C_L\alpha_{L^{2-}}}\frac{f_{\mathrm{AlL_2}^-}}{f_{\mathrm{AlL^+}}f_{L^{2-}}} \qquad (9)$$

In this case the preferred value of z is 2.00. Equation 6 now gives an equation containing two unknowns, so a second equation is needed to determine $[\mathrm{AlL_2}^-]$ and $[\mathrm{AlL^+}]$. Let y be the fraction of aluminum–ligand complex present as $\mathrm{AlL^+}$.

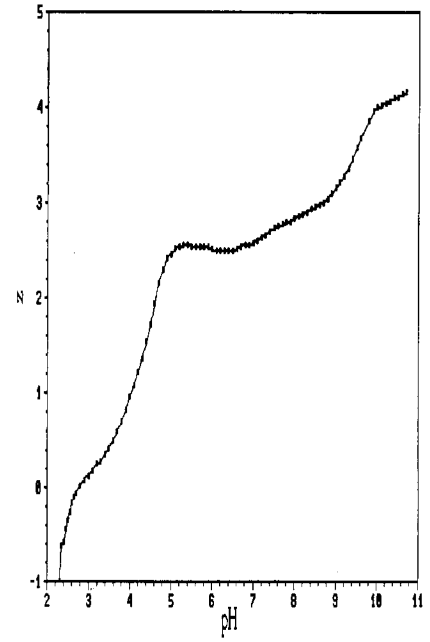

Figure 3. Formation curve determined from potentiometric titration data for solutions 7 and 8 of Table I.

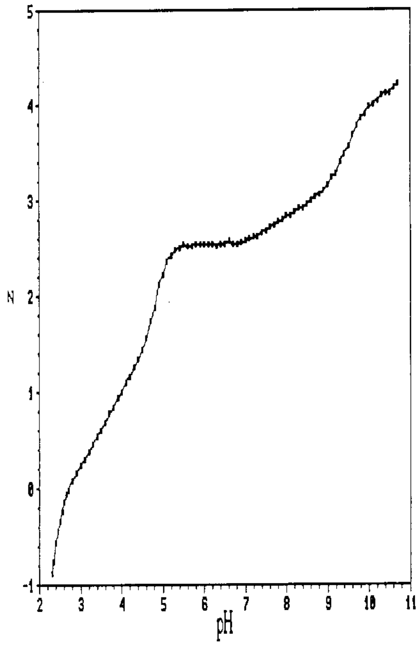

Figure 4. Formation curve determined from potentiometric titration data for solutions 9 and 10 of Table I.

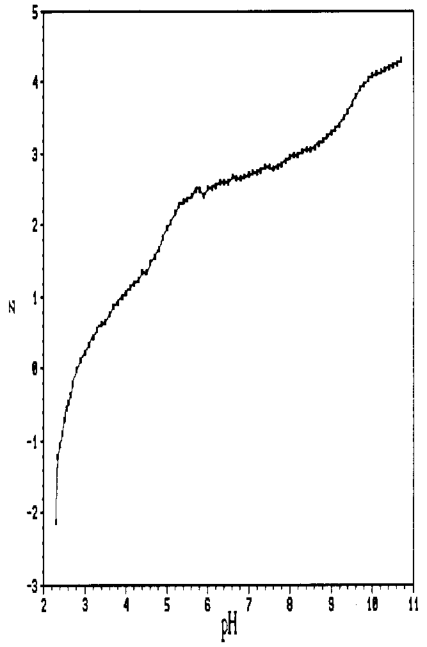

Figure 5. Formation curve determined from potentiometric titration data for solutions 11 and 12 of Table I.

Then it can be shown that

$$z = 1.34y + 2.67(1 - y) \qquad (10)$$

Solving for y allows $[AlL^+]$ to be expressed in terms of $[AlL_2^-]$. The calculation then proceeds as for that of K_1.

None of the solutions have a concentration of organic ligand sufficient for the determination of a K_3 value. Higher concentrations of ligand were not tried, for reasons that are discussed below. The results for K_1 and K_2 are shown in Table III.

The results in Table III show that when the concentration of excess ligand is small, the complex formation constant is larger than when the excess ligand concentration is larger. When the excess ligand concentration is too small (about that of the metal species), dissociation of the excess ligand becomes important. Thus, the best values in this study are the ones based on Figure 5. In going from Figure 4 conditions to Figure 5 conditions, the value of K_1 does not change much. Conservative estimates for the first and second complex formation constants are (3 ± 1) × 10^5 and (2 ± 1) × 10^3, respectively. The complex formation constants for Al^{3+}–maleate are smaller than the corresponding constants for Al^{3+}–oxalate ($K_1 = 1.3 \times 10^6$; $K_2 = 1.0 \times 10^5$) (*12*), but larger than the single complex formation constant for Al^{3+}–acetate ($\sim 10^3$) (*6*). Therefore, it seems likely that maleate is behaving as a bidentate ligand. This is in accordance with the behavior of maleate toward other terpositive ions (*3*). The values which we have determined for Al^{3+}–maleate are close to those reported for In^{3+}–maleate; $\log K_1 = 5.0$ and $\log \beta_2 = 7.1$ at 25 °C and an ionic strength of 0.2 mol L^{-1} (*3*). For 25 °C and an ionic strength of 0.2 mol L^{-1}, our values for $\log K_1$ and $\log \beta_2$ are 4.2 and 7.0, respectively.

It is necessary, but not sufficient, that valid complex formation constants will give simulated titration curves that are highly correlated with the actual titration curves. We have simulated the titration curve for the solution with a total ligand to total metal ratio of 0.2. This is one of the two curves which have not been used in the determination of the complex formation constants. Sixteen solution species have been considered in the simulation, as follows: H_3O^+, OH^-, $Al(H_2O)_6^{3+}$, $Al(H_2O)_5OH^{2+}$, $Al(H_2O)_4(OH)_2^+$, $Al(H_2O)_3(OH)_3$, $Al(H_2O)_2(OH)_4^-$, $Al_2(H_2O)_8(OH)_2^{4+}$, $Al_{13}O_4(H_2O)_{12}(OH)_{24}^{7+}$, $Al(H_2O)_4L^+$, $Al(H_2O)_3(OH)L$, $Al(H_2O)_2(OH)_2L^-$, $Al(H_2O)_2L_2^-$, H_2L, HL^-, and L^{2-}, where L = maleate ion. Acid dissociation

Table III. Complex Formation Constants (K_1 and K_2) for Al^{3+}–Maleate (Z Is the Mean Number of Protons Splitt off and C_L Is the Total Ligand Concentration)[a]

curve	z	K_1	C_L (mol L^{-1})	K_2	C_L (mol L^{-1})
Figure 3	0.707	(9.6 ± 0.4) × 10^5	(2.36 × 0.02) × 10^{-3}		
Figure 4	0.610	(4.4 ± 0.3) × 10^5	(1.02 × 0.007) × 10^{-2}		
	0.682	(4.4 × 0.3) × 10^5	(9.96 ± 0.07) × 10^{-3}		
Figure 5	0.648	(3.1 ± 0.3) × 10^5	(2.26 ± 0.02) × 10^{-2}		
	0.754	(3.1 ± 0.5) × 10^5	(2.22 × 0.02) × 10^{-2}		
Figure 4	1.88			(7.9 ± 0.4) × 10^3	(5.47 ± 0.04) × 10^{-3}
	2.13			(1.7 ± 0.09) × 10^4	(4.53 ± 0.03) × 10^{-3}
Figure 5	1.95			(2.3 ± 0.1) × 10^3	(1.77 × 0.01) × 10^{-2}
	2.04			(2.5 ± 0.1) × 10^3	(1.74 × 0.01) × 10^{-2}

[a] The precision of α (eqs 7 and 8) is limited by the precision in pH, taken to be the precision of the calibration buffers, ±0.02. The precisions of the K values are limited by the precisions of the activity coefficients. Statistical analysis of the results in ref 15 gives the uncertainty in the ionic hydration radius as ±0.08 nm. The following equation, based on the extended Debye–Huckel equation, has been derived for the uncertainty in activity coefficients:

$$\sigma_f = \frac{f(\log f)^2}{Z^2}\left[14.971\sigma_a - \frac{2.273\sigma_\mu}{\mu^{3/2}}\right]$$

where a is the ionic hydration radius (nm) and μ is the ionic strength (mol L^{-1}).

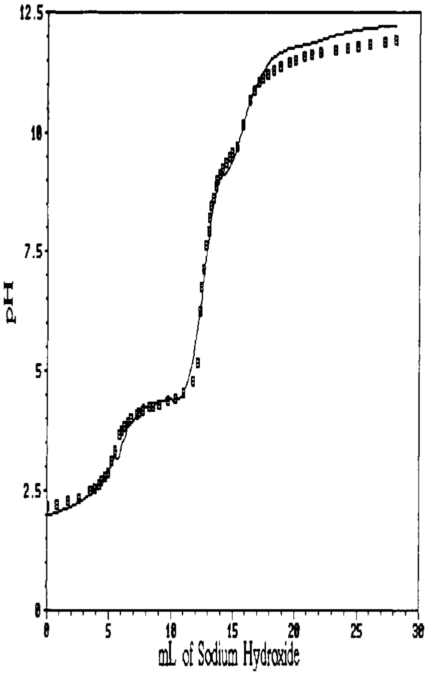

Figure 6. Potentiometric titration curve for solution 3 (symbols) and the simulated curve (solid line).

constants for aluminum ion and its hydroxo complexes and polymers have been taken from ref 13. Because the structure of $Al(H_2O)_2L_2^-$ is analogous to that of $Al(H_2O)_2(OH)_4^-$, which does not hydrolyze, it has been assumed that $Al(H_2O)_2L_2^-$ does not hydrolyze. Because the structure of $Al(H_2O)_4L^+$ is analogous to $Al(H_2O)_4(OH)_2^+$, it has been assumed that $Al(H_2O)_4L^+$ hydrolyzes in two steps with K_{a1} and K_{a2} equal to K_{a3} and K_{a4} of aluminum ion, respectively. A system of 32 simultaneous equations, 16 based on equilibrium constant expressions, material balance, and charge balance and 16 constraining each concentration to be non-negative, have been solved for the measured volumes of solution 4 using Mathcad version 3.1 (Mathsoft Inc., Cambridge, MA). As can be seen from Figure 6, there is excellent agreement between the simulation and the actual titration curve. The correlation coefficient is 0.9991.

Conclusion

It has been found that Al^{3+} complexes with maleate to form AlL^+ and AlL_2^- complexes. In^{3+}, which like Al^{3+} is in group 3A of the periodic table, has been reported to form InL^+, InL_2^-, and InL_3^{3-} complexes with maleate, with $\log K_1 = 5.0$, $\log \beta_2 = 7.1$, and $\log \beta_3 = 6.2$ at 25 °C and an ionic strength of 0.2 mol L^{-1}. It is readily apparent that the third stepwise formation constant is less than 10. No more than two stepwise formation constants have been reported for the entire series of lanthanide ion–maleate complexes, which we interpret to mean that ML_3^{3-} is not stable for this series. The Al^{3+} ion is by far the smallest metal ion, radius 0.51 Å (*14*), of all the metal ions which have previously been reported to form maleate complexes, radii 0.72–1.34 Å (*14*). It seems unlikely that AlL_3^{3-} can form in aqueous solution. Theoretical studies on the geometries of these complexes are now in progress, and will be reported elsewhere. We find it interesting that although seven-membered-ring formation is involved, molecular models show that ring formation can occur with no bond length distortion.

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