Kinetics and Mechanisms of Complex Formation of Gallium(III) and Indium(III). The Reactions with 4-(2-Pyridylazo)resorcinol in Water and other Mixed Solvents

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The reactions of 4-(2-pyridylazo)resorcinol (H_2par) with Ga^{III} and In^{III} have been studied in water and aqueous mixtures with methanol, acetonitrile, dimethyl sulphoxide, and *NN*-dimethylformamide at 25.0 °C and I 0.80 mol dm^{-3} ($NaClO_4$). The equilibrium constant, K_c, for $M(Hpar)^{2+}$ formation (M = In or Ga) has been evaluated spectrophotometrically and its variation with the medium composition has been discussed with reference to different properties of the solvents. The kinetics of dissociation of $M(Hpar)^{2+}$ by H^+ have been investigated. The derived formation rate constants are discussed with reference to the mechanisms which operate for the different reacting metal species.

In aqueous solution, the rate constants for many metal complex formation reactions depend only slightly on the nature of the ligand and are similar to the corresponding quantities for solvent exchange at metal centres.[1] In such cases the reaction has been represented by a dissociative interchange (I_d) mechanism. The experimental formation rate constant, k_f, for the I_d mechanism is given by $fK_{os}k_s$ where K_{os} is the outer-sphere complex formation constant which can be computed with the Eigen–Fuoss equation,[2,3] k_s is the rate constant for the solvent exchange on the metal, and f is the probability[4] that the ligand will enter a particular co-ordination site vacated by a solvent molecule. Evaluation of both K_{os} and f is uncertain due to the approximation that must be made in order to apply the Fuoss equation.[2] A value of $f = 0.75$ is now generally accepted.[4]

For a number of years, the I_d mechanism was thought to be generally applicable to divalent, six-co-ordinate metal ions,[5] with a greater degree of uncertainty as to the intimate mechanism for tervalent metals. Recent results, however, indicate that the degree of associative behaviour is much more prevalent than previously thought,[6] and that the degree of associative behaviour, even for divalent metal ions such as V and Mn, is large.[6] Among the +3 metal ions, Fe is the most investigated case.[7] It has been pointed out in several papers that on one side the free metal ion, Fe^{3+}, shows an associative mechanism, whereas $Fe(OH)^{2+}$ appears to show a dissociative interchange pattern.

Substitution reactions of Ga^{III} and In^{III} have been restricted to a few specific ligands, largely because of the absence of conveniently monitored spectral changes. The lack of extensive data on these systems has so far prevented definite conclusions on the operative mechanisms. Much of the available data could be interpreted in an associative or dissociative mode. Two particularly conflicting conclusions have been made. Secco and co-workers,[8] on the basis of variation of rate with ligand identity, have assigned an associative mode of activation (S_N2 ion pair) to the reaction of both Ga^{3+} and $Ga(OH)^{2+}$ with a series of substituted salicylates. Yamada *et al.*,[9] on the other hand, largely on the basis of activation volumes, have concluded that the reaction of both gallium species with tropolone is dissociative in nature.

In order to try to shed more light on the mechanism of substitution reactions of tervalent metal ions we have studied the equilibrium and kinetics of the complex formation of In^{III} and Ga^{III} with 4-(2-pyridylazo)resorcinol (H_2par) in aqueous and water–organic solvent mixtures. The effect of solvent composition is expected to provide additional insight into the intimate mechanisms of these substitution reactions.[10]

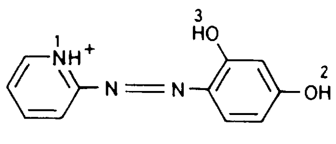
Experimental

Reagents.—All reagents were analytical grade chemicals; H_2par was supplied by E. Merck. Indium and gallium stock solutions were prepared from their nitrates, dissolved in appropriate H_2O–$HClO_4$ mixtures, and their concentrations were determined by standard ethylenediaminetetra-acetate titrations using 1-(2-pyridylazo)-2-naphthol. Aqueous solutions of H_2par were kept in the dark and were found stable for several weeks as shown by the constancy of u.v.–visible spectra.

Kinetic and equilibrium measurements were performed in aqueous and in aqueous–organic solvent mixtures of different composition using MeOH, MeCN, Me_2SO, and *NN*-dimethylformamide (dmf) of analytical grade (E. Merck). Me_2SO and dmf were purified by distillation before each series of measurements.

Measurements.—Equilibrium measurements were performed with a Cary 219 u.v.–visible spectrophotometer, whereas kinetic results were obtained from a Durrum-Gibson stopped-flow spectrophotometer, as previously described.[7] All measurements were made at 25.0 °C and at an ionic strength of 0.80 mol dm^{-3} ($NaClO_4$). Measurements were performed at pH $\leqslant$ 2.5 for In^{III} and $\leqslant$2.1 for Ga^{III}, at metal concentrations low enough to prevent metal (M) polymerization. The following equilibrium constants for $M(OH)^{2+}$ and $M(OH)_2^{+}$ formation were used:[11,12] Ga^{III}, $pK_{1H} = 2.91$, $pK_{2H} = 3.68$; In^{III}, $pK_{1H} = 3.28$, $pK_{2H} = 4.02$.

The fully protonated form of the ligand is H_3par^+, where the pK values[13] for the three indicated protons are: $pK_{1A} = 3.02$, $pK_{2A} = 5.5$, $pK_{3A} = 12.0$.



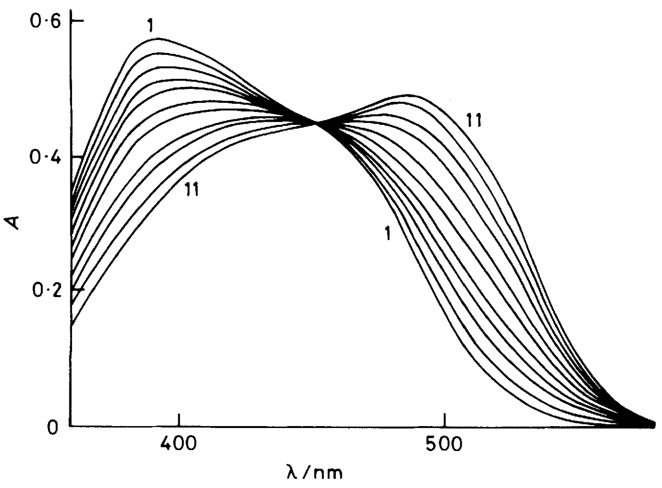


Figure 1. Absorption spectra for solutions of par, containing variable amounts of Ga^{III}, at pH 2.25 in pure water at 25.0 °C and $I = 0.80$ mol dm^{-3}, $C_{par} = 3.0 \times 10^{-5}$ mol dm^{-3}. From spectrum 1 to 11, $10^5 C_{Ga}$ as follows: 0, 1.25, 2.50, 3.75, 5.00, 7.50, 10.0, 15.0, 20.0, 30.0, and 45.0 mol dm^{-3} respectively

All these equilibrium constants (pK_H and pK_A) have been determined at $I = 0.10$ mol dm^{-3}. In order to compute rate constants and complex formation equilibrium constants, the values of pK_{1A}, pK_{1H}, and pK_{2H} have been used without correction. This approximation may be reasonable, especially for pK_{1A} which refers to the dissociation of a protonated pyridine nitrogen with no net charge variation, for which a very low variation with ionic strength is expected (the behaviour of pyridine confirms this assumption[12]). In the case of hydrolysis constants, their use allows the computation of upper limits for the derived rate constants and the expected variation with medium and ionic strength (which is here disregarded, and expected to decrease pK_H) does not invalidate the estimated upper limits. However, possible medium effects on the acid/base properties of metal and ligand are considered below.

Results and Discussion

Equilibria of Complex Formation.—Visible spectra of solutions of par in the presence of added quantities of M^{III} at constant pH show a maximum relative variation at $\lambda = 500$ nm (Figure 1) which was used to compute the equilibrium quotients for complexation. Reaction (1) represents the 1:1

$$M^{3+} + H_3par^+ \rightleftharpoons M(Hpar)^{2+} + 2H^+ \qquad (1)$$

complex formation (K_c) at pH $\leqslant$ 2.5, where protons H^1 and H^3 are displaced by the metal. Equations (2) and (3) define the

$$C_{par} = [H_3par^+] + [H_2par] + [M(Hpar)^{2+}] \qquad (2)$$

$$A = [H_3par^+]\varepsilon_{H_3par^+} + [H_2par]\varepsilon_{H_2par} + [M(Hpar)^{2+}]\varepsilon_{M(Hpar)^{2+}} \qquad (3)$$

partitioning of the ligand and the net absorbance, where C_{par} and A represent total ligand concentration and absorbance. Since there are no spectral changes for the ligand in the pH region around pK_{1A}, the molar absorptivity of H_3par^+ and H_2par must be similar: $\varepsilon_{H_3par^+} \simeq \varepsilon_{H_2par} = \varepsilon_{par}$, so that $A - C_{par}\varepsilon_{par} = [M(Hpar)^{2+}]\Delta\varepsilon$ where $\Delta\varepsilon = \varepsilon_{M(Hpar)^{2+}} - \varepsilon_{par}$.

From equations (1), (2), and (3) follow equations (4) and (5).

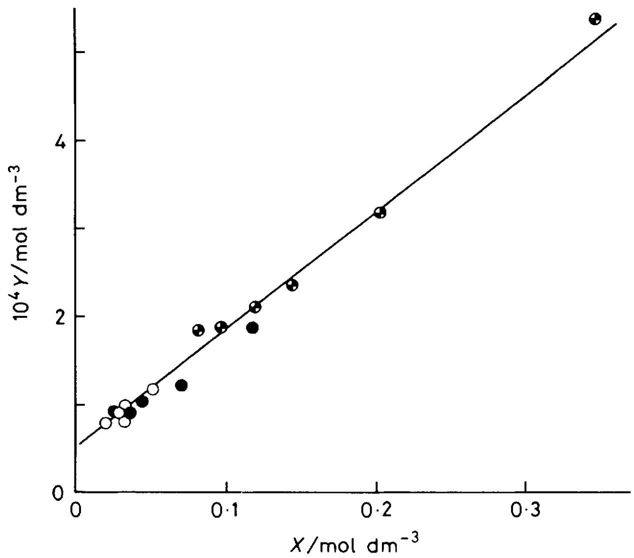


Figure 2. Variation of $Y = C_{par}/(A - C_{par}\varepsilon_{par})$ as a function of $X = ([H^+]^2/C_{In})(1 + K_{1A}[H^+]^{-1})(1 + K_{1H}[H^+]^{-1} + K_{1H}K_{2H}[H^+]^{-2})$ according to equations (4) and (5) for the complex formation of In^{III}–par in pure water; the different symbols represent different acidities

$$C_{par}/(A - C_{par}\varepsilon_{par}) = (\Delta\varepsilon)^{-1} + (\Delta\varepsilon K_{app})^{-1}(C_M - A/\Delta\varepsilon)^{-1} \qquad (4)$$

$$K_{app.} = [M(Hpar)^{2+}]/C_M C_{par} = K_c/\{[H^+]^2(1 + K_{1A}[H^+]^{-1})(1 + K_{1H}[H^+]^{-1} + K_{1H}K_{2H}[H^+]^{-2})\} \qquad (5)$$

Plots of $C_{par}/(A - C_{par}\varepsilon_{par})$ *vs.* C_M^{-1} were approximately linear for all experiments, confirming the 1:1 stoicheiometry. Final determinations of $\Delta\varepsilon$ and K_c were achieved after a series of successive approximations to account for the $A/\Delta\varepsilon$ term in equation (4).

Figure 2 shows a plot of absorbance data for the In^{III}–par reaction traced according to equations (4) and (5). From the slope of such plots, K_c values reported in Table 1 have been obtained.

Figure 3 shows the effect of the organic solvent composition on the stability of the Ga^{III} complex for different media. Similar behaviour is exhibited by In^{III}. As can be seen in Figure 3, opposite effects are displayed by MeOH–H_2O mixtures on one hand and the other water–organic solvent mixtures on the other. These differences have been observed not only for other complexation reactions but for a variety of phenomena.[14]

Several solvent properties seem to effect these results. A lowering of dielectric constant with increased x_{org} should increase the value of K_c for each solvent. This is observed only for methanol; other properties must therefore be important. Similarly, trends opposite from those predicted occur for MeOH and MeCN when compared with Gutmann's donor number,[14] and, although the relative ranking of the organic solvents is as predicted, Reichardt's E_t parameter[14] would predict virtually identical K_c values in mixtures of MeCN, Me_2SO, and dmf. All these considerations point to several terms being effective in determining the action of different media on $M(Hpar)^{2+}$ formation.

Kinetics of Complex Formation.—In order to investigate the mechanism of the formation of Ga and In complexes the rate of dissociation of each M–par complex was measured under different experimental conditions. The corresponding formation rate constants were obtained from the derived kinetic results

Table 1. Equilibrium constants, K_c, for the complex formation of Ga^{III} and In^{III} complexes with par according to equation (1), in different water–solvent mixtures: 25.0 °C, I = 0.80 mol dm^{-3}

Medium: organic solvent (v/v%)		Mole fraction [a]	K_c/mol dm^{-3}	
			Ga^{III}	In^{III}
H_2O	100	—	0.312	0.036
CH_3OH	5	0.023	0.60	0.048
	10	0.047	0.80	0.094
	20	0.100	1.15	0.111
	35	0.193	1.40	0.135
	50	0.310	1.64	0.160
CH_3CN	5	0.018	0.260	0.027
	10	0.037	0.220	0.024
	20	0.079	0.171	0.020
	35	0.156	0.149	0.015
Me_2SO	5	0.013	0.29	0.033
	10	0.027	0.26	0.030
	20	0.060	0.22	0.010
	35	0.120	0.101	0.0073
dmf	5	0.012	0.26	0.030
	10	0.025	0.22	0.022
	20	0.055	0.12	0.018
	35	0.112	0.031	0.010

[a] Of organic solvent.

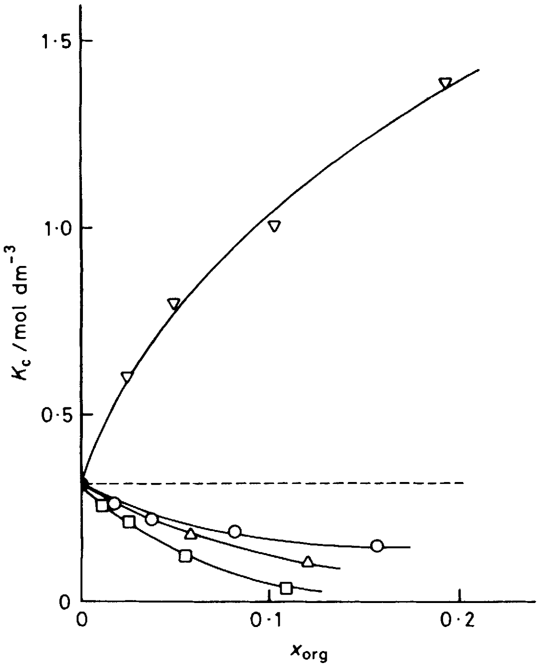


Figure 3. Variation of the equilibrium constant K_c for the formation of $Ga(HPar)^{2+}$ as a function of organic solvent mole fraction ($x_{org.}$): MeOH (▽), MeCN (○), Me_2SO (△), dmf (□)

with the aid of the equilibrium constants K_c previously obtained.

A solution containing par (C_{par} = 1.0 × 10^{-4} mol dm^{-3}) and an excess of Ga or In (C_M = 1.0 × 10^{-3} mol dm^{-3}) was brought to pH 4.0 and I = 0.80 mol dm^{-3}. Under these conditions, reaction (1) is completely displaced towards the formation of the complex. This solution was then mixed in the stopped-flow apparatus with a solution of $HClO_4$ brought to the same ionic strength so that the final acidity was within $[HClO_4]$ = (3.20—400) × 10^{-3} mol dm^{-3}. Under such conditions the complex dissociation could be easily followed by monitoring the decrease of absorbance at 500 nm. The reactions are first order with values of $k_{obs.}$ which are hydrogen-ion dependent of the form of equation (6), where, under our conditions, c is only significant

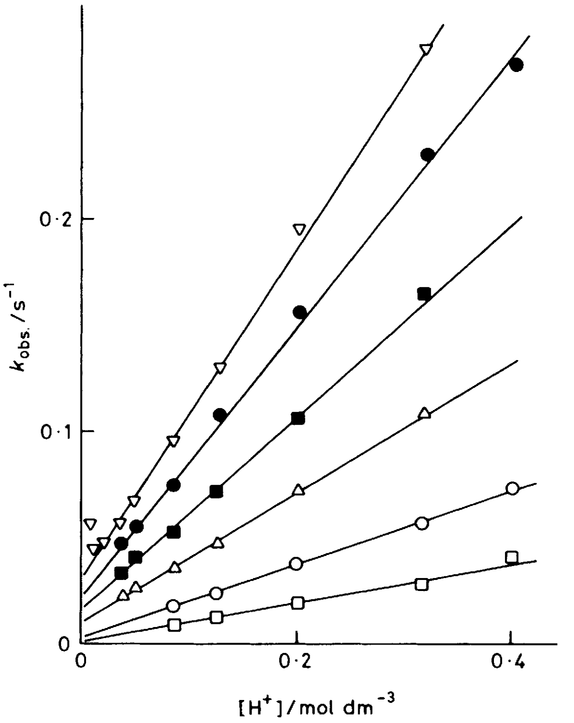


Figure 4. Variation of the observed rate constant $k_{obs.}$ for the dissociation of Ga^{III}–par complex as a function of $[H^+]$ for different MeOH–H_2O mixtures: 0 (▽), 5 (●), 10 (■), 20 (△), 35 (○), 50% (v/v) MeOH (□)

$$k_{obs.} = a + b[H^+] + c[H^+]^2 \qquad (6)$$

for the In system. Figures 4 and 5 show these different $[H^+]$ dependences. The reactions that are involved, written for complex formation, can be represented by the Scheme [steps (i)—(v)]. Under our experimental conditions the observed rate constants are essentially equal to those for the overall reverse process (7). The reaction sequence does not include interaction of $M(OH)_2{}^+$ with H_2par since its reverse reaction would give a

$$M^{3+} + H_3par^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M(Hpar)^{2+} + 2H^+ \qquad \text{(i)}$$

$$M(OH)^{2+} + H_3par^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M(Hpar)^{2+} + H^+ + H_2O \qquad \text{(ii)}$$

$$M(OH)_2{}^+ + H_3par^+ \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} M(Hpar)^{2+} + 2\,H_2O \qquad \text{(iii)}$$

$$M^{3+} + H_2par \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} M(Hpar)^{2+} + H^+ \qquad \text{(iv)}$$

$$M(OH)^{2+} + H_2par \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} M(Hpar)^{2+} + H_2O \qquad \text{(v)}$$

Scheme.

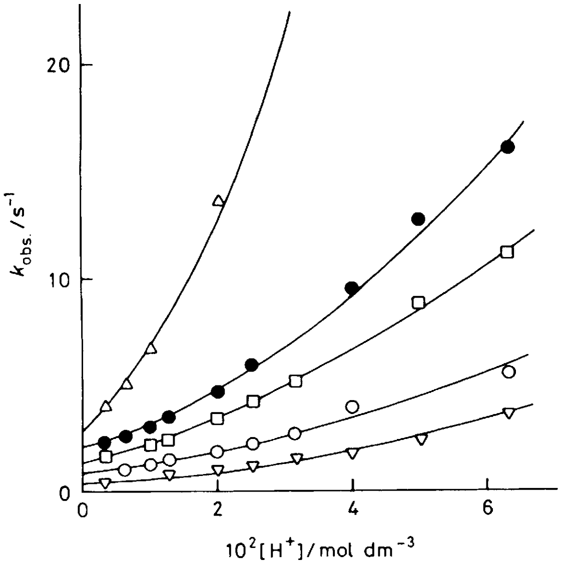


Figure 5. Varation of the observed rate constant $k_{obs.}$ for the dissociation of In^{III} par complex as a function of $[H^+]$ for different MeOH–H_2O mixtures: 100% H_2O (△); 10 (●), 20 (□), 35 (○), 50% (v/v) MeOH (▽)

$$k_{obs.} \simeq k_{rev.} = k_{-3} + k_{-5} + (k_{-2} + k_{-4})[H^+] + k_{-1}[H^+]^2 \quad (7)$$

$[H^+]^{-1}$ term in equation (7) that was not observed. Figure 6 shows an example of the linear determination of *b* and *c*, of equation (6), obtained when the intercepts *a* of Figure 5 were used in plots of $(k_{obs.} - a)/[H^+]$ *vs.* $[H^+]$, in the case of In. The empirical rate parameters thus obtained are listed in Table 2. Note that for dmf and mixtures with higher mole fractions of Me_2SO, there is no detectable contribution from the *c* term in the indium system. The small deviation from linearity seen in Figure 4 at very low acidities may be attributed to a contribution from the forward reactions of the Scheme.

We may now make the identification between the empirical parameters *a*, *b*, and *c* with the rate constants of equation (7), and introduce the appropriate equilibrium relationships for the forward reactions to obtain the expressions given below. The

$$a = k_{-3} + k_{-5} = (k_3K_{1H}K_{2H} + k_5K_{1H}K_{1A})/K_c$$

$$b = k_{-2} + k_{-4} = (k_2K_{1H} + k_4K_{1A})/K_c$$

$$c = k_{-1} = k_1/K_c$$

identical kinetic forms from steps (ii) and (iv) and steps (iii) and (v) prevent us from determining any of these values individually. However we may set upper limits for each of these rate constants by considering, in turn, the corresponding one to be negligible. The results of the analysis are given in Tables 3 and 4 along with values of k_1 for the indium reaction.

In Table 5 we have summarized formation rate constants, k_f, for reactions in water of Ga^{III} and In^{III} with a number of ligands including those derived from our data. In addition, we have listed values of K_{os} (based on an encounter distance of 5 Å) and the quotients k_f/K_{os} for comparison with fk_s (see Introduction).[2,3] As can be seen from Table 5, Ga^{3+} and H_2par species react, in water, with a value of k_4/K_{os} = 1 300 s^{-1}, to be compared with $0.75k_s$ = 570 s^{-1}.[8] For the reactions of In^{3+} with H_3par$^+$ and H_2par, values of $k_f/K_{os} = 2.4 \times 10^4$ s^{-1} and 5.0×10^4 s^{-1} should be compared with $0.75k_s = 1.5 \times 10^4$ s^{-1}.[15]

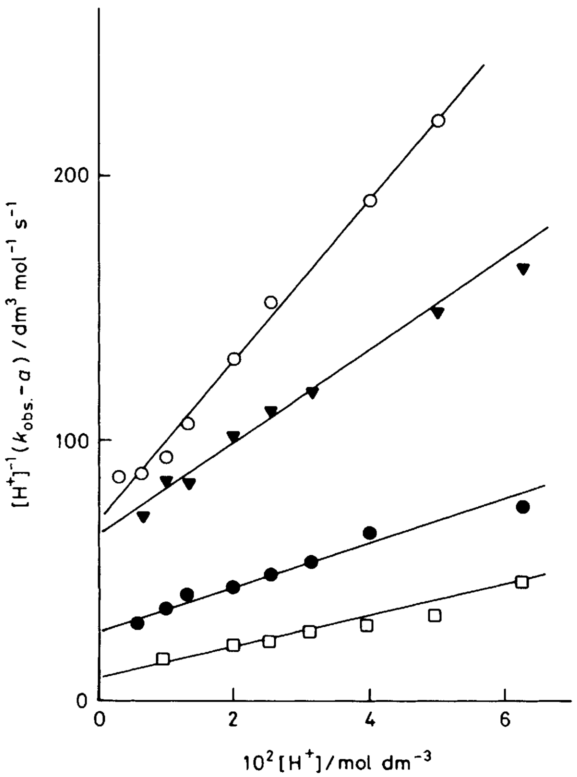


Figure 6. Variation of $(k_{obs} - a)/[H^+]$ as a function of $[H^+]$, according to equation (6), for the In^{III}–par complex dissociation in different MeOH–H_2O mixtures: 10 (○), 20 (▼), 35 (●), 50% (v/v) MeOH (□)

This agreement appears reasonably good and might seem to support an I_d mechanism based on the discussion given in the Introduction. However, if one compares the rate data of aquated Ga^{3+} and In^{3+} with other ligand species, see Table 5, a scatter of more than two orders of magnitude shows that both metal species have behaviour dependent on the nature of the ligand. The differences are much smaller for the limited data available for the hydrolysed species, for which water exchange rates are lacking. According to the Eigen–Wilkins mechanism,[2] complex formation in non-aqueous media[10] as well as in water goes through a series of steps including approach of the incoming ligand, release of a solvent molecule from the co-ordination sphere of the metal and its substitution by the ligand, and exit of the subsequent solvent molecule into the bulk solvent.

It has been observed that at low mole fraction of organic solvent ($\leqslant 0.2$ for MeOH and MeCN and $\leqslant 0.1$ for the more co-ordinating solvents dmf and Me_2SO for the conditions of this study) these co-solvents do not enter into the inner co-ordination sphere of the aquacations;[14,16] thus, the solvent effect must be considered as resulting from the different solvation energies of the prevailing media around the entering ligand molecule and around the leaving water molecule. At low mole fractions of organic component in water–solvent mixtures (x = 0.1—0.3), water structure becomes more ordered and 'stiffer'.[10] Thus, both reduced mobilities and energetic effects coupled with higher solvation (as pointed out for the different K_c values) tend to slow the exchange steps involved in a complex formation reaction.

The observed variations in rate with solvents (Tables 3 and 4) and with ligands (Table 5) cannot be rationalized on the basis of simple ligand properties such as, for example, basicity, polarizability, or nucleophilicity. Solvent composition plays an

Table 2. Values of parameters *a*, *b*, and *c* for the dissociation reaction of Ga^{III} and In^{III} complexes with par at 25.0 °C and I = 0.80 mol dm^{-3}

Medium: organic solvent (v/v %)		Ga^{III} + par		In^{III} + par		
		10^2a/ s^{-1}	$10b$/ dm^3 mol^{-1} s^{-1}	a/ s^{-1}	b/ dm^3 mol^{-1} s^{-1}	10^{-3} c/ dm^6 mol^{-2} s^{-1}
H_2O	100	2.87	7.96	2.9	260	13.2
CH_3OH	2			2.4	240	16.0
	5	2.47	6.37	2.25	270	11.0
	10	1.62	4.51	2.0	70	3.0
	20	1.12	3.03	1.3	60	1.75
	35	0.25	1.73	0.95	25	0.83
	50	0.13	0.94	0.60	10	0.58
CH_3CN	5	1.9	6.62	1.8	240	9.4
	10	1.5	5.84	1.5	240	8.0
	20	1.0	4.31	1.3	220	3.2
	35	0.50	3.00	1.0	120	3.1
Me_2SO	5	2.25	6.8	2.2	220	12
	10	1.9	5.5	1.8	220	8.0
	20	1.6	4.56	1.5	200	1.2
	35	1.25	2.76	1.2	125	—
dmf	5	1.3	8.35	1.8	350	—
	10	1.3	4.21	1.6	260	—
	20	1.3	2.17	1.2	140	—
	35	1.3	0.72	0.90	48	—

Table 3. Computed rate constants for Ga^{III}–par complex formation in different water–solvent mixtures, at 25.0 °C and I = 0.80 mol dm^{-3}

Medium: organic solvent (v/v %)		k_2/dm^3 mol^{-1} s^{-1}	$10^{-4}k_3$/dm^3 mol^{-1} s^{-1}	k_4/dm^3 mol^{-1} s^{-1}	$10^{-4}k_5$/dm^3 mol^{-1} s^{-1}
H_2O	100	$\leqslant 200$	$\leqslant 3.4$	$\leqslant 260$	$\leqslant 0.76$
CH_3OH	5	$\leqslant 310$	$\leqslant 5.7$	$\leqslant 402$	$\leqslant 1.30$
	10	$\leqslant 293$	$\leqslant 5.0$	$\leqslant 379$	$\leqslant 1.10$
	20	$\leqslant 283$	$\leqslant 5.0$	$\leqslant 367$	$\leqslant 1.10$
	35	$\leqslant 197$	$\leqslant 1.35$	$\leqslant 255$	$\leqslant 0.30$
	50	$\leqslant 283$	$\leqslant 0.8$	$\leqslant 367$	$\leqslant 0.18$
CH_3CN	5	$\leqslant 140$	$\leqslant 1.9$	$\leqslant 181$	$\leqslant 0.42$
	10	$\leqslant 105$	$\leqslant 1.3$	$\leqslant 135$	$\leqslant 0.29$
	20	$\leqslant 60$	$\leqslant 0.66$	$\leqslant 78$	$\leqslant 0.15$
	35	$\leqslant 35$	$\leqslant 0.29$	$\leqslant 46$	$\leqslant 0.064$
Me_2SO	5	$\leqslant 160$	$\leqslant 2.5$	$\leqslant 210$	$\leqslant 0.56$
	10	$\leqslant 116$	$\leqslant 1.9$	$\leqslant 150$	$\leqslant 0.42$
	20	$\leqslant 82$	$\leqslant 1.4$	$\leqslant 106$	$\leqslant 0.30$
	35	$\leqslant 23$	$\leqslant 0.49$	$\leqslant 29$	$\leqslant 0.11$
dmf	5	$\leqslant 176$	$\leqslant 1.4$	$\leqslant 228$	$\leqslant 0.29$
	10	$\leqslant 76$	$\leqslant 1.1$	$\leqslant 98$	$\leqslant 0.24$
	20	$\leqslant 21$	$\leqslant 0.60$	$\leqslant 27$	$\leqslant 0.13$
	35	$\leqslant 1.8$	$\leqslant 0.16$	$\leqslant 2.3$	$\leqslant 0.035$

important role in the complex formation mechanism with a general reduction of rates with decrease in water content for every reaction step of both metals. The reduced dielectric constant should increase the tendency for hydrolysis (increase of K_{1H} and K_{2H})[17] as well as the tendency of the proton on the pyridine nitrogen to dissociate (increase of K_{1A}). These trends have been confirmed, for example, for iron(III).[17] Thus the values listed for k_2—k_5 in Tables 3 and 4 (which were determined without correction for changes in hydrolysis) probably underestimate the relative decrease in rate with increasing organic component. The values of k_1 in Table 4 are, however, a true reflection of this effect.

The labilizing effect of OH^-, which increases the reactivity of $M(OH)^{2+}$ and $M(OH)_2{}^+$ with respect to the corresponding aquacation, is here (since k_1 is undetectably small) displayed in a more pronounced way than previously observed for other Ga^{III} reactions. For example,[18] $Ga(OH)_2{}^+$ reacts with the 3-nitrosalicylate monoanion *ca.* 15 times faster than $Ga(OH)^{2+}$

Table 4. Computed rate constants for In^{III}–par complex formation in different water–solvent mixtures, at 25.0 °C and I = 0.80 mol dm^{-3}

Medium: organic solvent (v/v %)		k_1/ dm^3 mol^{-1} s^{-1}	$10^{-4}k_2$/ dm^3 mol^{-1} s^{-1}	$10^{-6}k_3$/ dm^3 mol^{-1} s^{-1}	$10^{-4}k_4$/ dm^3 mol^{-1} s^{-1}	$10^{-5}k_5$/ dm^3 mol^{-1} s^{-1}
H_2O	100	475	$\leqslant$1.8	$\leqslant$2.1	$\leqslant$1.0	$\leqslant$2.1
CH_3OH	2	640	$\leqslant$1.8	$\leqslant$1.9	$\leqslant$1.0	$\leqslant$1.9
	5	528	$\leqslant$2.5	$\leqslant$2.2	$\leqslant$1.4	$\leqslant$2.2
	10	282	$\leqslant$1.26	$\leqslant$3.8	$\leqslant$0.69	$\leqslant$3.8
	20	194	$\leqslant$1.28	$\leqslant$2.9	$\leqslant$0.70	$\leqslant$2.9
	35	112	$\leqslant$0.65	$\leqslant$2.6	$\leqslant$0.36	$\leqslant$2.6
	50	93	$\leqslant$0.31	$\leqslant$1.9	$\leqslant$0.17	$\leqslant$1.9
CH_3CN	5	253	$\leqslant$1.20	$\leqslant$0.97	$\leqslant$0.65	$\leqslant$0.97
	10	192	$\leqslant$1.10	$\leqslant$0.72	$\leqslant$0.60	$\leqslant$0.72
	20	63	$\leqslant$0.84	$\leqslant$0.52	$\leqslant$0.46	$\leqslant$0.52
	35	46	$\leqslant$0.34	$\leqslant$0.30	$\leqslant$0.19	$\leqslant$0.30
Me_2SO	5	400	$\leqslant$1.4	$\leqslant$1.5	$\leqslant$0.76	$\leqslant$1.5
	10	240	$\leqslant$1.3	$\leqslant$1.1	$\leqslant$0.71	$\leqslant$1.1
	20	$\leqslant$12	$\leqslant$0.38	$\leqslant$0.30	$\leqslant$0.21	$\leqslant$0.30
	35	—	$\leqslant$0.175	$\leqslant$0.18	$\leqslant$0.10	$\leqslant$0.18
dmf	5	—	$\leqslant$2.0	$\leqslant$1.1	$\leqslant$1.1	$\leqslant$1.1
	10	—	$\leqslant$1.1	$\leqslant$0.71	$\leqslant$0.60	$\leqslant$0.71
	20	—	$\leqslant$0.48	$\leqslant$0.43	$\leqslant$0.26	$\leqslant$0.43
	35	—	$\leqslant$0.09	$\leqslant$0.18	$\leqslant$0.05	$\leqslant$0.18

Table 5. Kinetic parameters for the complex formation of Ga^{III} and In^{III} complexes with various ligands in water

Metal ion	Ligand[a]	k_f/dm^3 mol^{-1} s^{-1}	K_{os}/dm^3 mol^{-1}	$k_fK_{os}^{-1}$/ s^{-1}
Ga^{3+}	H_2par	$\leqslant$260	0.2	$\leqslant$1 300
	$Hsal^{-}$[b]	$\leqslant$670	5	$\leqslant$130
	$H_2semixyl^{2-}$[c]	$\leqslant$690	87	$\leqslant$8
	H_3pcv[17]	$\leqslant$80	5	$\leqslant$16
	SO_4^{2-}[d]	2×10^4	10^3	20
	Tropolone[e]	38		
	H_2O			570[f]
$Ga(OH)^{2+}$	H_3par^+	$\leqslant$200	0.02	$\leqslant 1 \times 10^4$
	H_2par	$\leqslant$7 600	0.2	$\leqslant 4 \times 10^4$
	$Hsal^{-}$[b]	$\leqslant 3.4 \times 10^4$	2	$\leqslant 1.7 \times 10^4$
	H_2sal[b]	$\leqslant$1 100	0.2	$\leqslant 3 \times 10^3$
	$H_3semixyl^{-}$[c]	$\leqslant$1 100	2	$\leqslant$550
	$H_2semixyl^{2-}$[c]	1.2×10^4	13	920
	SO_4^{2-}[d]	1.4×10^4	13	1 100
$Ga(OH)_2^+$	H_3par^+	$\leqslant 3.4 \times 10^4$	0.04	$\leqslant 8 \times 10^5$
	$Hsal^{-}$[b]	2.1×10^5	1	2×10^5
	H_2sal[b]	$\leqslant 3.5 \times 10^5$	0.3	$\leqslant 1 \times 10^6$
In^{3+}	H_3par^+	475	0.02	2.4×10^4
	H_2par	$\leqslant 1.0 \times 10^4$	0.2	$\leqslant 5.0 \times 10^4$
	$H_2ferron$[g]	1 080	0.3	3.5×10^3
	$Hferron^{-}$[g]	$\leqslant 9.7 \times 10^4$	3	$\leqslant 3.8 \times 10^4$
	Murexide(1−)[h]	6×10^5	5	1.2×10^5
	$H_2semixyl^{2-}$[c]	2.8×10^5	80	3.7×10^3
	SO_4^{2-}[d]	2.6×10^5	10^3	2.6×10^2
	H_2O			1.5×10^4[i]

[a] Abbreviations: H_2sal = salicylic acid, $H_4semixyl$ = semixylenol orange, H_3pcv = pyrocatechol violet, $H_2ferron$ = 8-hydroxy-7-iodoquinolinesulphonic acid. [b] B. Perlmutter-Hayman, F. Secco, E. Tapuhi, and M. Venturini, *J. Chem. Soc., Dalton Trans.*, 1977, 2220. [c] Y. Kawai, T. Takamashi, K. Hayashi, T. Imamura, H. Nakayama, and M. Funimoto, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1972. [d] J. Miceli and J. Stuehr, *J. Am. Chem. Soc.*, 1968, **90**, 6967. [e] Ref. 9. [f] $0.75k_{H_2O}$; from ref. 8. [g] Ref. 23. [h] Y. Kaway, T. Imamura, and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 3142; Y. Ohtani, S. Yagihashi, and M. Fujimoto, *ibid.*, 1977, **50**, 1345. [i] $0.75k_{H_2O}$; from ref. 15.

and *ca.* 500 times faster than Ga^{3+}. Similarly, $In(OH)_2{}^+$ reacts with H_3par^+ species up to 100 times faster than $In(OH)^{2+}$ and 4×10^3 times greater than In^{3+} (these factors are upper limits both for 3-nitrosalicylate and par).

For several reactions involving ligands with co-ordinating groups engaged in intramolecular hydrogen bonds a noticeable decrease in rate has been observed for complex formation, owing to the slowness of dissociation of these bonds.[19] This decrease in rate has not been observed here for par, even though the *ortho*-phenolic group is certainly engaged in a strong intramolecular interaction with the azo-moiety (this causes a very low acidity of the corresponding proton: $pK_{3A} = 12.0$).

A general trend of increased dissociative behaviour along the first-row transition series for both divalent and trivalent high-spin metal ions has been pointed out.[20] A trend towards more associative behaviour also occurs[6] down the groups in the Periodic Table. This is seen from the variation of the volume of activation for solvent exchange, with the more positive (or less negative) volume of activation for the more dissociative (or less associative) character.[21] In the case of gallium, as for aluminium, in a series of pure organic solvents, both entropy and volume of activation are positive, indicating a dissociative mode.[22] On the other hand, in water an associative mode of activation has been put forward for In,[23] Ga,[8,24] and Al.[25]

In the present systems, the observed decrease in rate with mole fraction of organic solvent is probably due to the increased ordering of the water. Since an increase in solvent structure might be expected to introduce an additional barrier to either associative attack by an incoming par or a release of solvent to the bulk solution (as in the Ni^{II}–bipyridine system[16]), we are unable definitely to assign a mechanism on this basis; thus it appears that in order to be able to make more meaningful conclusions on the basis of solvent effects, further work will have to concentrate on systems with simpler acid/base properties.

Conclusions

Although the Ga^{III}–tropolone[9] complexation has been described to occur by an I_d mechanism, the data collected in Table 5 certainly do not allow us to conclude that this is a mechanism operative for all the tabulated reactions. This is especially true for the series of substituted salicylate monoanion reactions[8] with both Ga^{3+} and $Ga(OH)^{2+}$ for which the strong correlation between reaction rates and ligand basicities seems to indicate an associative mechanism. Tanaka and co-workers[9] have noted the rather large difference between the computed values of k_f/K_{os} for Ga^{3+} and the directly measured value of the water exchange, but have discounted it in favour of the similarity of k_f/K_{os} values in his tabulation (which differs somewhat from ours). They have attributed the variation in rates for the salicylate series as being due to reactions of 'only modest dissociative character'.

We may conclude, then, that there is a great need for additional work on these metals to determine whether substitution reactions are uniformly associative or dissociative for each particular metal species, how solvent composition effects the mechanism or if, indeed, the mechanism is simply a function of the incoming ligand.

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