Solvent Effect on Stabilities of Binuclear Complexes of Oxalatopentaamminecobalt(III) with Fe(III), Al(III) & Ni(II)

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The effect of solvent dielectric constant on the stability constant (K_2) of $[(NH_3)_5CoC_2O_4M]^{n+}$ {M = Fe(III), Al(III) and Ni(II)} species has been investigated at 30 C and $I = 0.3\ M$. The dielectric constant of the medium has been varied using methanol-water solvent mixture (10-60%, v/v). The effect of dielectric constant of the medium on acid dissociation constant of $[(NH_3)_5CoC_2O_4H]^{2+}$ (K_1) and on hydrolysis constant of $Fe^{3+}(aq)$ (K_h) has been examined. The stabilities of the proton complex and the binuclear complexes of $[(NH_3)_5CoC_2O_4]^+$ increase with decrease in the dielectric constant of the medium. Log K_1, log K_2 and log K_h versus $(1/D) \times 10^2$ plots are found to be linear.

The stability constants of the binuclear species resulting from the interaction of oxalatopentaamminecobalt(III) with metal ions like Mn^{2+}, Ni^{2+}, Cu^{2+}, Fe^{3+}, Al^{3+}, Ga^{3+} and In^{3+} have been reported earlier in aqueous medium[1]. We are currently investigating the effect of solvents on the metal ion catalysed aquation of oxalatopentaamminecobalt(III) as a sequel to our earlierwork[2]. This prompted us to determine the stability constants of the binuclear species cited above and also the acid dissociation constant of $[(NH_3)_5CoC_2O_4H]^{2+}$ in different methanol-water mixtures.

Materials and Methods

$[(NH_3)_5CoC_2O_4H]\,(ClO_4)_2$ was prepared by the published method[3]. Metal perchlorate solutions were prepared and estimated as reported earlier[2]. Methanol (AnalaR, BDH) was used to prepare the solvent mixtures. $HClO_4$ (E. Merck) and $NaClO_4$ (Riedel) were used to adjust the acidity and the ionic strength of the reaction medium respectively. Absorbance measurements were made with a Beckman DU-2 spectrophotometer using matched 1 cm quartz cells. The cell block was thermostated to the desired temperature during the measurement, by circulating water from a thermostat.

Acid dissociation constant (K_1)—Oxalatopentaamminecobalt(III) solution was first neutralised with required amount of standard alkali. Requisite amounts of sodium perchlorate, perchloric acid and methanol were mixed in 25 ml volumetric flasks. Required volume of neutralised complex solution was then transferred into the reaction flasks which were allowed to attain thermal equilibrium. The absorbances of such mixtures were measured at 300 nm.

Stability constant (K_2) of binuclear complexes—Complex formation between oxalatopentaammine-cobalt(III) and the added metal ions in different methanol-water mixtures (10-60%, v/v) was studied spectrophotometrically. Requisite volume of sodium perchlorate, perchloric acid, metal perchlorate and methanol were allowed to equilibrate at 30 C in 25 ml volumetric flasks. A measured volume of a freshly prepared solution of the complex previously equilibrated at 30 C was added to the flasks and the volume made up to the mark and the solutions allowed to attain thermal equilibrium. The absorbances of such mixtures were measured at 300 nm for Ni(II) and Al(III) and at 380 nm for Fe(III) to study the formation of the $[(NH_3)_5CoC_2O_4M]^{(n+1)+}$ species.

Hydrolysis constant of Fe(III) (K_h)—The hydrolysis constant of $Fe(OH_2)_6^{3+}$ was also measured in 10-60% methanol-water (v/v) and at 35° and 40° and $I = 0.3\ M$. For hydrolysis constant measurement, requisite volumes of sodium perchlorate, perchloric acid, ferric perchlorate and methanol were mixed in 25 ml volumetric flasks and thermostated. After thermal equilibrium was attained the absorbances of these solutions were measured at 380 nm at 35° and 40°.

Results

The acid dissociation equilibrium of Hoxalatopentaamminecobalt(III) is represented by Eq. (1)

$$[(NH_3)_5CoC_2O_4H]^{2+} \underset{\rightleftharpoons}{\overset{K_1}{}} [(NH_3)_5CoC_2O_4]^+ + H^+ \qquad \ldots (1)$$
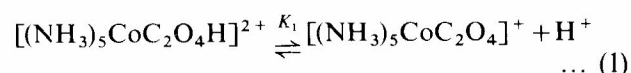
For such an equilibrium it can be shown[1] that

$$\frac{a}{d_1 - d_2} = \frac{1}{(\varepsilon_1 - \varepsilon_2)l} + \frac{K_1}{(\varepsilon_1 - \varepsilon_2)l[H^+]} \qquad \ldots (2)$$

where $a = [\text{complex}]_{\text{total}} =$ concentration of $[(NH_3)_5CoC_2O_4]^+ + [(NH_3)_5CoC_2O_4H]^{2+}$, ε_1 and ε_2 are the molar extinction coefficients of

Table 1—Dissociation Constant of $(NH_3)_5CoC_2O_4H^{2+}$ in Methanol-Water Mixtures[a] Determined Spectrophotometrically at 300 nm

MeOH (%, v/v)	Absorbance at different $[HClO_4] \times 10^2\ M$							
	0	1.0	2.0	2.6	3.0	4.0	5.0	8.0
10	0.845 (0.825)	0.460 (0.451)	0.339 (0.326)	0.308 (0.295)	0.287 (0.274)	0.254 (0.238)	0.237 (0.219)	0.204 (0.180)
20	0.910 (0.880)	0.440 (0.430)	0.308 (0.320)	0.270 (0.285)	0.250 (0.270)	0.218 (0.235)	0.201 (0.224)	0.163 (0.182)
30	0.900 (0.890)	0.378 (0.401)	0.275 (0.300)	0.238 (0.270)	0.230 (0.250)	0.195 (0.225)	0.174 (0.206)	0.147 (0.180)
40	0.900 (0.870)	0.355 (0.366)	0.247 (0.263)	0.220 (0.250)	0.202 (0.227)	0.179 (0.206)	0.160 (0.197)	0.143 (0.170)
50	1.01 (0.860)	0.360 (0.336)	0.264 (0.245)	0.235 (0.226)	0.216 (0.212)	0.194 (0.198)	0.185 (0.180)	0.161 (0.167)
60	1.120 (0.880)	0.364 (0.305)	0.268 (0.229)	0.240 (0.210)	0.235 (0.203)	0.217 (0.191)	0.208 (0.182)	0.180 (0.162)
70	0.940 (0.830)	0.250 (0.270)	0.195 (0.210)	0.185 (0.198)	0.174 (0.190)	0.166 (0.185)	0.155 (0.180)	0.145 (0.165)
80	1.00 (0.785)	0.260 (0.215)	0.204 (0.185)	0.197 (—)	0.193 (0.178)	0.185 (0.170)	0.177 (0.168)	0.169 (0.155)

(a) $I = 0.3\ M$, complex $= (5.0 \pm 0.20) \times 10^{-4}\ M$, temp $= 30°C$, absorbance values given in parentheses are at 40°C

$(NH_3)_5CoC_2O_4^+$ and $(NH_3)_5CoC_2O_4H^{2+}$ respectively, l is the cell path length in cm, $d_1 = \varepsilon_1 al$ and d_2 = absorbance due to the total complex of concentration (a) at a definite $[H^+]$. K_1 was evaluated from the least squares slope and intercept of $a/(d_1 - d_2)$ versus $1/[H^+]$ plot. The results are collected in Tables 1 and 2.

The equilibrium involving M^{n+}, $[(NH_3)_5CoC_2O_4]^+$ and $[(NH_3)_5CoC_2O_4M]^{(n+1)+}$ may be represented by Eq. (3).

$$M^{n+} + [(NH_3)_5CoC_2O_4]^+ \underset{\rightleftharpoons}{\overset{K_2}{}} [(NH_3)_5CoC_2O_4M]^{(n+1)+} \quad \dots (3)$$
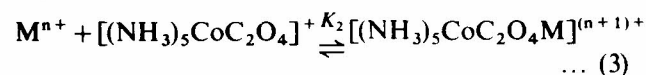
At constant ionic strength, the stability constant (K_2) of the binuclear complexes may be defined as,

$$K_2 = [(NH_3)_5CoC_2O_4M^{(n+1)+}]/([M^{n+}][(NH_3)_5CoC_2O_4]^+) \quad \dots (4)$$

The observed absorbance (d) of the solutions containing the metal ion, acid and the oxalato complex[1] may be expressed as,

$$d - \varepsilon_4[M^{n+}]l =$$

$$\frac{\varepsilon_1 K_1/[H^+] + \varepsilon_2 + \varepsilon_3 K_1 K_2[M^{n+}]/[H^+]}{1 + K_1/[H^+] + K_1 K_2[M^{n+}]/[H^+]} a.l \quad \dots (5)$$

where $a = [complex]_{total}$, ε_3 and ε_4 are the molar extinction coefficients of $(NH_3)_5CoC_2O_4M^{(n+1)+}$ and M^{n+} ions respectively and all other terms have their

Table 2—Calculated Values of Dissociation Constant (K_1) and the Extinction Coefficient Parameter $(\varepsilon_1 - \varepsilon_2)$ of the Oxalatopentaamminecobalt(III) Complex

MeOH (%, v/v)	$K_1 \times 10^3$ (M)	$(\varepsilon_1 - \varepsilon_2) \times 10^{-3}$ $(M^{-1}cm^{-1})$
10	7.11 ± 0.01 (9.28 ± 0.46)	1.35 ± 0.10 (1.45 ± 0.24)
20	6.68 ± 0.72) (6.64 ± 0.10)	1.25 ± 0.27 (1.43 ± 0.21)
30	5.48 ± 0.13 (5.60 ± 0.18)	1.56 ± 0.25 (1.45 ± 0.20)
40	4.86 ± 0.08 (4.85 ± 0.30)	1.57 ± 0.22 (1.43 ± 0.19)
50	3.70 ± 0.03 (3.93 ± 0.20)	1.73 ± 0.22 (1.41 ± 0.17)
60	2.78 ± 0.06 (3.04 ± 0.07)	1.88 ± 0.22 (1.45 ± 0.18)
70	1.78 ± 0.06 (2.17 ± 0.05)	1.57 ± 0.18 (1.32 ± 0.13)
80	1.52 ± 0.19 (1.23 ± 0.12)	1.66 ± 0.23 (1.23 ± 0.12)

Values given in parentheses are at 40°C

usual meanings as defined earlier. In terms of d (absorbance of the mixture in the absence of M^{n+}) and d' (absorbance of the mixture in the absence of complex) Eqn (5) can easily be transformed to Eq (6).

$$\frac{d-d''}{a} = \varepsilon_3 l + \frac{d'-d+d''}{a[M^{n+}]} \cdot \frac{[H^+]+K_1}{K_1K_2} \qquad \dots (6)$$

K_2 was evaluated from the least squares slope of the linear plot of $(d-d'')/a$ versus $\{(d'-d+d'')/a[M^{n+}]\} \cdot \{([H^+]+K_1)/K_1\}$ in 10-60% methanol-water medium. The relevant data are presented in Table 3. For the hydrolytic equilibrium,

$$Fe^{3+} + H_2O \underset{\rightleftharpoons}{\overset{K_h}{\longrightarrow}} FeOH^{2+} + H^+ \qquad \dots (7)$$

the hydrolysis constant is given by,

$$K_h = \frac{[FeOH^{2+}][H^+]}{[Fe^{3+}]} \qquad \dots (8)$$

Table 3—Stability Constants of Binuclear Complexes, $(NH_3)_5CoC_2O_4M^{(n+1)+}$

$[I = 0.3\ M;\ \text{temp.} = 30°C]$

Methanol (%, v/v)	$10^4[\text{Comp}]$ (M)	$10^2[M^{n+}]$ (M)	d	d''	d'	$K_2(M^{-1})$	$\varepsilon_3(M^{-1}\text{cm}^{-1})$
M = Fe³⁺; λ = 380 nm; [HClO₄] = 0.1 M							
10	7.5	0.450	0.122	0.071	0.015	1000	200
		0.675	0.178	0.115			
		0.900	0.224	0.152			
		1.000	0.260	0.185			
		1.328	0.345	0.259			
20	7.5	0.257	0.105	0.067	0.015	1500	180
		0.450	0.185	0.135			
		0.675	0.291	0.230			
		0.900	0.370	0.300			
		1.350	0.550	0.469			
30	7.5	0.225	0.163	0.132	0.006	1905	192
		0.450	0.290	0.245			
		0.675	0.440	0.380			
		0.900	0.550	0.480			
		1.350	0.840	0.755			
40	7.5	0.300	0.240	0.206	0.005	2667	175
		0.450	0.440	0.397			
		0.675	0.705	0.650			
		0.900	0.900	0.838			
		1.125	1.100	1.032			
50	5.0	0.150	0.227	0.200	0.005	4375	215
		0.225	0.305	0.270			
		0.300	0.470	0.428			
		0.375	0.530	0.480			
		0.450	0.660	0.600			
60	5.0	0.150	0.350	0.330	—	8000	215
		0.225	0.490	0.464			
		0.300	0.680	0.647			
		0.345	0.750	0.715			
		0.440	0.970	0.930			
M = Al³⁺; λ = 300 nm; [HClO₄] = 0.005 M							
10	3.577	0.36	0.304	—	0.330	90	460
		0.72	0.285				
		1.08	0.272				
		1.44	0.260				
		1.80	0.251				
20	3.577	0.36	0.270	—	0.305	110	390
		0.54	0.265				
		0.72	0.255				
		1.08	0.233				
		1.44	0.220				
		1.80	0.210				
30	3.756	0.36	0.275	—	0.314	125	240
		0.72	0.245				
		1.08	0.220				
		1.44	0.206				
		1.80	0.194				

(contd)

Table 3—Stability Constants of Binuclear Complexes, $(NH_3)_5CoC_2O_4M^{(n+1)+}$ —*Contd*

Methanol ($\%$, v/v)	10^4[Comp] (M)	10^2[M^{n+}] (M)	d	d''	d'	$K_2(M^{-1})$	$\varepsilon_3(M^{-1}cm^{-1})$
			$M = Al^{3+}$; $\lambda = 300$ nm; [HClO$_4$] = 0.005 M				
40	3.734	0.36	0.243	—	0.284	144.2	180
		0.54	0.225				
		0.72	0.214				
		1.08	0.190				
		1.44	0.175				
		1.80	0.168				
50	3.652	0.36	0.174	—	0.235	267	90
		0.54	0.161				
		0.72	0.142				
		1.08	0.121				
		1.44	0.108				
60	3.652	0.36	0.145	—	0.208	500	60
		0.54	0.130				
		0.72	0.120				
		1.08	0.100				
		1.26	0.092				
			$M = Ni^{2+}$; $\lambda = 300$ nm; [HClO$_4$] = 0.005 M				
10	3.616	0.5	0.320	—	0.345	66.6	655
		1.0	0.300				
		1.5	0.290	0.005			
		2.0	0.282	0.010			
		3.0	0.275	0.015			
		4.0	0.270	0.020			
20	3.616	0.5	0.264	—	0.290	93.3	475
		1.0	0.255	0.005			
		1.5	0.250	0.010			
		2.0	0.243	0.017			
		3.0	0.238	0.020			
		4.0	0.233	0.025			
30	3.498	0.5	0.287	0.017	0.306	125	570
		1.0	0.281	0.021			
		1.5	0.277	0.025			
		2.0	0.270	0.030			
		3.0	0.270	0.036			
		4.0	0.268	0.040			
40	3.498	1.0	0.270	0.020	0.285	150	535
		1.5	0.265	0.025			
		2.0	0.260	0.030			
		3.0	0.260	0.035			
		4.0	0.260	0.040			
50	3.498	1.0	0.235	0.015	0.255	185	460
		1.5	0.230	0.021			
		2.0	0.230	0.025			
		3.0	0.230	0.030			
		4.0	0.230	0.037			
60	3.525	1.0	0.260	0.025	0.285	233	520
		1.5	0.255	0.030			
		2.0	0.255	0.036			
		3.0	0.255	0.042			
		4.0	0.255	0.050			

Table 4—Hydrolysis Constant (K_h) of Fe^{3+} in Methanol-water Mixtures[a] Determined Spectrophotometrically at 380 nm[b]

(Absorbance at different $[HClO_4] \times 10^2 M$)

MeOH (%, v/v)	0.25	0.5	0.75	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
10	0.255	0.195	0.163	0.125	0.085	0.072	0.058	0.050	0.042	0.037	0.031
	(0.251)	(0.205)	(0.164)	(0.145)	—	(0.082)	(0.066)	(0.058)	(0.052)	(0.041)	(0.036)
20	0.422	0.330	0.258	0.230	0.170	0.140	0.117	0.100	0.095	0.075	0.064
	(0.440)	(0.354)	(0.290)	(0.257)	—	(0.150)	(0.128)	(0.110)	(0.093)	(0.080)	(0.076)
30	0.610	0.503	0.408	0.352	0.290	0.225	0.195	0.160	0.145	0.125	0.110
	(0.615)	(0.540)	(0.450)	(0.400)	(0.315)	(0.245)	(0.215)	(0.185)	(0.164)	(0.138)	(0.125)
40	0.800	0.673	0.580	0.500	0.400	0.360	0.296	0.247	0.227	0.195	0.179
	—	(0.710)	(0.620)	(0.555)	(0.460)	(0.375)	(0.310)	(0.280)	(0.250)	(0.235)	(0.200)
50		0.447	0.400	0.355	0.300	0.245	0.216	0.185	0.166	0.150	0.140
		(0.440)	(0.400)	(0.368)	(0.311)	(0.260)	(0.225)	(0.200)	(0.175)	(0.160)	(0.150)
60	—	0.560	0.500	0.455	0.395	0.350	0.310	0.265	0.245	0.230	0.185
	—	(0.580)	(0.510)	(0.485)	(0.400)	(0.370)	(0.310)	(0.290)	(0.260)	(0.245)	(0.217)

(a) $I = 0.3 M$, temp. $= 35$ C; Absorbance values given in parentheses are at 40 C
(b) $[Fe^{3+}]_T = 1.0 \times 10^{-3} M$ (10-40% MeOH) and $0.5 \times 10^{-3} M$ (50 and 60% MeOH)

Table 5—Calculated Values of the Hydrolysis Constant (K_h) and the Extinction Coefficient Parameter ($\varepsilon_1 - \varepsilon_2$) of Fe(III)

MeOH (%, v/v)	$K_h \times 10^3 M$	$(\varepsilon_1 - \varepsilon_2)^\dagger \times 10$ $M^{-2} cm^{-1}$
10	2.60	5.00
	(3.60)	(4.50)
20	3.40	7.10
	(4.10)	(7.10)
30	4.10	10.00
	(5.00)	(10.00)
40	4.60	12.50
	(6.30)	(11.11)
50	6.50	15.30
	(7.00)	(14.30)
60	6.80	18.20
	(9.30)	(16.00)

Values given in parentheses are at 40 C
†See Eqn (4)

For such an equilibrium it can easily be shown that

$$\frac{a}{d - \varepsilon_2 al} = \frac{1}{(\varepsilon_1 - \varepsilon_2)l} + \frac{H^+}{(\varepsilon_1 - \varepsilon_2)lK_h} \quad \ldots (9)$$

where $a = [Fe^{3+}] + [FeOH^{2+}]$, ε_1 and ε_2 are the molar extinction coefficients of $FeOH^{2+}$ and Fe^{3+} respectively, l is the cell path length in cm and d is the observed absorbances at a given acidity. K_h was evaluated from the least squares slope and intercept of $a/(d - \varepsilon_2 al)$ versus $[H^+]$ plot. The absorption data and the calculated equilibrium constants are presented in Tables 4 and 5 respectively.

Discussion

The acid dissociation constant (K_1) of $[(NH_3)_5CoC_2O_4H]^{2+}$ decreases smoothly from 7.0×10^{-3} to $1.5 \times 10^{-3} M$ ($I = 0.3 M$) at $30°$ when percentage of methanol in the water-methanol mixture is increased from 10 to 80 (v/v). Similar behaviour is also noted at $40°$. Values of the dielectric constant of the methanol-water mixtures were obtained from literature[4] and were used to construct the plot of $\log K_1$ versus $(1/D) \times 10^2$ which yielded linear plots with intercepts $-1.25(30°)$, $-1.15(40°)$ and slopes $= -67.3$ $(30°)$, $-66.7(40°)$, (see Fig. 1). Values of the acid dissociation constant K_1 at $D^{-1} = 0$ turns out to be 5.62×10^{-2} and $7.08 \times 10^{-2} M$ at $30°$ and $40°$ respectively. It is pertinent to note that even though the complex ion is bipositive, the $\log K_1$ versus $(1/D)$ plot is still observed to be linear (Fig. 1). Unlike the acid dissociation constant of $[(NH_3)_5CoC_2O_4H]^{2+}$, the hydrolysis constant (K_h) of Fe^{3+}(aq) increases with increase in methanol content of medium. This means that Fe^{3+}(aq) behaves as a stronger acid as the dielectric constant of the medium decreases consequent upon addition of methanol (Fig. 2). This is not unlikely as the electrostatic repulsion between the departing proton and the positive Fe^{3+} center becomes stronger as the dielectric constant of the medium decreases. Another reason for the observed variation of the $pK_h(Fe^{3+})$ may be due to replacement of some of the aquo ligands around Fe^{3+} by MeOH, which is likely to produce a steric pressure on the Fe^{3+}(aq) hydrolysis equilibria.

The stability constant (K_2) of $[(NH_3)_5CoC_2O_4M]^{(n+1)+}$ [M = Fe(III), Al(III) and Ni(II)] species are reported at $30°C$, ($I = 0.3 M$) and in methanol-water media containing 10-60% methanol (v/v). The plots of $\log K_2$ versus $(1/D) \times 10^2$ are linear
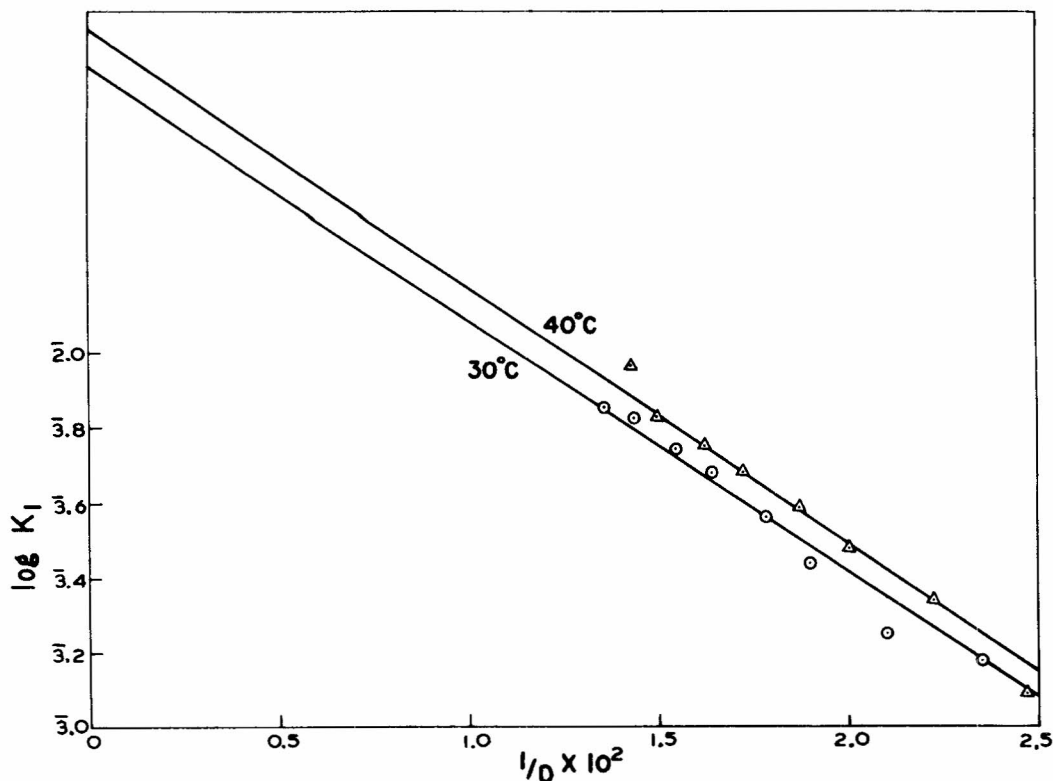
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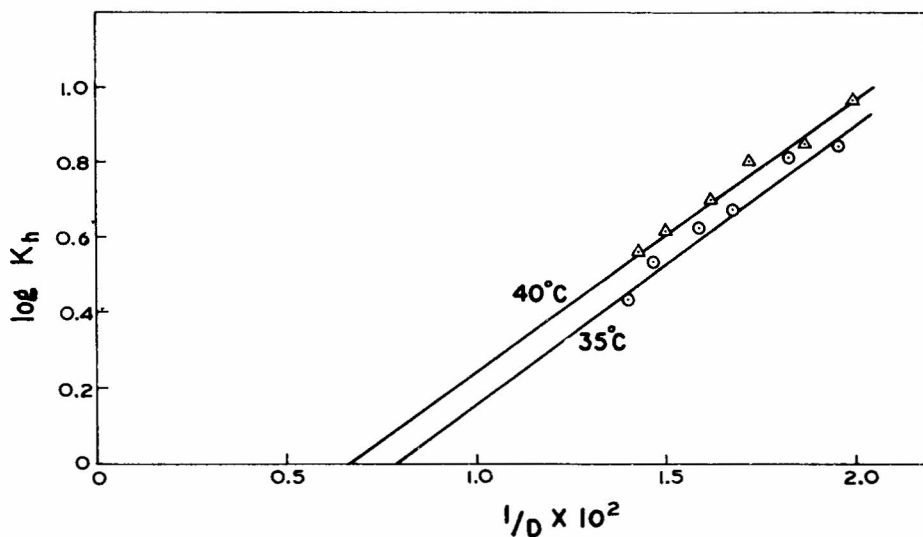Fig. 1—Plot of $\log K_1$ versus $(1/D) \times 10^2$

Fig. 2—Plot of $\log K_h$ versus $(1/D) \times 10^2$

(Fig. 3). The slope of the plot is positive and is sensitive to the charge of the metal ion. It is observed that the stability of the binuclear species increases with decreasing dielectric constant of the medium. This is perfectly in agreement with the fact that the electrostatic attraction between the unbound carboxylate group and M^{n+} ions has the major contribution to the overall free energy change associated with the formation of the binuclear complexes. The stability constants of the binuclear species at $D^{-1} = 0$ [obtained from the intercept of $\log K_2$ versus $(1/D) \times 10^2$ plot] are 7.6, 2.5 and 6.0 M^{-1}
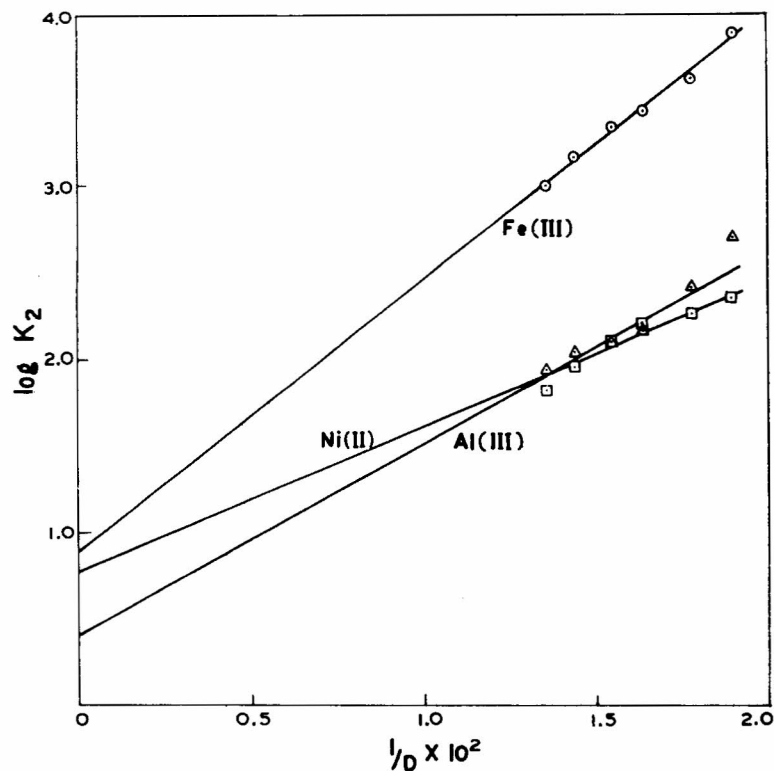
Fig. 3—Plot of $\log K_2$ versus $(1/D) \times 10^2$

for Fe(III), Al(III) and Ni(II) respectively. The values of K_2 at $D^{-1} = 0$ stand for the non-electrostatic component of the stability constant. It is observed that K_2 at $D^{-1} = 0$ for Al^{3+} is significantly lower than that for Fe^{3+} and Ni^{2+}. This is believed to be due to intense solvation of Al^{3+}.

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