

STABILITY CONSTANTS OF Al(III) COMPLEXES IN AQUEOUS SOLUTION OBTAINED FROM KINETIC MEASUREMENTS

WILHELM KNOCHE

Universität Bielefeld, Fakultät für Chemie, Postfach 86 40, D-4800 Bielefeld 1 (F.R.G.)

M. ARTURO LÓPEZ-QUINTELA

Max-Planck-Institut für Biophysikalische Chemie, Postfach 968, D-3400 Göttingen (F.R.G.)

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ABSTRACT

Many aluminium complexes are formed from the aquo-metal ion in the time range 0.01 to 100 s. Therefore, this process can be conveniently studied by stopped-flow techniques. Complex formation is associated with a change in the electrical conductivity of the solutions and the stability constants have been evaluated from the size of this change. Either the inner-sphere stability constant, K_i , or the overall association constant, K_a , can be determined. The following values have been obtained: for AlSO_4^+ , $\text{p}K_i = 0.78 \pm 0.10$; for $\text{AlFe}(\text{CN})_6$ and $\text{AlCo}(\text{CN})_6$, $\text{p}K_i = 0.89 \pm 0.10$; for HCOOAl^{2+} , $\text{p}K_i = -0.76 \pm 0.10$; $\text{p}K_a = -2.10 \pm 0.07$; and for $\text{H}_2\text{CitAl}^{2+}$, $\text{p}K_a = -2.62 \pm 0.10$.

INTRODUCTION

Generally, the thermodynamics of a chemical reaction are studied and the relevant equilibrium constants are determined before the kinetics of the reaction are investigated. However, there are some cases where the equilibrium data of a reaction can only be obtained by kinetic measurements. The most well-known example is the determination of the true dissociation constant of H_2CO_3 in aqueous solution. From equilibrium measurements (e.g. potentiometric or spectrophotometric) only the overall dissociation constant can be evaluated. This does not differentiate between CO_2 and H_2CO_3 . The splitting of this constant into the dissociation constant of H_2CO_3 and the hydration constant of CO_2 is possible by flow or chemical relaxation measurements [1] which yield both forward and backward rate constants for the hydration of CO_2 separately and the hydration constant as the quotient of these rate constants. The outer-sphere/inner-sphere equilibrium constants for metal complexes in solution have been determined by chemical relaxation measurements in a similar way [2].

In these examples pseudo monomolecular equilibria (the solvent molecule

is one of the reacting species) are established, which cannot be shifted by concentration changes, and the equilibrium cannot be determined since there is no possibility to differentiate between different species. However, kinetic measurements can discriminate between different complexes, if they are formed at different rates. This may be used advantageously to obtain equilibrium constants in those chemical systems where several different complexes are present simultaneously and therefore an unambiguous evaluation of spectrophotometric, conductometric, or potentiometric measurements seems to be impossible.

In this paper the stability constant is determined for the complex HCOOAl^{2+} , for which values between 3.6 and $61 \text{ dm}^3 \text{ mole}^{-1}$ are quoted at an ionic strength, I , of 1 mole dm^{-3} [3–5]. The uncertainty is caused mainly by the fact that the complex is relatively weak and that the Al^{3+} ion reacts with water forming several stoichiometrically different hydroxy complexes. In a kinetic experiment, on the other hand, the formation of the HCOOAl^{2+} inner-sphere complex can be followed conductometrically and thus the influence of this complex formation on the electrical conductance of the solution can be measured in isolation. In this way, we have determined kinetically the equilibrium constants for different aluminium complexes in aqueous solution with an accuracy which compares well with other methods. Hence the potentialities of the method can be demonstrated and it can be used further to study interactions between the Al^{3+} ion and chelating ligands.

METHODS AND MATERIALS

At room temperature many aluminium complexes are formed in the time range 10^{-2} to 100 s , and therefore these reactions can conveniently be studied by the stopped-flow technique. [Only the mononuclear hydroxy-complexes $\text{Al}(\text{OH})_n^{(3-n)+}$ are in very fast equilibrium with the solvated Al^{3+} ion since they are formed by the release of protons from the hydration shell of the metal ion.] The reactions are initiated by mixing solutions of $\text{Al}(\text{NO}_3)_3$ with solutions of a salt of the ligand, which is also completely dissociated. By adding perchloric acid, the pH value of the $\text{Al}(\text{NO}_3)_3$ solution is kept below 2.5 to avoid complications due to the presence of polynuclear hydroxy complexes [6] which are formed very slowly (aging processes). The pH of the ligand solution is adjusted by adding sodium hydroxide, so that after mixing the desired proton concentration is established.

The formation of the complexes is accompanied by a change in electrical conductance. The equivalent conductivities of the ions involved are either known or can be estimated with sufficient accuracy, and therefore it is possible to calculate the concentrations of the complexes from the change in conductance due to their formation. Therefore, in this investigation we are

predominantly interested in the amplitude of kinetic effects rather than in time constants as is usual in kinetic studies. The experiments are carried out under pseudo first-order conditions. Thus the conductance change decays exponentially with time and the conductance at the time of mixing can be extrapolated accurately.

The stopped-flow equipment is a conventional all-glass apparatus except that electrical conductance is measured instead of optical absorbance. The conductivity cell is immersed in a thermostatted bath and the temperature is kept constant at $25 \pm 0.1^\circ\text{C}$. The area of the platinum electrodes is about 10 mm^2 and all electrical connections are well shielded. The change in conductance is measured with a 40 kHz bridge as used in the pressure-jump relaxation technique, and the data are digitized and fitted to an exponential curve by a computer program. The observed changes in conductance are below 1%. Measurements are disturbed mainly by pressure variations after the stopping of flow and by concentration fluctuations caused by incomplete mixing. Conductivity detection is more sensitive to these disturbances than spectrophotometric detection. Therefore, the flow is arrested by stopping the driving syringes instead of using a stopping syringe. On stopping the flow, the driving pressure is suddenly released from the solution and the formation of gas bubbles is thereby facilitated. In order to avoid this, the solutions are degassed in the driving syringes. The effect of inhomogeneous mixing is minimised by mixing solutions of the same conductance obtained by adding inert electrolyte to the less conducting solution.

All chemicals are p.a. grade from Merck (W. Germany). Triply distilled water is used.

MEASUREMENTS

Solutions of $\text{Al}(\text{NO}_3)_3$ are mixed with solutions of the potassium salts of SO_4^{2-} , $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Co}(\text{CN})_6^{3-}$. Sodium nitrate is added to the ligand solutions in order to obtain equal conductivities of the solutions to be mixed. Complex formation between NO_3^- and Al^{3+} as well as between K^+ or Na^+ and the ligands can be neglected. Solutions of $\text{Al}(\text{NO}_3)_3$ are mixed with dilute formic acid to study the binding of a simple carboxylate ion to aluminium. Preliminary measurements of the reaction of the aluminium ion with the tridentate citrate ion are also reported.

In all experiments, exponentially decaying changes in conductance are observed, which can be described as relaxation effects with relaxation time τ and relaxation amplitude $\delta\kappa/\kappa$ (which equals the relative change in conductivity). The results are summarised in Table 1. The pH of the solutions is measured with a standard glass electrode and all concentrations given are total concentrations as calculated from the weighed-in concentrations of salts and acids.

TABLE I

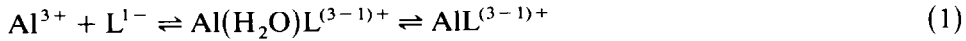
Relaxation effects observed after mixing solutions of $\text{Al}(\text{NO}_3)_3$ with solutions containing the ligands L , for $\text{L} = \text{SO}_4^{2-}$, $\text{Fe}(\text{CN})_6^{3-}$, $\text{Co}(\text{CN})_6^{3-}$, HCOO^- and citrate

All concentrations are given in 10^{-3} mole dm^{-3} and the conductivity is given in 10^{-3} ohm $^{-1}$ cm^{-1} . The concentrations and the conductivity refer to the solutions after mixing.

No.	Ligand	$[\text{Al}^{3+}]$	$[\text{L}]$	pH	$[\text{Na}^+]$	$[\text{K}^+]$	$[\text{ClO}_4^-]$	$[\text{NO}_3^-]$	κ	$10^3 \delta\kappa/\kappa$	τ (s)
1	SO_4^{2-}	2.50	3.50	2.50	1.03	7.0	10.7	10.7	2.76	- 3.0	0.130
2		5.00	5.00	2.90	2.10	10.0	18.0	18.0	2.96	- 5.7	0.067
3		2.50	3.50	2.90	0.34	7.0	8.8	8.8	1.95	- 6.0	0.066
4		1.25	1.75	2.90	0.53	3.5	5.1	5.1	1.37	- 4.0	0.068
5	$\text{Fe}(\text{CN})_6^{3-}$	2.50	2.50	2.50	2.28	7.5	1.2	1.2	3.00	- 5.0	0.206
6		5.00	5.00	2.90	5.00	15.0	20.8	20.8	3.58	- 6.6	0.084
7		1.25	1.25	2.90	0.97	3.7	5.5	5.5	1.35	- 6.0	0.094
8		2.50	2.50	2.94	2.45	7.5	10.8	10.8	2.18	- 6.3	0.093
9	$\text{Co}(\text{CN})_6^{3-}$	2.50	2.50	2.86	2.30	7.5	10.8	10.8	2.17	- 6.0	0.104
10		5.00	5.00	2.90	2.70	15.0	18.9	18.9	3.41	- 6.7	0.129
11		2.50	2.50	2.90	2.10	7.5	10.5	10.5	2.13	- 7.0	0.098
12		1.50	5.00	2.50	4.65		10.8	10.8	2.06	3.7	0.490
13	HCOO^-	1.50	5.00	2.50	5.00		11.1	11.1	2.09	4.0	0.493
14		1.50	5.00	2.70	4.20		9.6	9.6	1.57	5.0	0.378
15		5.00	5.00	2.90	14.6		30.0	30.0	3.57	5.3	0.300
16		2.50	5.00	2.90	7.40		15.4	15.4	2.06	6.5	0.315
17	Citrate	5.10	6.20	2.90	14.1		30.0	30.0	3.43	6.9	0.320
18		40.0	40.0	1.36	92.0		32.4	212	31.0	63	10.9
19		10.2	10.1	1.46	29.2		35.0	59.8	18.7	20	17.0
20		3.1	3.09	1.52	2.55		31.0	14.4	13.4	4.0	13.4

RESULTS

The general mechanism of metal-complex formation can be written (with Al^{3+} as metal ion) as



Al^{3+} and L^{1-} are the abbreviations for the solvated metal ion and ligand, respectively. $\text{Al}(\text{H}_2\text{O})\text{L}^{(3-1)+}$ is the outer-sphere complex. In the pH range studied, the concentrations of the hydrolysis products of Al^{3+} are relatively small and can be neglected, but the protonation of SO_4^{2-} and HCOO^- as well as of the citrate anion has to be taken into account.

The equilibrium concentrations of the different species involved are determined by the three stability constants

$$K_0 = \frac{[\text{Al}(\text{H}_2\text{O})\text{L}^{(3-1)+}]}{[\text{Al}^{3+}][\text{L}^{1-}]} \frac{f_{3-1}}{f_3 f_1} \quad (2)$$

$$K_i = \frac{[\text{AlL}^{(3-1)+}]}{[\text{Al}(\text{H}_2\text{O})\text{L}^{(3-1)+}]} \quad (3)$$

$$K_H = \frac{[\text{HL}^{(1-1)-}]}{[\text{H}^+][\text{L}^{1-}]} \frac{f_{1-1}}{f_1 f_1} \quad (4)$$

It is assumed that the activity coefficients, f_i , depend only on the charge of the ions and on the ionic strength I of the solution (therefore the number of charges is taken as an index of f). For their estimation the equation proposed by Davies [7]

$$-\log f_i = 0.5 z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 I \right) \quad (5)$$

is used. The proton concentration is calculated by

$$[\text{H}^+] = 10^{-\text{pH}} \times f_1^{-1} \quad (6)$$

The association constant, K_a , as determined by equilibrium measurements, is related to K_0 and K_i by

$$K_a = \frac{[\text{Al}(\text{H}_2\text{O})\text{L}^{(3-1)+}] + [\text{AlL}^{(3-1)+}]}{[\text{Al}^{3+}][\text{L}^{1-}]} \frac{f_{3-1}}{f_3 f_1} \quad (7a)$$

or

$$K_a = K_0(1 + K_i) \quad (7b)$$

The conductivity of the solution can be calculated from the concentrations and the equivalent conductivities λ_i of the charged species. Table 2 summarises the equivalent conductivities at infinite dilution of the ions involved. Where possible, these are taken from the literature; the other values are

TABLE 2

Equivalent conductivities at infinite dilution

Ion	λ^0 (cm ² ohm ⁻¹ mole ⁻¹)	
	298.2 K	293.7 K
Al ³⁺	61	55
H ⁺	350	327
Na ⁺	50.1	45.4
NO ₃ ⁻	71.5	66
K ⁺	73.5	
SO ₄ ²⁻	80	
HSO ₄ ⁻	50 ^a	
AlSO ₄ ⁺	50 ^a	
HCOO ⁻	55	
AlHCOO ²⁺	50 ^a	
Fe(CN) ₆ ³⁻	100	
Co(CN) ₆ ³⁻	100 ^a	
ClO ₄ ⁻		62
H ₂ Cit ⁻		30 ^a
AlH ₂ Cit ²⁺		30 ^a
AlHCit ⁺		30 ^a

^a Estimated values

estimated by comparing the ions with other ones of the same charge and similar size. The conductivities of the inner-sphere and outer-sphere complexes are assumed to be equal.

The total conductivity of a solution is given by

$$\kappa = \sum z_i \lambda_i^0 f_{\lambda_i} c_i \quad (8)$$

The conductivity coefficients, f_{λ_i} , are calculated by the equation of Robinson and Stokes [8], where the distance of closest approach has been estimated to be 0.5 nm and the counterions have been statistically weighed to take account of their influence on f_{λ_i} .

In order to obtain K_a from conductivity measurements, κ has been calculated as a function of K_a for all solutions listed in Table 1 by applying eqn. (4) to eqn. (8). The functions are mathematically fitted to polynomials of fourth order. As an example, Fig. 1(a) shows the plot of κ vs. K_a for solution 1. It can be seen that κ changes by no more than 5% when K_a is changed from 100 to 3000 dm³ mole⁻¹ (the region for which values of K_a are reported [9]). κ would increase by another 1% if we assume $K_a = 0$. On the other hand, the uncertainty in the calculations of κ may exceed this range since some errors accumulate; these include approximate validity of the equations for f_i

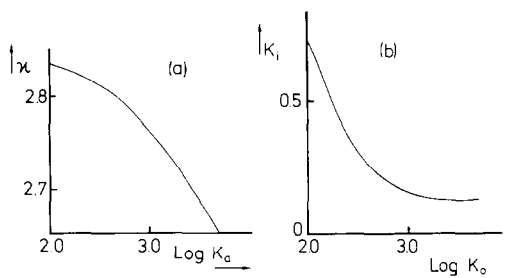


Fig. 1. (a) Conductivity, κ , calculated as a function of the stability constant, K_a , for solution 1 of Table 1. (b) Dependence of K_i on the choice of K_0 calculated from $\delta\kappa/\kappa$ for solution 1 of Table 1.

and f_{λ_i} , the complete neglect of hydrolysis products of Al^{3+} , and the error in the determination of pH.

Therefore, it is clear that these conductivity measurements are inappropriate to determine K_a for AlSO_4 or even to prove the existence of this complex. However, it is clearly indicated by the existence of the relaxation effect. On mixing $\text{Al}(\text{NO}_3)_3$ and K_2SO_4 , the equilibria between the outer-sphere complex and the free solvated ions and ligand/protonated ligand are established rapidly ($\sim 10^{-9}$ s), and the much slower formation of the inner-sphere complex is observed in the stopped-flow experiment. If we define a quotient X as

$$X = \frac{[\text{Al}(\text{H}_2\text{O})\text{SO}_4^+] + [\text{AlSO}_4^+]}{[\text{Al}^{3+}][\text{SO}_4^{2-}]} \frac{f_1}{f_3 f_2} \quad (9)$$

and time $t = 0$ as the time at which the flow is stopped, then X will change from $X = K_0$ at time $t = 0$ to $X = K_a$ at a time which is long compared with the relaxation time.

For the evaluation of the relaxation measurements, we have to assume a value of K_0 to be able to calculate $\kappa(t = 0)$. The change in conductivity during the relaxation process will then be used to obtain a value of K_i . Since the outer-sphere complex is formed mainly by electrostatic interactions, the stability constant K_0 is approximately given by Fuoss' equation [10] which yields $K_0 = 1550 \text{ dm}^3 \text{ mole}^{-1}$ for AlSO_4^+ , with $a = 0.51 \text{ nm}$ as the distance of closest approach of the metal ion and ligand in the solvent-separated complex. With $X = K_0$ (Fuoss) we calculate $\kappa = 2.73 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ which refers to $t = 0$. The experimental value is $\kappa = 2.76 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ at $t = 0$. If we estimate that Fuoss' equation leads to results for K_0 which may be wrong by a factor of two, then we obtain for the conductivity of the solution values between 2.68×10^{-3} and $2.78 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$, i.e. κ deviates by $\approx 2\%$ from the mean value. The calculation of κ is less accurate due to the uncertainties mentioned earlier and therefore the experimental value cannot be used to obtain K_0 . The influence of these uncertainties on

the evaluation of the kinetic measurements can be reduced enormously by discussing relative instead of absolute changes in conductivity. From the experimental $\delta\kappa/\kappa = 3.0 \times 10^{-3}$, we obtain the change in X caused by the formation of the inner-sphere complex, and this change is equal to $K_a - K_0 = K_0 K_i$, i.e. knowing K_0 we can obtain K_i from the experimentally determined change in conductivity. This procedure is indicated in Fig. 2. Figure 1(b) shows how much the value of K_i depends on the choice of K_0 in order to account for the approximations made by applying Fuoss' equation. If we assume again that this equation leads to results for K_0 which may be wrong by a factor of two, then K_i varies between 0.120 and 0.171 with $K_i = 0.131$ for $K_0 = K_0$ (Fuoss). From these considerations we obtain $K_i = 0.145 \pm 0.025$ and $K_a = 2200 \pm 1300 \text{ dm}^3 \text{ mole}^{-1}$. Our evaluation relies completely on the measurements of relative changes of conductivity. Therefore the stability constants depend only weakly on the errors in calculating κ , and the probable error in K_i and K_a are determined only by the uncertainty of K_0 . The measurements have been evaluated analogously for the complexes between the Al^{3+} ion and the ligands $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Co}(\text{CN})_6^{3-}$ [$K_0(\text{Fuoss}) = 2 \cdot 10^4 \text{ dm}^3 \text{ mole}^{-1}$ for $a = 0.62 \text{ nm}$]. The results are summarised in Table 3, where the equilibrium constants are given as pK's and the error is determined by the assumption that the uncertainty in K_0 (Fuoss) is within a factor of two, i.e. $\delta(\text{p}K_0) = \pm 0.3$.

In the examples discussed so far, only values of K_i have been extracted from relaxation amplitudes, but K_0 had to be assumed. This is because the inner-sphere complexes are very weak and therefore do not much influence the overall conductivity of the solutions. The situation is more favourable if stronger inner-sphere complexes are formed, as will now be shown for aluminium formate. At the pH values of experiments 12–17 to Table 1, the formic acid is only weakly dissociated. Therefore, in the stopped flow experiments, the reaction observed is mainly the reaction of the aluminium ion with formic acid forming the aluminium formate complex under the release of a proton. Due to the high mobility of protons, this reaction is accompanied by an increase of conductivity. If, for example, the conductivity is calculated for solution No. 12, it increases from 1.816×10^{-3} to

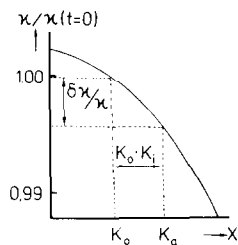


Fig. 2. Relation between relative change in conductivity and X at the relaxation process when X changes from $X = K_0$ at $t = 0$ to $X = K_a$ at $t \rightarrow \infty$.

TABLE 3

Values of pK_0 , pK_i , pK_a , ($pK = -\log K$) and κ_{cal} for solutions given in Table 1.

κ_{cal} (10^{-3} ohm $^{-1}$ cm $^{-1}$) is calculated using the data of Table 2 with the association constants obtained for each solution.

No.	pK_0	pK_i	pK_a	κ_{cal}
1	-3.19 ± 0.30^a	0.84 ± 0.08	-3.34 ± 0.30	2.73 ± 0.05
2	-3.19 ± 0.30^a	0.70 ± 0.10	-3.37 ± 0.30	2.92 ± 0.06
3	-3.19 ± 0.30^a	0.72 ± 0.08	-3.36 ± 0.30	1.93 ± 0.05
4	-3.19 ± 0.30^a	0.84 ± 0.10	-3.35 ± 0.30	1.30 ± 0.03
5	-4.30 ± 0.30^a	0.87 ± 0.10	-4.46 ± 0.30	2.85 ± 0.09
6	-4.30 ± 0.30^a	0.87 ± 0.07	-4.49 ± 0.30	3.43 ± 0.13
7	-4.30 ± 0.30^a	0.89 ± 0.07	-4.46 ± 0.30	1.30 ± 0.05
8	-4.30 ± 0.30^a	0.89 ± 0.07	-4.46 ± 0.30	2.03 ± 0.08
9	-4.30 ± 0.30^a	0.92 ± 0.04	-4.49 ± 0.30	2.10 ± 0.08
10	-4.30 ± 0.30^a	0.90 ± 0.04	-4.49 ± 0.30	3.20 ± 0.15
11	-4.30 ± 0.30^a	0.87 ± 0.06	-4.51 ± 0.30	2.03 ± 0.08
12	-1.23 ± 0.10	-0.76 ± 0.10	-2.07 ± 0.02	1.82 ± 0.01
13	-1.28 ± 0.10	-0.76 ± 0.10	-2.11 ± 0.02	1.83 ± 0.01
14	-1.28 ± 0.10	-0.76 ± 0.10	-2.11 ± 0.02	1.54 ± 0.01
15	-1.22 ± 0.10	-0.76 ± 0.10	-2.05 ± 0.02	3.27 ± 0.01
16	-1.34 ± 0.10	-0.76 ± 0.10	-2.17 ± 0.02	2.02 ± 0.01
17	-1.28 ± 0.10	-0.76 ± 0.10	-2.11 ± 0.02	3.35 ± 0.01
18			-2.76 ± 0.10	34.3 ± 0.03
19			-2.51 ± 0.10	19.3 ± 0.02
20			-2.59 ± 0.10	13.2 ± 0.01

^a Estimated value

1.860×10^{-3} ohm $^{-1}$ cm $^{-1}$ for an increase of X [eqn. (6)] from 0 to 1000 dm 3 mole $^{-1}$. Fuoss' equation gives a value of $K_0 \approx 20$ dm 3 mole $^{-1}$ for a 3:1 complex of this size, but it is known that this equation may not be reliable for carboxylates [11,12]. On the other hand, the conductivity depends only weakly on X for $X < 100$ dm 3 mole $^{-1}$ (from 1.816×10^{-3} to 1.828×10^{-3} ohm $^{-1}$ cm $^{-1}$). Thus from $\delta\kappa/\kappa = 3.7 \times 10^{-3}$ we obtain $K_a = (125 \pm 25)$ dm 3 mole $^{-1}$ based on the sole assumption that $K_0 < 50$ dm 3 mole $^{-1}$. Thus, in this case, K_a is obtained with a reasonably small error, although no value is obtained for K_0 and for K_i we only get $K_i < 2$. The reaction between aluminium and formate has been studied previously using the pressure-jump relaxation technique [13] and, from the dependence of the relaxation time on concentration, K_i has been estimated to be 5.8 ± 1.2 . Inserting this restriction yields $K_a = 130 \pm 20$ dm 3 mole $^{-1}$, and $K_0 = 19 \pm 3$ dm 3 mole $^{-1}$.

If K_i has a value between about 1 and 10 (as in the case of aluminium formate), both K_0 and K_i can be obtained from kinetic measurements. If K_i is further increased, no conclusions regarding K_i and K_0 can be made, but only K_a can be determined, as will be demonstrated using the reaction of

aluminium with the chelating ligand citrate. For the measurements reported in Table 1, aluminium nitrate is mixed with citric acid at $\text{pH} < 1.6$. In this range the acid is fully protonated ($\text{p}K_1 = 3.14$) and protons are released on complex formation. Since the pH is far below the $\text{p}K_1$, the system is not buffered (as for the formic acid system) and the relaxation process is associated with an increase in conductivity due to the high mobility of the protons. The results agree with the formation of the complex $\text{H}_2\text{CitAl}^{2+}$ from Al^{3+} and H_3Cit under release of a proton (Cit^{3-} stands for the trivalent citrate anion). Fuoss predicts $K_0 < 1$ for this reaction since the entering ligand is uncharged. Therefore, the concentration of the outer-sphere complex is small enough to be neglected when the relaxation amplitude is evaluated and we obtain the association constant $K_a = 430 \pm 130 \text{ dm}^3 \text{ mole}^{-1}$ for the reaction of Al^{3+} with H_2Cit^- as ligand. Despite the large possible error in K_0 (Fuoss) we can conclude from this value that $K_i \gg 1$ and therefore $K_a = K_0 K_i$. This means that the concentration of the outer-sphere complex is too small to be detectable and, therefore, a splitting of K_a into K_0 and K_i is not possible.

DISCUSSION

The existence of the inner-sphere complexes is unambiguously indicated by the slow relaxation process occurring after mixing solutions of aluminium nitrate with solutions containing the ligands. The relaxation amplitudes depend on the strength of the inner-sphere as well as of the outer-sphere complexes. The evaluation of the kinetic measurements yields: for AlSO_4^+ , $K_i = 0.17 \pm 0.03$, $K_a = (2.3 \pm 1.3) \times 10^3 \text{ dm}^3 \text{ mole}^{-1}$, with the estimation $K_0 = 1550 \text{ dm}^3 \text{ mole}^{-1}$; for $\text{AlFe}(\text{CN})_6$ and $\text{AlCo}(\text{CN})_6$, $K_i = 0.13 \pm 0.02$, $K_a = (3.0 \pm 1.9) \times 10^4 \text{ dm}^3 \text{ mole}^{-1}$, with the estimation $K_0 = 2 \times 10^4 \text{ dm}^3 \text{ mole}^{-1}$; for HCOOAl^{2+} , $K_i = 5.8 \pm 1.2$, $K_0 = (19 \pm 3) \text{ dm}^3 \text{ mole}^{-1}$, $K_a = (130 \pm 20) \text{ dm}^3 \text{ mole}^{-1}$; and for $\text{H}_2\text{CitAl}^{2+}$, $K_a = (430 \pm 130) \text{ dm}^3 \text{ mole}^{-1}$.

The magnitude of these constants is the factor controlling their determination. No relaxation effect is observed in dilute solutions (to which this study is restricted) if both K_0 and K_i are small, since in this case complexes are hardly formed at all. For relatively large values of the constant K_0 (as in 2:3 and 3:3 complexes), K_i can be obtained even if this latter constant is small. Both K_i and K_0 can be evaluated if K_i is larger than about unity and if K_0 is large enough to ensure that outer-sphere complexes have to be taken into account. For large values of K_i ($K_i > 10$) the concentration of the outer-sphere complex can be neglected compared to that of the inner-sphere complex, [$K_0(1 + K_i) \approx K_0 K_i$], and the overall association constant, K_a , defines the relaxation amplitude.

For $\text{AlFe}(\text{CN})_6$ and $\text{AlCo}(\text{CN})_6$ the overall association constants have been determined conductometrically to be $(1.4 \pm 0.2) \times 10^4$ [14] and $(2.0 \pm$

$0.3) \times 10^4 \text{ dm}^3 \text{ mole}^{-1}$ [15], respectively, which is in satisfactory agreement with our values. The conductometric determination is more reliable for these complexes than for aluminium sulphate, since the complexes are more stable and they themselves are uncharged. K_i has been calculated to be 0.05 ± 0.02 for $\text{AlCo}(\text{CN})_6$ [15] and 0.9 ± 0.3 for $\text{AlFe}(\text{CN})_6$ [14] by evaluating the amplitudes of pressure-jump relaxation measurements. This large difference cannot be understood since the two ligands are very similar, and only the first value agrees reasonably well with $K_i = 0.13 \pm 0.02$ obtained in this study. With our value of K_i and the values of K_a reported in refs. [14] and [15], we can calculate $K_0 = 1.2 \times 10^4 \text{ mole dm}^{-3}$ for $\text{AlFe}(\text{CN})_6$ and $K_0 = 1.8 \times 10^4 \text{ mole dm}^{-3}$ for $\text{AlCo}(\text{CN})_6$ compared with $K_0 = 2.0 \times 10^4$ calculated by Fuoss' equation. The comparison indicates that this equation gives an approximative estimate for K_0 .

Values of K_a of 3.6, 23, and $61 \text{ dm}^3 \text{ mole}^{-1}$ are reported in the literature for HCOOAl^{2+} [3–5] at an ionic strength of 1 mole dm^{-3} . A rough estimation predicts $K_a(I=0) \approx 5 K_a(I=1)$, so that the value reported by Kereichuk and Il'icheva [4] approximately agrees with our result. $K_0 = 19 \pm 3 \text{ dm}^3 \text{ mole}^{-1}$ agrees with the value calculated for the Fuoss' equation ($20 \text{ dm}^3 \text{ mole}^{-1}$ for a distance of closest approach $a = 60 \pm 10 \text{ nm}$), whereas for beryllium formate [11] and nickel acetate [12], it has been found that the outer-sphere association constants are much larger than obtained by Fuoss. So far, we cannot explain when Fuoss' equation may be applied for carboxylates.

The measurements in solutions of aluminium citrate are restricted to very acidic solutions, where the complex $\text{H}_2\text{CitAl}^{2+}$ has been detected. No experimental results have been reported previously. Even increasing the pH to only 2.0 causes stoichiometrically different complexes to appear and at pH = 3.5 three relaxation processes are observed and, therefore, at least three different complexes are formed. A careful study to evaluate these data is being undertaken and more details concerning the binding of aluminium to multidentate ligands is being obtained. It was the aim of this contribution to show that it may be possible to extract these details from kinetic measurements.

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