

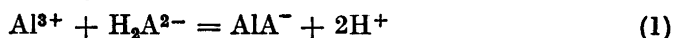
## Studies on the Stability of Aluminium Chelates of Catecholdisulphonic Acid in Aqueous Solutions

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The complex formation between the aluminium ion and catecholdisulphonic acid ( $H_4A$ ) has been investigated. The stability constant of  $AlA^-$  was determined. The effect of some added electrolytes on the stabilities of  $AlA^-$  and  $AlA_2^{5-}$  has been studied. The effects of potassium chloride and nitrate on the stability of  $AlA_2^{5-}$  were nearly equal. The effects of sodium perchlorate, chloride and nitrate were mutually nearly equal but differed considerably from the effect of potassium salts. The effect of one pentavalent ion ( $AlA_2^{5-}$ ) appeared to be nearly equal to that of five monovalent ions.

In a recent paper from this laboratory<sup>1</sup>, it was concluded that the types of the complexes formed between the aluminium ion and catecholdisulphonic acid ( $H_4A$ ) are  $AlA^-$ ,  $AlA_2^{5-}$  and  $AlA_3^{9-}$ . At that time the equilibrium



was not investigated in detail. Data concerning equilibrium (1) are now presented.

The previous potentiometric method was used and the equilibrium constant

$$K_I = [AlA^-][H^+]^2 / [Al^{3+}][H_2A^{2-}] \quad (2)$$

was calculated from the equations

$$[H_2A^{2-}] = (c - 0.5c_B - 0.5[H^+]) / (1 + 0.5K_3 / [H^+]) \quad (3)$$

$$c' = c - [H_2A^{2-}](1 + K_3 / [H^+]) \quad (4)$$

$$x = [H_2A^{2-}] / [H^+]^2 \quad (5)$$

$$K_I = c' / x(c_{Al} - c') \quad (6)$$

where  $c$ ,  $c_B$  and  $c_{Al}$  are the total molar concentrations of tiron, sodium hydroxide and aluminium perchlorate, respectively.

Table 1. Determination of constant  $K_I$  at 25°C.

Titration I:			Titration II:				Titration III:			
$\frac{c \cdot 10^3}{c_{Al} \cdot 10^3}$	$\sqrt{I}$	$pK_I$	$c \cdot 10^3$	$c_{Al} \cdot 10^3$	$\sqrt{I}$	$pK_I$	$c \cdot 10^3$	$c_{Al} \cdot 10^3$	$\sqrt{I}$	$pK_I$
1.364	0.092	2.69	4.092	1.364	0.179	2.84	14.21	4.737	0.34	3.01
1.357	0.089	2.68	4.071	1.357	0.178	2.84	13.93	4.639	0.34	3.06
1.351	0.087	2.66	4.053	1.351	0.176	2.82	13.64	4.545	0.33	3.05
1.341	0.084	2.64	4.023	1.341	0.174	2.82	13.37	4.455	0.32	3.06
1.339	0.081	2.64	4.017	1.339	0.173	2.83	13.11	4.369	0.31	3.05
1.333	0.077	2.63	3.999	1.333	0.172	2.84				

In Table 1 the results of some titrations for the determination of the constant  $K_I$  are presented. The ionic strength is calculated from  $I = \frac{1}{2} \sum z_i^2 c_i$ . The constant  $K_I$  is seen to vary in a way to be expected from the Debye-Hückel equation, which in this case has the form

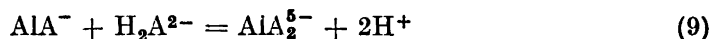
$$pK_I = pK_I^\circ + \frac{5.09 \sqrt{I}}{1 + a \sqrt{I}} - BI. \quad (7)$$

The results do not suggest the formation of the complex  $AlHA$ , a type which is found among the  $Fe(III)$  complexes of tiron<sup>2</sup>. The effect of addition of potassium chloride on the constant  $K_I$  was also investigated and the results are presented in Table 2. These results can be represented satisfactorily by the equation

$$pK_I = 2.32 + \frac{5.09 \sqrt{I}}{1 + 2.35 \sqrt{I}} + 0.06I \quad (8)$$

On comparing the values in Tables 1 and 2, one sees they differ at higher ionic strengths, as would be expected from the differences in ionic medium.

The equilibrium constant of the reaction



defined by

$$K_{II} = [AlA_2^{5-}][H^+]^2 / [AlA^-][H_2A^{2-}] \quad (10)$$

has been determined previously by Näsänen and Veivo<sup>1</sup>. They became aware that the points of both the second and the third buffer ranges of the titration curve give almost constant values for  $K_{II}$  and  $K_{III}$ , respectively,

Table 2. Constant  $K_I$  in potassium chloride solutions at 25°C.

$\sqrt{I}$	exptl. $pK_I$	eqn. (8) $pK_I$	$\sqrt{I}$	exptl. $pK_I$	eqn (8) $pK_I$
0.084	2.67	2.67	1.02	3.90	3.91
0.32	3.26	3.25	1.39	4.10	4.09

Table 3. The effect of pentavalent ions  $AlA_3^-$  on the equilibrium constant  $K_{II}$ .

Titration I. $c/c_{Al} = 3$						
$c \cdot 10^3$	$c_B/c_{Al}$	$c'/c_{Al}$	pH	$\sqrt{\frac{1}{2}\sum z_i^2 c_i}$	$\sqrt{\frac{1}{2}\sum z_i c_i}$	$pK_{II}$
3.974	2.12	1.07	4.801	0.110	0.104	8.06
3.965	2.29	1.15	5.017	0.118	0.105	8.09
3.947	2.62	1.31	5.246	0.127	0.107	8.08
3.930	2.91	1.48	5.438	0.134	0.108	8.11
3.913	3.08	1.64	5.607	0.145	0.110	8.10
3.896	3.62	1.81	5.820	0.152	0.112	8.09
3.888	3.79	1.89	5.972	0.155	0.113	8.04

Titration II. $c/c_{Al} = 3$						
$c \cdot 10^3$	$c_B/c_{Al}$	$c'/c_{Al}$	pH	$\sqrt{\frac{1}{2}\sum z_i^2 c_i}$	$\sqrt{\frac{1}{2}\sum z_i c_i}$	$pK_{II}$
12.86	2.18	1.09	4.373	0.203	0.188	7.51
12.62	2.71	1.31	4.732	0.225	0.190	7.52
12.24	3.07	1.53	4.973	0.244	0.192	7.51
12.16	3.51	1.75	5.235	0.262	0.196	7.53
12.05	3.73	1.87	5.421	0.270	0.198	7.54

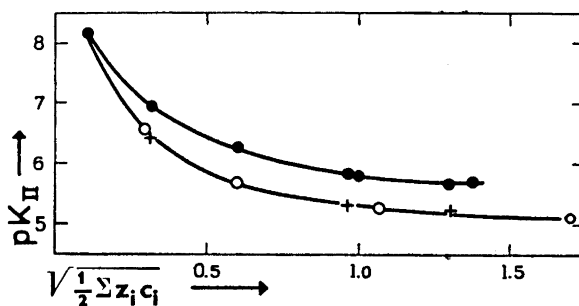
Titration III. $c/c_{Al} = 3$						
$c \cdot 10^3$	$c_B/c_{Al}$	$c'/c_{Al}$	pH	$\sqrt{\frac{1}{2}\sum z_i^2 c_i}$	$\sqrt{\frac{1}{2}\sum z_i c_i}$	$pK_{II}$
58.8	2.35	1.18	3.802	0.435	0.404	6.63
57.7	2.75	1.33	4.064	0.515	0.410	6.62
56.6	3.17	1.58	4.240	0.550	0.416	6.59
55.6	3.55	1.78	4.522	0.580	0.421	6.68

although the increase in the concentrations of the ions  $AlA_2^{5-}$  and  $AlA_3^{9-}$  during the titrations causes a considerable change in ionic strength as calculated from  $I = \frac{1}{2}\sum z_i^2 \cdot c_i$ . More complete measurements have since been carried out by the present author in the case of  $AlA_2^{5-}$ . In Table 3 some titrations with the ratio  $c/c_{Al} = 3$  but with different total concentrations are recorded. The results are in agreement with Brönsted's theory of specific ionic interaction<sup>3</sup> in the sense that one pentavalent negative ion has nearly the same effect on  $K_{II}$  as five univalent negative ions. The quantity  $\frac{1}{2}\sum z_i c_i$  also varies during the titration but much less than  $\frac{1}{2}\sum z_i^2 \cdot c_i$  and obviously the variation of  $K_{II}$  with  $\frac{1}{2}\sum z_i c_i$  is of the same order of magnitude as the accuracy reached in the case in question.

The specific ionic interaction in the case of equilibrium (9) was further investigated by means of some neutral salts. These results are presented in Table 4. From this table and from Fig. 1 one can see that sodium chloride, nitrate and perchlorate have a nearly equal effect. The effects of potassium chloride and nitrate are also mutually nearly equal but differ considerably from the effect of sodium salts. Thus these results are also in accordance with the theory of specific ionic interaction.

Table 4. The dependence of  $K_{II}$  on ionic strength in solutions of some neutral salts.

$\sqrt{\frac{1}{2}\sum z_i c_i}$	$pK_{II}$			$\sqrt{\frac{1}{2}\sum z_i c_i}$	$pK_{II}$	
	(NaClO <sub>4</sub> )	(NaCl)	(NaNO <sub>3</sub> )		(KCl)	(KNO <sub>3</sub> )
0.108	8.13	8.13	8.14	0.108	8.13	8.13
0.316	6.98	6.95	6.96	0.294	6.57	—
0.612	6.28	—	—	0.313	—	6.43
0.971	—	—	5.84	0.598	5.68	—
0.998	—	5.79	—	0.962	—	5.34
1.300	—	—	5.66	1.070	5.26	—
1.375	—	5.71	—	1.305	—	5.24
				1.700	5.14	

Fig. 1. The effect of some salts on the constant  $K_{II}$ . ● NaCl, NaNO<sub>3</sub>, NaClO<sub>4</sub>. ○ KCl, +KNO<sub>3</sub>.

Besides concentrations of negative ions, eqn. (10) also contains the concentration of hydrogen ion. The change in the activity coefficient of hydrogen ion with ionic medium is small compared with the respective changes of the activity coefficients of the high valent ions and obviously does not much influence the results.

For the calculation of the stability constants

$$k_p = [AlA_p^{(4p-3)-}] / [Al^{3+}][A^{4-}]^p, \quad (11)$$

the ionisation constants

$$K_3 = [H^+][HA^{3-}] / [H_2A^{2-}] \text{ and } K_4 = [H^+][A^{4-}] / [HA^{3-}] \quad (12)$$

Table 5. Some values of the stability constants of aluminium chelates of catecholdisulphonic acid in potassium chloride solutions at 25°C.

$\sqrt{\frac{1}{2}\sum z_i c_i}$	$\log k_1$	$\log k_2$
0.1	16.6	30.0
1.0	14.9	28.4
2.0	14.6	28.1

are needed. One obtains

$$k_1 = K_I/K_3K_4; \quad k_2 = K_IK_{II}/K_3^2K_4^2 \quad \text{and} \quad k_3 = K_IK_{II}K_{III}/K_3^3K_4^3 \quad (13)$$

The third and fourth ionisation constants have been determined recently by the present author<sup>4</sup>. The values of  $k_1$  and  $k_2$  at various ionic strength in potassium chloride solutions are given in Table 5.

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