The Hydrolysis of Metal Ions. Part 11.[1] The Ionic Strength Dependence of Gallium(III)

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An automated potentiometric titration technique has been used to study the behaviour of the gallium(III) ion in 0.10, 0.50, 1.0, and 1.5 mol dm^{-3} potassium nitrate at 25 °C. Data analysis indicates the presence of the monomeric species $[Ga(OH)]^{2+}$ and $[Ga(OH)_2]^+$. The $-\log \beta_{pq}$ values for these species are estimated to be 3.16 (0.02) and 7.07 (0.02), respectively, in 0.10 mol dm^{-3} KNO_3, 3.73 (0.03) and 7.15 (0.02) in 0.50 mol dm^{-3} KNO_3, 3.92 (0.02) and 7.79 (0.03) in 1.0 mol dm^{-3} KNO_3, and 4.02 (0.03) and 7.73 (0.03) in 1.5 mol dm^{-3} KNO_3 (the standard deviations have been given in parentheses). The dependence of the two formation constants on ionic strength has been determined.

The aqueous complexation chemistry of gallium(III) is poorly understood since it has received little attention. A literature review[2–10] of the hydrolytic equilibria of the ion, for instance, reveals poor agreement between the results of the various studies. Indeed, the stoicheiometry of the species is somewhat unclear. Even more unclear are the formation constants of the postulated species; for example, the formation constant of $[Ga(OH)]^{2+}$ varies by two to three orders of magnitude, when measured using the same experimental conditions. The most extensive study of the system is a recent one by Campisi and Tregloan[2] who, using a variety of experimental conditions (temperature and ionic strength), found evidence for only the monomeric species $[Ga(OH)]^{2+}$ and $[Ga(OH)_2]^+$. Earlier studies,[3–5] however, postulated a large-molecular-weight polymer with a hydroxide to metal ion ratio of *ca.* 2.5, in addition to the monomeric species.

In order better to elucidate the species which are formed in this system, and their relevant formation constants, it appeared appropriate to reinvestigate the system and to use the advanced experimental and computational techniques developed at this laboratory;[1,11–13] this paper reports a study carried out at 25 °C in 0.10, 0.50, 1.0, and 1.5 mol dm^{-3} potassium nitrate.

Table 1. Summary of titrations of gallium(III) at 25 °C

Total initial gallium(III) concentration (mmol dm^{-3})	pH range	Number of points
(*a*) 0.10 mol dm^{-3} data		
1.670	2.054—3.051	109
0.835	2.454—3.168	79
0.595	2.553—3.355	72
0.367	3.052—3.465	81
(*b*) 0.50 mol dm^{-3} data		
2.070	1.709—3.048	211
0.574	2.394—3.296	104
0.144	2.911—3.551	198
(*c*) 1.0 mol dm^{-3} data		
2.870	1.900—3.016	66
1.435	2.302—3.141	60
0.574	2.359—3.308	102
0.287	2.681—3.458	187
0.144	2.986—3.592	142
(*d*) 1.5 mol dm^{-3} data		
2.870	1.901—2.953	115
1.435	2.304—3.099	83
0.574	2.320—3.274	99
0.287	2.636—3.415	187
0.144	2.899—3.500	140

Experimental

Reagents.—The source of gallium was gallium metal (Alfa Puratonic). The base was potassium hydrogencarbonate (Fluka Garantie). All other chemicals were Merck Suprapur grade. Water was purified by ultrafiltration and ion exchange, followed by distillation. Gallium analyses were carried out using atomic absorption spectrophotometry.

Procedure.—The procedure used has been previously described.[1,11] The titrations were carried out using 0.10, 0.50, 1.0, and 1.5 mol dm^{-3} KNO_3 as the ionic media, and at 25.0 ± 0.1 °C. A summary of the titrations is given in Table 1; full details are available on request.

Results

The (hypothetical) hydrolysis reactions (1) can be used to define the *overall* stoicheiometric formation constants, β_{pq}, as in equation (2). Each species is represented by either its formula or by a (p,q) pair.

$$p\mathrm{Ga}^{3+} + q\mathrm{H_2O} \rightleftharpoons [\mathrm{Ga}_p(\mathrm{OH})_q]^{(3p-q)+} + q\mathrm{H}^+ \quad (1)$$

$$\beta_{pq} = \frac{[\mathrm{Ga}_p(\mathrm{OH})_q{}^{(3p-q)+}][\mathrm{H}^+]^q}{[\mathrm{Ga}^{3+}]^p} \quad (2)$$

Initial data analysis involved models containing the species (1,1), (1,2), (2,2), (3,4), (3,5), and high-molecular-weight polymers with a q/p ratio of *ca.* 2.5, in various combinations. This numerical analysis demonstrated that the only likely species which may be involved in this system, under the experimental conditions stated, are (1,1) and (1,2), and possibly a polymeric species of low molecular weight. The postulated species and the models containing them were determined by using previously outlined acceptance criteria.[1,11–16] Namely, the agreement factor, R, is less than 0.002 and the estimated standard deviation (e.s.d.) of each species is $\leqslant 10\%$. If this does not resolve the ambiguity then chemical reasoning must be used to select the correct model. This reasoning has been given in detail by Khoe *et al.*[11]

Table 2. Comparison of models of the hydrolysis of gallium(III) at 25 °C

Model no.	Model	$-\log \beta_{pq}$	E.s.d. (%) of β_{pq}	R	$-\log \beta_{pq}$	E.s.d. (%) of β_{pq}	R
		(*a*) 0.10 mol dm^{-3} data			(*b*) 0.50 mol dm^{-3} data		
1	(1,1)	3.16	4.89	0.0012	3.73	5.80	0.0019
	(1,2)	7.07	5.58		7.15	4.77	
2	(1,2)	7.49	10.93	0.0012	7.13	4.54	0.0020
	(2,2)	3.55	4.69		4.26	7.01	
3	(1,1)	3.54	26.25	0.0012	Model rejected:		
	(1,2)	7.29	12.38		(2,2) became negative		
	(2,2)	3.76	18.31				
4	(1,1)	3.32	6.76	0.0011	Model rejected:		
	(1,2)	7.37	15.12		(3,4) became negative		
	(3,4)	7.14	13.02				
5	(1,1)	3.16	5.26	0.0012	Model rejected:		
	(1,2)	7.08	5.93		(13,32) became negative		
	(13,32)	63.67	156.26				
6	(1,1)	3.31	7.05	0.0011	Model rejected		
	(1,2)	7.40	16.61		(3,4) and (13.32) became		
	(3,4)	7.14	12.93		negative		
	(13,32)	64.60	115.49				
		(*c*) 1.0 mol dm^{-3} data			(*d*) 1.5 mol dm^{-3} data		
1	(1,1)	3.92	4.70	0.0017	4.02	6.05	0.0017
	(1,2)	7.79	6.77		7.73	6.59	
2	(1,2)	7.68	3.35	0.0015	7.61	4.11	0.0018
	(2.2)	4.64	3.75		4.86	7.12	
3	(1,1)	Model rejected:			Model rejected:		
	(1,2)	(1,1) became negative			(2,2) became negative		
	(2.2)						
4	(1,1)	4.19	5.78	0.0016	4.02	9.16	0.0017
	(1,2)	7.77	5.38		7.73	6.59	
	(3,4)	8.53	8.50		10.12	458.46	
5	(1,1)	3.91	4.68	0.0017	4.00	5.97	0.0017
	(1,2)	7.83	8.61		7.78	8.58	
	(13.32)	68.31	57.15		68.60	47.84	
6	(1,1)	4.17	11.27	0.0016	4.00	9.10	0.0017
	(1,2)	7.78	6.61		7.78	8.60	
	(3,4)	8.55	10.47		10.42	949.56	
	(13,32)	69.52	222.00		68.61	50.95	

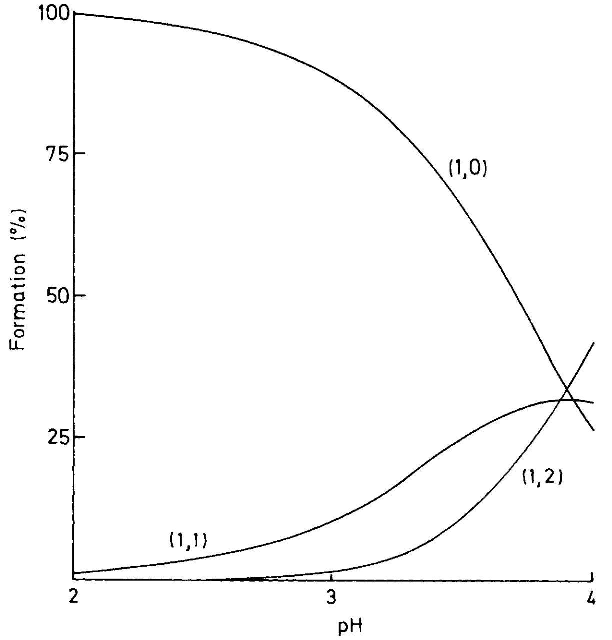

Figure 1. Percentage distribution of gallium(III) in various species in 1.0 mol dm^{-3} potassium nitrate and at 25 °C

Table 2 contains the results of computations of a number of models for comparative purposes. Use of the developed criteria[1,11–16] led to the choice of the model containing only the monomers (1,1) and (1,2) as the 'best' model to fit the data at each ionic strength. Model 2 must be rejected since it contains the (1,2) species in the absence of (1,1) and, indeed, the model does not meet the acceptance criteria for either the 0.10 or the 0.50 mol dm^{-3} data. Model 4, for the 1.0 mol dm^{-3} data, is rejected since the contribution of the (3,4) species to the data is virtually negligible, and, furthermore, in the remaining data the model fails to meet the acceptance criteria. Figure 1 illustrates the percentage distribution of each species of gallium(III) in Model 1 in 1.0 mol dm^{-3} potassium nitrate. Since only monomeric species are formed, the percentage speciation is independent of the gallium(III) concentration. As expected, the (1,1) species is more important at low pH and the (1,2) species at higher pH.

In the equation (3), the value of λ is 0.866, 0.899, 0.993,

$$[H^+] = 10^{-pH}/\lambda \qquad (3)$$

and 1.123 for the 0.10, 0.50, 1.0, and 1.5 mol dm^{-3} data, respectively. These values are in good agreement with values obtained previously[1,11–16] at these ionic strengths in this laboratory and they demonstrate that λ depends on ionic strength most significantly. The pH range of the reactions allows the ionisation reaction of water to be ignored.

Table 3. Survey of some results of the potentiometric investigation of gallium(III)

Concentration/ mol dm^{-3} (medium)	Temp. (°C)	Total gallium(III) concentration (mmol dm^{-3})	$-\log \beta_{1q}$ (1,1)	(1,2)	(1,3)	Ref.
0.5 ($NaClO_4$)	10	0.4—10	4.17	8.21		2
0.1 ($NaClO_4$)	25	0.4—10	3.50	7.67		2
0.5 ($NaClO_4$)	25	0.4—10	3.69	7.43		2
1.5 ($NaClO_4$)	25	0.4—10	4.15	6.97		2
0.1 ($NaClO_4$)	25	0.0003	2.87	6.55	11.07	7
0.3 ($NaClO_4$)	25	0.0003	2.48	5.67	9.69	7
0.5 ($NaClO_4$)	25	0.0003	2.30	5.20	8.65	7
1.0 ($NaClO_4$)	25	0.0003	1.78	3.88	6.16	7
0.1 (NaCl)	25	0.01	2.91	6.61	11.02	9
0.01 (GaX_3)[a]	25	0.01	2.90			17[b]
0.02 (GaX_3)[a]	25	0.02	3.00			17[b]
0.05 (GaX_3)[a]	25	0.05	3.17			17[b]
0.10 (KNO_3)	25	0.367—1.670	3.16	7.07		This work
0.50 (KNO_3)	25	0.144—2.070	3.73	7.15		
1.0 (KNO_3)	25	0.144—2.870	3.92	7.79		
1.5 (KNO_3)	25	0.144—2.870	4.02	7.73		
Predicted values for zero ionic strength						
	25		2.6	5.9	10.3	17
	25		2.56	6.37	11.30	18

[a] X = Cl, Br, or NO_3. [b] Calculated from ref. 6.

Table 4. Ionic strength dependence of β_{11} and β_{12}: calculated and experimental

Ionic strength (mol dm^{-3})	$-\log \beta_{11}$ Calc.	$-\log \beta_{11}$ Exp.	$-\log \beta_{12}$ Calc.	$-\log \beta_{12}$ Exp.
0	2.56		6.07	
0.10	3.12	3.16	6.82	7.07
0.50	3.64	3.73	7.39	7.15
1.0	3.94	3.92	7.70	7.79
1.5	4.14	4.02	7.91	7.73
3.0	4.52		8.31	
Constants				
b	0.5		1.0	
c	−0.021		−0.10	

Discussion

Table 3 compares the results of earlier investigations with those of the present study and shows excellent agreement between the present results and those of Campisi and Tregloan[2] for the (1,1) complex at higher ionic strengths. Much poorer agreement is found for the second monomeric species at all ionic strengths, and for the first species at the lowest ionic strength. Overall, the agreement between the various studies is extremely poor because of the following.

(*a*) Uncertainties in some of the experimental techniques used; specifically, the colorimetric technique.[17]

(*b*) In some studies[7,9] only one metal-ion concentration was used. To justify the selection of a model it is essential that as wide a range of concentration as is experimentally practicable, of both metal ion and proton, be studied.[16]

(*c*) Compositional changes caused by the use of high gallium(III) and/or proton concentrations (relative to the ionic strength), which in some instances[2,9] are as high as 20% of the total ionic strength.

The formation constants from Brown[18] given in Table 3 (at zero ionic strength) were determined using the numerical equations developed for the Brown–Sylva electronicity principle.[19] The value of the ionic radius used for Ga^{3+} in these calculations, however, was 0.006 nm larger (*i.e.* 0.068 nm) than the value given by Shannon and Prewitt.[20] Indeed, in this regard, it has been previously suggested[14] that the earlier value[20] was in error since it gave predicted formation constants which could not be supported by experimental evidence.[14,19] Use of the larger ionic radius in the equations of Brown and Sylva[19] gives predicted formation constants which are consistent with those calculated by Baes and Mesmer.[17]

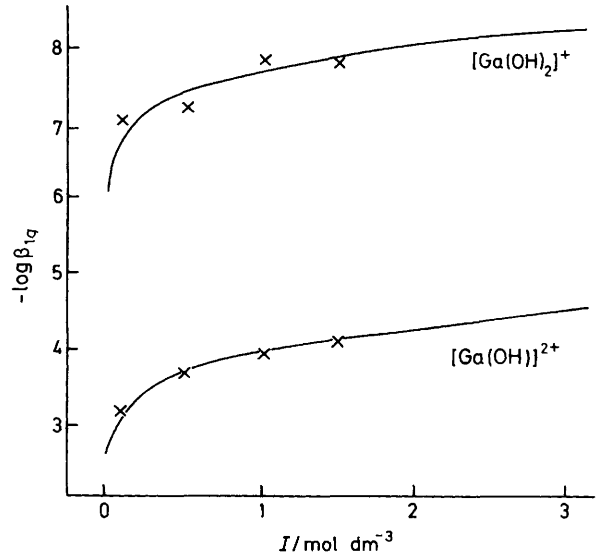

Figure 2. Ionic strength dependence of β_{11} and β_{12} at 25 °C: calculated (solid lines) and experimental (×)

Formation constants at zero ionic strength are usually calculated by using a version of the Debye–Hückel equation which may be represented by equation (4):[21] where *a*, *b*, and *c*

$$\log\beta_{pq} = \log\beta_{pq^0} + a\Delta z^2 I^{\frac{1}{2}}/(1 + bI^{\frac{1}{2}}) + cI \qquad (4)$$

are constants (*a* is the Debye–Hückel constant), *I* is the ionic strength, β_{pq^0} is the formation constant at zero ionic strength, β_{pq} is the same constant at *I*, and Δz^2 is the sum of the charge of each species summed over the formation reaction of the complex. Using equation (4) in conjunction with the data determined in this study allows the constants *b* and *c* to be determined which, in turn, permits the ionic strength dependence of each formation constant to be calculated. Table 4 gives the calculated values of *b* and *c* using the present data, as well as the calculated formation constant using these two values in the Debye–Hückel equation. The dependence of the two constants on ionic strength is illustrated in Figure 2. In the figure, the line of best fit is given for both of the formation constants (solid line). When these lines are compared to the average of the more reliable data given in Table 3 very satisfactory agreement is obtained.

The data given in Table 4 reveal an interesting trend. At low ionic strength the value of the first step-wise formation constant is, as expected, greater than the second (*i.e.* $K_1 > K_2$). However, at higher ionic strength an apparent anomaly arises, since K_2 becomes larger than K_1 (the crossover point occurs when the ionic strength is *ca.* 0.66 mol dm^{-3}). Thus, at 1.5 mol dm^{-3} the value of $-\log K_1$ has increased by 1.58 log units, from the value at zero ionic strength, whereas the increase in $-\log K_2$ is only 0.26 units. This anomaly arises because the two overall formation constants are, in real terms, similarly dependent on ionic strength. Thus, the change in β_{12} with increasing ionic strength is due almost solely to the change in β_{11}. Indeed, the value of $-\log K_2$, as calculated from equation (4), is virtually independent of ionic strength.

Comparison of the present data with previous studies is somewhat misleading since, although satisfactory agreement is obtained with some studies, much poorer agreement is found with other studies, especially at lower ionic strengths. It is believed that this poor agreement results from the deficiencies in the experimental design of these studies as has been outlined earlier. Indeed, these deficiencies have resulted [2,7] in apparently anomalous data where a species becomes more stable as ionic strength increases, when usually the opposite occurs as the present data clearly show.

The experimental techniques developed at this laboratory [1,11-13] have been used to describe definitively the hydrolysis behaviour of gallium(III). Numerical analysis has shown that the only species which form, in the experimental conditions studied, are the monomeric species $[Ga(OH)]^{2+}$ and $[Ga(OH)_2]^{+}$. However, it is likely that the use of lower concentrations of gallium(III) would permit the detection of $[Ga(OH)_3]$ but, in the present study, its formation is limited by precipitation reactions. The present study has also emphasised the importance of experimental design, since without due attention in this regard model postulations cannot be justified.

References

1 Part 10, P. L. Brown, M. E. Shying, and R. N. Sylva, *J. Chem. Soc., Dalton Trans.*, 1987, 2149.
2 A. Campisi and P. Tregloan, *Inorg. Chim. Acta*, 1985, **100**, 251.
3 J. Haladjian and G. Carpeni, *J. Chim. Phys. Physiochim. Biol.*, 1967, **64**, 1338.
4 J. K. Ruff and S. Y. Tyree, *J. Am. Chem. Soc.*, 1958, **80**, 5654.
5 H. Gamsjäger and P. Schindler, *Helv. Chim. Acta*, 1967, **50**, 2053.
6 T. Moeller and G. L. King, *J. Phys. Chem.*, 1950, **54**, 999.
7 E. A. Biryuk and V. A. Nazarenko, *Russ. J. Inorg. Chem.*, 1973, **18**, 1576.
8 A. P. Savostin, *Russ. J. Inorg. Chem.*, 1966, **11**, 1514.
9 V. A. Nazarenko, V. P. Antonovich, and E. M. Nevskaya, *Russ. J. Inorg. Chem.*, 1968, **13**, 825.
10 I. P. Alimarin, S. A. Khamid, and I. V. Puzdrenkova, *Russ. J. Inorg. Chem.*, 1965, **10**, 209.
11 Part 9, G. H. Khoe, P. L. Brown, R. N. Sylva, and R. G. Robins, *J. Chem. Soc., Dalton Trans.*, 1986, 1901.
12 Part 7, P. L. Brown, J. Ellis, and R. N. Sylva, *J. Chem. Soc., Dalton Trans.*, 1983, 2001.
13 Part 1, R. N. Sylva and M. R. Davidson, *J. Chem. Soc., Dalton Trans.*, 1979, 232.
14 P. L. Brown, R. N. Sylva, and J. Ellis, *J. Chem. Soc., Dalton Trans.*, 1985, 723.
15 Part 5, P. L. Brown, J. Ellis, and R. N. Sylva, *J. Chem. Soc., Dalton Trans.*, 1983, 31.
16 Part 8, P. L. Brown, R. N. Sylva, and J. Ellis, *J. Chem. Soc., Dalton Trans.*, 1985, 1967.
17 C. F. Baes and R. E. Mesmer, 'The Hydrolysis of Cations,' Wiley-Interscience, New York, 1976.
18 P. L. Brown, unpublished work.
19 P. L. Brown and R. N. Sylva, *J. Chem. Res.*, 1987, (*S*) 4; (*M*) 0110.
20 R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, 1969, **25**, 925.
21 S. L. Phillips, 'Hydrolysis and Formation Constants at 25 °C,' Report LBL-14313, University of California, Berkeley, 1982.

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