Chloride-exchange Processes on Gallium(III) in Concentrated Aqueous Chloride Solutions: a Chlorine-35 and Gallium-71 Magnetic Resonance Study

By **Stephen F. Lincoln** * and **Alan C. Sandercock,** Department of Physical and Inorganic Chemistry, University of Adelaide, South Australia 5001
Donald R. Stranks, Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia

The equilibria between gallium(III) species have been investigated by ^{71}Ga n.m.r. and the rates of chloride exchange determined by ^{35}Cl n.m.r. in two series of solutions in which the total chloride concentrations were 11·0 and 7·0M, and in which the ratio [HCl] : [LiCl] was varied over a wide range. The chloride-exchange dynamics are rationalised in terms of an associative exchange of chloride on $[GaCl_4]^-$. In 11M-hydrochloric acid: $10^5 k_{ex.}'$ (298 K) = 164 ± 8 l mol^{-1} s^{-1}; $\Delta H^‡ = 30{\cdot}1 \pm 1{\cdot}5$ kJ mol^{-1}; and $\Delta S^‡ = -44 \pm 5$ J K^{-1} mol^{-1}.

VARIABLE-TEMPERATURE studies of the nuclear relaxation times of quadrupolar halogen nuclei may be employed to determine rates of halide-ion chemical exchange in labile diamagnetic systems.[1-3] However, the number of such studies has been limited probably due to uncertainty as to the stoicheiometry of the species present in solution. One system which does appear to be reasonably well characterised is the aqueous gallium(III)–chloride system, which has accordingly been selected for this study. Raman[4,5] and ^{71}Ga n.m.r.[6] studies of aqueous gallium(III)–chloride solutions indicate that the sequential equilibria shown in equation (1) characterise this system. The stoicheiometry of

$$[Ga(OH_2)_6]^{3+} \rightleftharpoons [GaCl_n(OH_2)_m]^{(3-n)+} \rightleftharpoons [GaCl_4]^-;\ n = 1\text{—}4 \quad (1)$$

$[Ga(OH_2)_6]^{3+}$ and $[GaCl_4]^-$ is well established by n.m.r.,[7,8] Raman,[4,5] and *X*-ray[9] studies, but it appears that for some values of *n* the value of *m* may be compatible with either six- or four-co-ordination. This is discussed later.

RESULTS AND DATA TREATMENT

^{71}Ga *Studies*.—In this study the rates of chloride exchange on gallium(III) were determined by a ^{35}Cl n.m.r. method[3,10] which requires that the mole fraction of co-ordinated chloride should not exceed *ca.* 0·1. This requirement limits the total gallium(III) concentrations permitted in solution to values considerably less than those in the reported ^{71}Ga n.m.r. equilibrium studies.† Consequently ^{71}Ga n.m.r. studies were carried out at lower gallium(III) concentrations, and also over a range of [HCl] : [LiCl] ratios to determine medium effects on the equilibria shown in equation (1). Accordingly the ^{71}Ga n.m.r. spectra (Figure 1) of the solutions given in Table 1 were determined. The spectra of solutions (*i*)—(*iv*) were each characterised by single resonances of identical width, within experimental error (±0·1 mT), 240 ± 10 p.p.m. downfield from $[Ga(OH_2)_6]^{3+}$ (which compares with a value of 257 ± 5 p.p.m. reported for $[GaCl_4]^-$ in the earlier study[6]), and it is concluded that $[GaCl_4]^-$ is the predominant species in these solutions. The difference in chemical shift between the two studies may indicate a small difference in the position of equilibrium (1) or may be a consequence of the different total gallium(III) concentrations employed in the two studies, for it has been shown that the ^{71}Ga shift of $[GaCl_4]^-$ can vary by as much as 60 p.p.m., and the linewidth can also vary, as the environment is varied.[6]

TABLE 1

Composition of solutions for ^{71}Ga n.m.r. studies

Solution	$[Ga^{3+}]$/M	$[H^+]$ [a]/M	$[Li^+]$ [b]/M	$[Cl^-]_T$/M
(*i*)	0·50	9·50	0	11·00
(*ii*)	0·50	4·50	5·00	11·00
(*iii*)	0·50	1·00	8·50	11·00
(*iv*)	0·25	0·50	9·75	11·00
(*v*)	0·50	5·50	0	7·00
(*vi*)	0·50	3·50	2·00	7·00
(*vii*)	0·25	0·60	5·65	7·00

[a,b] Formal hydrochloric acid and lithium chloride concentrations respectively.

In the 7M-chloride solutions it is evident (Figure 1) from the ^{71}Ga spectra that several gallium(III) species are present, and furthermore that the ^{71}Ga n.m.r. spectra are dependent on the $[H^+]:[Li^+]$ ratio. A major component of the high-field signal observed in solutions (*v*)—(*vii*) is probably the $[Ga(OH_2)_6]^{3+}$ resonance, which increased in magnitude from (*v*) to (*vii*), even though all three solutions are formally 7M in chloride. This spectral variation of the 7M solutions is consistent with a shift of the equilibria in equation (1) to the right as the $[H^+]:[Li^+]$ ratio increases. The variation of the linewidth of the low-field signal indicates rapid environmental averaging of $[GaCl_4]^-$ with lower chloro-species. Akitt *et al.*[6] also observed an analogous modification of these equilibria on addition of $MgCl_2$ to acidic chloride solutions of gallium(III).

^{35}Cl *Studies*.—Application of the exchange-modified Bloch equations to ligand-exchange processes has been discussed in detail elsewhere[10] and hence only those aspects applicable to the system under study are considered here. The relaxation of the ^{35}Cl nucleus in the first co-ordination sphere of gallium(III) is very rapid by comparison to that in the free chloride ion and consequently chloride-exchange studies are most conveniently carried out under conditions where the mole fraction of co-ordinated

---

† The total gallium(III) concentration employed is calculated to be *ca.* 1·7M from data in ref. 6; 1M = 1 mol dm^{-3}.

[1] H. G. Hertz, *Z. Electrochem.*, 1961, **65**, 36.

[2] C. Hall, *Quart Rev.*, 1971, **25**, 87.

[3] S. F. Lincoln, A. Sandercock, and D. R. Stranks, *J.C.S. Chem. Comm.*, 1972, 1069.

[4] L. A. Woodward and A. A. Nord, *J. Chem. Soc.*, 1956, 3721.

[5] K. Schug and L. Katzin, *J. Phys. Chem.*, 1962, **66**, 907.

[6] J. W. Akitt, N. N. Greenwood, and A. Storr, *J. Chem. Soc.*, 1965, 4410.

[7] D. Fiat and R. E. Connick, *J. Amer. Chem. Soc.*, 1968, **90**, 608.

[8] A. Fratiello, R. E. Lee, V. M. Nishida, and R. E. Schuster, *J. Chem. Phys.*, 1968, **48**, 3705.

[9] G. Garton and H. M. Powell, *J. Inorg. Nuclear Chem.*, 1957, **4**, 84.

[10] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 1962, **37**, 307; 1964, **41**, 2553.

chloride, x_{Cl}, is less than *ca.* 0·1. Under these conditions only the free-chloride ^{35}Cl resonance is observed, the broadening of which is proportional to the gallium(III) concentration (0·10—0·30 and 0·05—0·15M for the 11 and 7M-chloride solutions respectively given in Table 2). The modification of the free-chloride ^{35}Cl relaxation caused by gallium(III) is given by equation (2), where γ is the

$$2\gamma^{-1}(W - W_A)^{-1} = [(1/T_2) - (1/T_{2A})]^{-1} = T_{2ex.}\ \mathrm{s} \quad (2)$$

^{35}Cl magnetogyric ratio ($2\ 620 \times 10^4$ rad T^{-1} s^{-1}), W and W_A are the full widths (T) at half maximum amplitude of the ^{35}Cl free-chloride resonance in the gallium(III) chloride solution and the reference solution of the same total chloride concentration but containing no gallium(III), respectively, and T_2 and T_{2A} are the respective free-chloride ^{35}Cl transverse relaxation times.

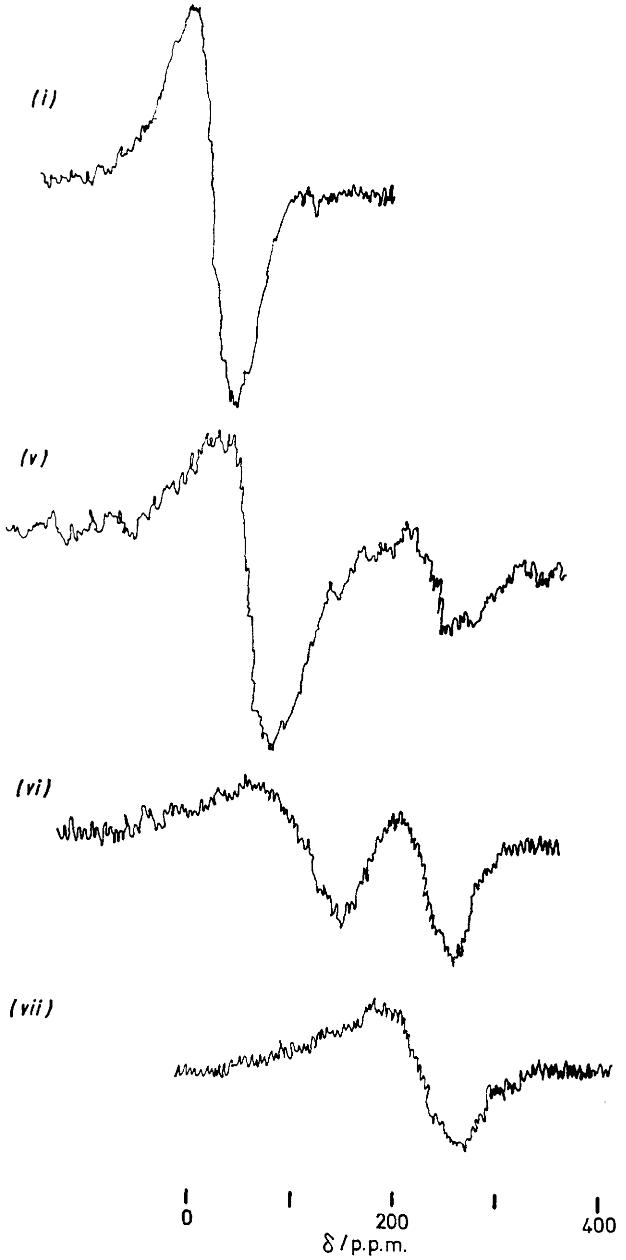

Figure 1 ^{71}Ga N.m.r. spectra of gallium(III)–chloride solutions. All solutions are stoicheiometrically 0·50M in $GaCl_3$ except (*vii*) which is 0·25M, and the hydrochloric acid and lithium chloride concentrations are respectively (*i*) 9·50 and 0, (*v*) 5·50 and 0, (*vi*) 3·50 and 2·00, and (*vii*) 0·60 and 5·65M

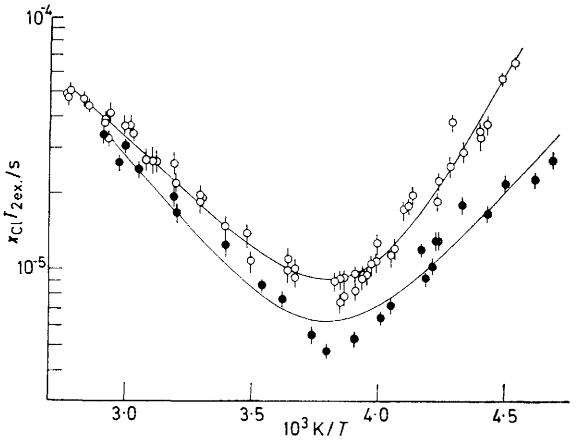

Figure 2 ^{35}Cl N.m.r. $x_{Cl}T_{2ex.}$ data for 11M total chloride solutions (*viii*) (○) and (*x*) (●). (——), Best fit of the data to equation (3)

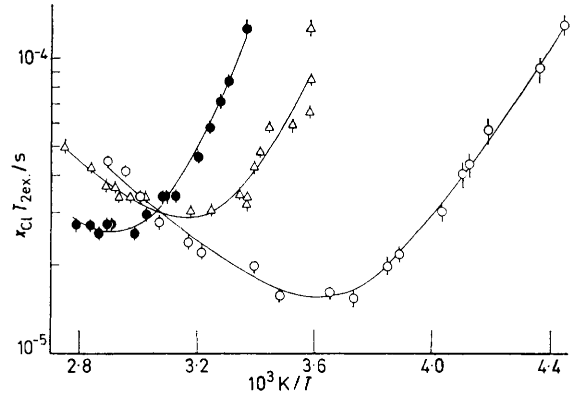

Figure 3 ^{35}Cl N.m.r. $x_{Cl}T_{2ex.}$ data for 7M total chloride solutions (*xii*) (○), (*xiii*) (△), and (*xiv*) (●). (——), Best fit of the data to equation (3)

The temperature dependences of $T_{2ex.}$ (Figures 2 and 3) for all the solution studies were consistent with an environmental averaging process occurring between the co-ordinated- and free-chloride environments. No chemical shift of the free ^{35}Cl resonance (limit of detection *ca.* 20 p.p.m.) from the ^{35}Cl resonance in the reference solution was observed in solutions (*viii*)—(*xiv*). No reduction was observed in $T_{2ex.}$ (294 K) characterising solution (*viii*) on reduction of the spectrometer frequency from 4·170 to 2·085 MHz; this indicates that the predominant ^{35}Cl relaxation process arises from the interaction of the electric quadrupole moment, *eQ*, of that nucleus with the electric-field gradient, *eq*, which arises on co-ordination to gallium(III). The two-site equation of Swift and Connick[10] consequently reduces to (3) for the 11M-chloride solutions,[2]

$$T_{2ex.} = (\tau_{Cl}/x_{Cl}) + [\hbar^2(e^2Qq)^{-2}\,(1 + \frac{\eta^2}{3})^{-1}/x_{Cl}\tau_c] \quad (3)$$

where τ_{Cl} is the mean life time of a co-ordinated chloride ion, η is the n.q.r. asymmetry parameter (in the absence of η values for this system it was assumed that $\eta^2 \ll 1$ as found for CCl_4 and PhCl[11]), and τ_c is the correlation time

---

[11] Y. Saito, *Canad. J. Chem.*, 1965, **43**, 2530.

TABLE 2

^{35}Cl N.m.r. kinetic data and solution compositions

11·00M Total chloride solutions [a]

Solution	[H$^+$] M	[Li$^+$] M	$10^{-4}k_{ex.}$ (298 K) [b] s^{-1}	$10^{-3}k_{ex.}'$ (298 K) [c] l mol^{-1} s^{-1}	$\Delta H^\ddagger$ kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1} b	$\Delta S^\ddagger$/J K^{-1} mol^{-1} c	$10^{12}\tau_c$ (298 K) s	E_Q kJ mol^{-1}
(*viii*)	9·80—10·70	0	180 ± 9	164 ± 8	30·1 ± 1·5	−24 ± 5	−44 ± 5	16 ± 2	17·6 ± 1·5
(*ix*)	5·80—6·70	4·00	97 ± 5	88 ± 5	16·3 ± 1·0	−76 ± 4	−96 ± 4	24 ± 2	23·5 ± 1
(*x*)	3·00—3·70	7·00	83 ± 4	75 ± 4	16·7 ± 1·0	−74 ± 4	−96 ± 4	24 ± 2	23·4 ± 1
(*xi*)	0·40—0·70	10·00	250 ± 1·0	227 ± 1·0	19·7 ± 1·0	−56 ± 3	−76 ± 3	30 ± 2	26·7 ± 1

7·00M Total chloride solutions [d]

Solution	[H$^+$] M	[Li$^+$] M	$10^{-3}k_{ex.}$ (298 K) [b] s^{-1}	$E^\ddagger$ kJ mol^{-1}
(*xii*)	6·28	0	430 ± 30	28·9 ± 1·5
(*xiii*)	3·28	3·00	47 ± 3	43·9 ± 2·0
(*xiv*)	0·28	6·00	11 ± 0·5	51·0 ± 2·0

[a,d] The total chloride was adjusted to 11·00 and 7·00M respectively with hydrochloric acid and gallium(III) chloride solution, as described in the Experimental section. [b] Calculated from the pseudo-first-order rate expression, Rate = $k_{ex.}4[GaCl_4^-]$. [c] Calculated from the pseudo-second-order rate expression, Rate = $k_{ex.}'4[GaCl_4^-][Cl^-]$.

for the quadrupole-induced nuclear relaxation process. The best fits of equation (3) to two of the 11M-chloride data sets {where x_{Cl} is calculated on the assumption that all of the gallium(III) exists as $[GaCl_4]^-$} are shown as solid curves in Figure 2, from which it is apparent that the chemical-exchange term (τ_{Cl}/x_{Cl}) dominates $T_{2ex.}$ at low temperatures whilst the quadrupolar term of equation (3) predominates at high temperature. On the assumption that $[GaCl_4]^-$ is the predominant source of free ^{35}Cl relaxation, the observed first-order chloride-exchange rate is given by equation (4). The kinetic parameters for the 11M-chloride solutions are given in Table 2.

$$\text{Rate} = k_{ex.}4[GaCl_4^-] \qquad (4)$$

where

$$k_{ex.} = \tau_{Cl}^{-1} = (\boldsymbol{k}T/\boldsymbol{h})\exp[(-\Delta H^\ddagger/RT) + (\Delta S^\ddagger/R)] \quad (5)$$

Values of τ_c calculated using an $e^2Qq\boldsymbol{h}^{-1}$ value of 32·2 MHz (the value obtained from Ga[GaCl$_4$] data) [12] are also given in Table 1 as are the associated ' activation energies,' E_Q, for the quadrupolar relaxation process. These E_Q values are greater than those reported [13] for pure CCl$_4$ and TiCl$_4$, but are similar to those reported for metal complexes in solution [14] and may reflect a modification of the tumbling process for $[GaCl_4]^-$ by solvation which may also explain the variance of τ_c values for solutions (*viii*)—(*xi*).

The $T_{2ex.}$ temperature dependences of the 7M-chloride solutions (Figure 3) qualitatively show similar temperature dependences to those of the 11M solutions and have also been fitted to equation (3). The value $x_{Cl} = 4 \times$ [mole fraction of total gallium(III) in solution] was employed, in the absence of a precise knowledge of the equilibrium species existent in solution, to derive the kinetic parameters given in Table 2. This procedure is adopted solely to provide a basis for comparison, and does not infer that all gallium(III) in these solutions exists as $[GaCl_4]^-$. The use of equation (3) in the $T_{2ex.}$ data treatment is justified mainly on the grounds that the observed $T_{2ex.}$ temperature variations for solutions (*xii*)—(*xiv*) were consistent with free ^{35}Cl relaxation occurring on a single gallium(III) species for a given [H$^+$] : [Li$^+$] ratio despite the obvious differences (Figure 3) between the data sets characterising the three solutions. As significant ΔH values may be associated with the equilibria between gallium(III) species in the 7M-chloride solutions, it is inappropriate to consider the activation parameters for the chloride-exchange process in more detail than the observed activation energy, $E^\ddagger$.

DISCUSSION

In the equilibrium (1) existing between the gallium(III) chloro-species, exchange of chloride between the co-ordinated and free states is possible for each chloro-species, but only those exchange processes occurring sufficiently rapidly, as defined by equations (2) and (3), induce detectable ^{35}Cl relaxation of the free chloride ion. [In this study the maximum accurately detectable value of $T_{2ex.} \approx 3 \times 10^{-3}$ s and, as the maximum permissible value of $x_{Cl} \approx 0{\cdot}1$, $x_{Cl}T_{2ex.} = 2 \times 10^{-4}$ s is the maximum observable value of $\tau_{Cl} = k_{ex.}^{-1}$ when the first term to the right of equation (3) is dominant.] Thus discussion is necessarily restricted to those exchange processes detected through such ^{35}Cl relaxation. It is apparent from Table 2 that the decrease of $k_{ex.}$ (298 K) in the 7M solutions occurs simultaneously with a shift of equilibrium (1) to the left, and that the $k_{ex.}$ values typifying the 11M solutions are considerably greater than the analogous 7M values. This is clearly consistent with exchange of chloride on $[GaCl_4]^-$, providing the greatly predominant source of free-chloride ^{35}Cl relaxation in the 11 and 7M solutions, as is now considered in detail.

Exchange in 11M-*Chloride Media*.—The chloride-exchange process on $[GaCl_4]^-$ in all of the 11M solutions is characterised by a large negative entropy of activation (Table 2). In general, two limiting reaction mechanisms might be envisaged for chloride exchange, a dissociative *D* scheme [equations (6) and (7)] and an associative *A* scheme [equation (8)]. An *approximate* estimate of $\Delta S^\ddagger$ values for these schemes may

$$[GaCl_4]^- \rightleftharpoons [GaCl_3Cl]^{-\ddagger} \longrightarrow GaCl_3 + Cl^- \text{ (slow)} \quad (6)$$

$$GaCl_3 + {}^*Cl^- \longrightarrow [GaCl_3{}^*Cl]^- \text{ (fast)} \quad (7)$$

$$[GaCl_4]^- + {}^*Cl^- \rightleftharpoons [GaCl_4{}^*Cl]^{2-\ddagger} \longrightarrow [GaCl_3{}^*Cl]^- + Cl^- \quad (8)$$

---

[12] D. A. Tong, *Chem. Comm.*, 1969, 790.

[13] D. E. O'Reilly and G. E. Schacher, *J. Chem. Phys.*, 1963, **39**, 1768.

[14] R. A. Bernheim, T. H. Brown, H. S. Gutowsky, and D. E. Woessner, *J. Chem. Phys.*, 1959, **30**, 950.

be derived using the admittedly crude Born equation for the electrostatic contribution to the entropy changes for ions of charge Z and radii r immersed in a dielectric continuum of dielectric constant D, namely[15] $S = (Z^2/2Dr)(\partial D/\partial T)$. Assuming that at 298 K, $(\partial D/\partial T) = -0{\cdot}0046$ (the value for water) and $r(\mathrm{Ga}^{3+}) = 0{\cdot}60$ and $r(\mathrm{Cl}^-) = 1{\cdot}81$ Å, for the D process the electrostatic contribution $\Delta S_{\mathrm{el.}}^{\ddagger} \simeq -13$ J K^{-1} mol^{-1} and for the A process $\Delta S_{\mathrm{el.}}^{\ddagger} \simeq -5$ J K^{-1} mol^{-1}. To these electrostatic contributions must be added a cratic entropy term[15] of $+33$ J K^{-1} mol^{-1} for the D process and -33 J K^{-1} mol^{-1} for the A process. Then for the limiting D reaction $\Delta S^{\ddagger} = +33 - 13 = +20$ J K^{-1} mol^{-1}, whilst for the A reaction $\Delta S^{\ddagger} = -33 - 5 = -38$ J K^{-1} mol^{-1}. The observed values, ranging from -24 to -76 J K^{-1} mol^{-1}, appear to exclude the D-type reaction mechanism. These estimates ignore additional more specific solvent–solute contributions to $\Delta S^{\ddagger}$, but, since non-electrostatic chlorine–solvent interactions are present in both ground and transition states of both mechanisms, the sign of $\Delta S^{\ddagger}$ estimated for the D mechanism is unlikely to be reversed. We therefore exclude D mechanisms from our subsequent discussions.

Table 2 shows that variation of the $[\mathrm{H}^+]:[\mathrm{Li}^+]$ ratio at 11M total chloride causes variations in $k_{\mathrm{ex.}}$ by a factor of only 3, but there are marked differences in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for exchange in the various chloride media. Exchange in the presence of hydrochloric acid alone proceeds with a noticeably larger $\Delta H^{\ddagger}$ value and a less negative $\Delta S^{\ddagger}$ value than exchanges in the presence of H^+ and Li^+ cations. These kinetic variations are unlikely to arise from significantly different bulk-solution properties of HCl and LiCl, since the osmotic and activity coefficients, and the hydration numbers, of these species are very similar[16] in this concentration range. An exchange path involving molecular HCl

$$[\mathrm{GaCl_4}]^- + \mathrm{H^*Cl} \rightleftharpoons [\mathrm{GaCl_3^*Cl}]^- + \mathrm{HCl} \quad (9a)$$

seems excluded by the low[16] (0·3%) proportion of HCl molecules even in 10·5M-HCl.

Cationic association with $[\mathrm{GaCl_4}]^-$ might also provide two concurrent associative reaction paths, so that

$$\mathrm{H[GaCl_4]} + {}^*\mathrm{Cl}^- \rightleftharpoons \mathrm{H[GaCl_3^*Cl]} + \mathrm{Cl}^- \quad (9b)$$

$$\mathrm{Li[GaCl_4]} + {}^*\mathrm{Cl}^- \rightleftharpoons \mathrm{Li[GaCl_3^*Cl]}^- + \mathrm{Cl}^- \quad (9c)$$

observed values of $k_{\mathrm{ex.}}$ could contain different contributions from (9b) and (9c) depending on the $[\mathrm{H}^+]$ and $[\mathrm{Li}^+]$ values. However, this scheme is incompatible with the approximately constant values of $k_{\mathrm{ex.}}$ in solutions (*ix*) and (*x*) compared with the sharp rise in $k_{\mathrm{ex.}}$ in both solutions (*viii*) and (*xi*). Paths involving specific protonated species such as $\mathrm{H[GaCl_4]}$ and HCl thus seem to be excluded, in contrast to the iron(III)–chloride system for which an exchange rate law has been suggested[17] of the form Rate $= k_{\mathrm{ex.}}4[\mathrm{FeCl_4}^-]a_{\mathrm{HCl}}$. Although the formation of $\mathrm{Li[GaCl_4]}$ might be expected to reduce the activation energy for exchange with Cl^-, the expected dependence of $k_{\mathrm{ex.}}$ on $[\mathrm{Li}^+]$ is not observed, and path (9c) cannot be justified.

The different kinetic effects of H^+ and Li^+ must therefore be attributed to different influences of these ions on the secondary solvation sphere of $[\mathrm{GaCl_4}]^-$. In the $[\mathrm{GaCl_4}]^-$ system, changes in $\Delta H^{\ddagger}$ are largely compensated by changes in $\Delta S^{\ddagger}$ as is also observed for many solvent-exchange and ligand-substitution processes on a variety of metal ions,[18] but the dilute-solution model postulated by Bennetto and Caldin[18] to explain these thermodynamic variations is inapplicable to concentrated chloride solutions. In rationalising the observed kinetic parameters, it is then necessary to postulate that, although bulk-solution properties of HCl and LiCl are similar, their influence on the secondary solvation sphere of $[\mathrm{GaCl_4}]^-$ is different, with the exchange process involving an enthalpy–entropy balance for associative reactions in the different solvent media.

Exchange in 7M-*Chloride Media*.—The relative concentrations of aquachlorogallium(III) species in 7M-chloride solutions has been shown to vary as the $[\mathrm{H}^+]:[\mathrm{Li}^+]$ ratio varies. The ^{71}Ga data for 7M solutions clearly indicate a shift in the equilibria in equation (1) to the left as $[\mathrm{H}^+]$ decreases. This effect cannot be attributed to a change in the activity of water a_{w} since a_{w} is known[19] to be virtually constant in HCl–LiCl solutions in this concentration range. In the analogous iron(III)–chloride systems, the preferential formation of four-co-ordinate $[\mathrm{FeCl_3(OH_2)}]$ over six-co-ordinate $[\mathrm{FeCl_3(OH_2)_3}]$ has been proposed[17] in solutions of low a_{w}. A similar change in co-ordination number of the type $[\mathrm{GaCl_3(OH_2)_3}] \rightleftharpoons [\mathrm{GaCl_3(OH_2)}]$ has therefore been incorporated into equation (1) and this equilibrium could be influenced by the different values of a_{w} in the 7 and 11M-chloride solutions.

The existence of several gallium(III) species in solution suggests that ^{35}Cl relaxation may arise as a consequence of exchange on lower chloro-species in addition to $[\mathrm{GaCl_4}]^-$. The relaxation curves in Figure 3, however, are consistent with relaxation occurring predominantly on a single species which, on the basis of the 11M data, is most likely to be $[\mathrm{GaCl_4}]^-$. Thus whilst chloride exchange must occur on the lower chloro-species, it appears that the rate of such exchange is too small to induce significant ^{35}Cl relaxation of free chloride ion. (It should be noted, however, that in the fortuitous circumstances that chloride exchange occurs on different chloro-species at rates producing ^{35}Cl relaxation of free chloride ion, and that these exchange processes are characterised by rates differing by not more than a factor of three, and by similar activation energies,

---

[15] R. W. Gurney in 'Ionic Processes in Solution,' Dover, New York, 1953, chs. 1 and 10.

[16] R. J. Robinson and R. K. Stokes in 'Electrolyte Solutions,' 2nd edn., Butterworths, London, 1959, pp. 51, 307, 504.

[17] A. H. Zeltmann and L. O. Morgan, *J. Phys. Chem.*, 1966, **70**, 2807.

[18] H. P. Bennetto and E. F. Caldin, *J. Chem. Soc.* (*A*), 1971, 2198.

[19] E. Högfeldt and P. J. Staples, *J. Chem. Soc.* (*A*), 1971, 2074. These authors show that variation of the [HCl] : [LiCl] ratio at a constant total chloride concentration up to 6M produces no detectable variation of a_{w}.

it is unlikely that these two exchanges processes will be distinguished by observation of ^{35}Cl relaxation of free chloride ion.)

If the decrease in $k_{ex.}$ observed in the 7M solutions as $[H^+]$ decreases is attributed predominantly to the concomitant decrease in $[GaCl_4^-]$, as a first approximation, $k_{ex.}$ for the 7M solutions may be equated to $k_{ex.}$ observed in 11M-chloride media in which $[GaCl_4]^-$ predominates. If $k_{ex.} = 180 \times 10^4$ s^{-1} is chosen, it follows that the mole fraction of gallium(III) existing as $[GaCl_4]^-$ is 0·239 ([HCl] = 6·28M), 0·026 ([HCl] = 3·28, [LiCl] = 3·00M), and 0·0061 ([HCl] = 0·28, [LiCl] = 6·00M) and $10^{12}\tau_c$ (298 K) for these solutions is respectively 6·1, 66, and 240 s. These estimates of $[GaCl_4]^-$ mole fraction, and qualitatively similar ones obtained from the other 11M $k_{ex.}$ values, ignore variations in activity of the chloride ion, but they are consistent with the significant changes in the proportions of chlorogallium(III) complexes revealed by the ^{71}Ga spectra. The derived τ_c values are of a similar order of magnitude to the 11M ones and qualitatively indicate a decrease in the tumbling rate of $[GaCl_4]^-$ as $[H^+]$ decreases. A similar but less pronounced trend is also seen in the 11M data. It is possible that ion association between $[GaCl_4]^-$ and $[Ga(OH_2)_6]^{3+}$ may become important in decreasing τ_c as $[H^+]$ decreases in the 7M solutions, but in view of the qualitative origin of the derivation of τ_c further discussion is inappropriate.

The variation in activation energies for chemical exchange in 7M-chloride media (Table 2) is probably a consequence of ΔH terms associated with the equilibria in equation (1) to a large extent.

Associative mechanisms of the type envisaged in reaction (9) are not unusual in metal complexes where the maximum co-ordination number is not exhibited.[20] In view of the apparently associative solvent-exchange and ligand-substitution mechanisms observed[7,21,22] in the $[Ga(OH_2)_6]^{3+}$ and $[Ga(dmf)_6]^{3+}$ systems (dmf = *NN*-dimethylformamide), associative exchange of Cl^- with $[GaCl_4]^-$ is not unexpected. The greater lability of $[GaCl_4]^-$ compared to the lower chloro-complexes of gallium is consistent with similar trends observed in aqueous-chloride solutions of iron(III),[17] oxovanadium(IV),[23] and cobalt(II),[24] and also in the cobalt(II)–thiocyanate system.[25] Ligand exchange on the tetrahedral iron(III) and cobalt(II) chloro- and thiocyanato-species is considerably more rapid than on the coexistent hexa-aqua-, aquathiocyanato-, and aquachloro-octahedral species. This behaviour is also exhibited in the gallium(III) species. Values of $k_{ex.}$ for chloride exchange of $[GaCl_4]^-$ are in the region of 10^6 s^{-1} (298 K) whilst the corresponding rate constant for exchange of a single aqua-ligand[7] in $[Ga(OH_2)_6]^{3+}$ is $1{\cdot}8 \times 10^3$ s^{-1} (298 K). A rationalisation of this generality of behaviour is that the energetics of formation of an associative transition state are more favourable for tetrahedral species than for the sterically inhibited octahedral species.

EXPERIMENTAL

Gallium(III) stock solutions were prepared by the dissolution of gallium metal (Alfa, 99·999%) in analytical grade hydrochloric acid. All other gallium(III)–chloride solutions were prepared from gallium(III) stock solutions and analytical grade hydrochloric acid and lithium chloride. In solutions (*viii*)—(*xi*) the gallium(III) concentration varied in the range 0·10—0·30M and the hydrochloric acid concentration was accordingly varied to give 11·0M total chloride. Thus three examples of solution (*viii*) were prepared 0·10, 0·20, and 0·30M in gallium(III) and so on. In the case of solutions (*xii*)—(*xiv*), single examples of each, 0·18M in gallium(III), were prepared in 7·0M total chloride media over a range of hydrochloric acid concentrations. The reference chloride solutions were of the same total chloride and hydrochloric acid concentration as the gallium(III)–chloride solution, the total chloride concentration being adjusted with lithium chloride. The variation in ^{35}Cl linewidth of the reference solution of identical total chloride was negligible compared to the gallium(III)-induced line broadening. Hexa-aquagallium(III) perchlorate was dissolved in 1M-perchloric acid for use as a ^{71}Ga shift reference sample.

The ^{35}Cl and ^{71}Ga n.m.r. measurements were made in the first-derivative absorption mode on a Varian V4502 wide-line spectrometer at 4·170 and 2·085 and 12·978 MHz respectively at radio-frequency power levels well below saturation. Samples for ^{35}Cl measurements were sealed into 9 mm-diameter glass n.m.r. tubes, and their temperature was continuously monitored by a thermocouple inserted into a 2 mm diameter thermocouple well in the n.m.r. tube. The samples were thermostatted in the probe using a standard Varian gas-flow thermostat (±1 K). The first-derivative spectra were run in triplicate and were corrected for modulation broadening (which never exceeded 7% of the full absorption linewidth at half maximum signal amplitude) by the method of Wahlquist.[26] The ^{71}Ga first-derivative spectra were run on samples in 15 mm diameter n.m.r. tubes at 298 K and shift measurements were achieved by placing a reference sample of $[Ga(OH_2)_6][ClO_4]_3$ in 1M-HClO$_4$, sealed into a 5 mm diameter n.m.r. tube, into the larger n.m.r. tube and recording the signals arising from both solutions simultaneously. All ^{35}Cl modulation-broadening corrections and $T_{2ex.}$ curve fittings to equation (3), using standard regression-analysis procedures, were made on a CDC 6400 computer.

We thank the Australian Research Grants Committee for support.

[4/1764 *Received*, 21*st August*, 1974]

---

[20] F. Basolo and R. G. Pearson in ' Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, p. 435 *et seq.*

[21] J. Miceli and J. Stuehr, *J. Amer. Chem. Soc.*, 1968, **90**, 6967; C. Kalidas, W. Knoche, and D. Papadopoulas, *Ber. Bunsengesellschaft Phys. Chem.*, 1971, **75**, 106.

[22] W. G. Movius and N. A. Matwiyoff, *Inorg. Chem.*, 1969, **8**, 925.

[23] A. H. Zeltmann and L. O. Morgan, *Inorg. Chem.*, 1971, **10**, 2739.

[24] A. H. Zeltmann, N. A. Matwiyoff, and L. O. Morgan, *J. Phys. Chem.*, 1969, **73**, 2689.

[25] A. H. Zeltmann and L. O. Morgan, *Inorg. Chem.*, 1970, **9**, 2522.

[26] H. J. Wahlquist, *J. Chem. Phys.*, 1961, **35**, 1708.