A ^{35}Cl Nuclear Relaxation Study of the Exchange of Chloride Ion on Tetrachlorogallate(III) Ion

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Summary The rate parameters for the exchange of chloride ion on tetrachlorogallate ion in concentrated hydrochloric acid have been determined by ^{35}Cl magnetic resonance.

THE exchange modified Bloch equations have been used extensively to derive kinetic parameters for ligand exchange on paramagnetic metal ions in dilute solution from ligand nuclear relaxation data,[1-3] but the extension of this method to diamagnetic systems has been limited. We report this type of nuclear relaxation study for the exchange of chloride ion on tetrachlorogallate(III) ion over the temperature range 220·5—361·5 K.

In concentrated hydrochloric acid tetrachlorogallate(III) ion is the only detectable gallium(III) species in solution[4] and a broadening, Δ, of the single ^{35}Cl magnetic resonance line of uncomplexed, or bulk, chloride ion is observed. The magnitude of the induced ^{35}Cl relaxation is proportional to the tetrachlorogallate(III) ion concentration at constant total chloride concentration and exhibits a temperature dependence consistent with the rapid exchange of chloride between the bulk and complexed environments. No chemical shift (experimental limit of detection *ca.* 20 p.p.m.) of the bulk ^{35}Cl line of the tetrachlorogallate solutions from the ^{35}Cl line in the 11·00M hydrochloric acid reference solution is observed over the temperature and concentration ranges studied. No variation of Δ at 294 K occurs upon reduction of the spectrometer frequency from 4·170 MHz to 2·085 MHz. This is consistent with the predominant relaxation process for the ^{35}Cl nucleus occurring through interaction of the nuclear electric quadrupole moment with the electric field gradient experienced by that nucleus in the tetrachlorogallate(III) ion.[5] The two site exchange equation of Swift and Connick[1] therefore reduces to equation (1),

$$2\gamma^{-1}\Delta^{-1} = T_{2ex} = \frac{\tau_M}{P_M} + \frac{\hbar^2(e^2Qq)^{-2}}{P_M A \tau_c} \qquad (1)$$

where Δ is the difference in the bulk ^{35}Cl absorption line widths at half maximum amplitude for the pure hydro-

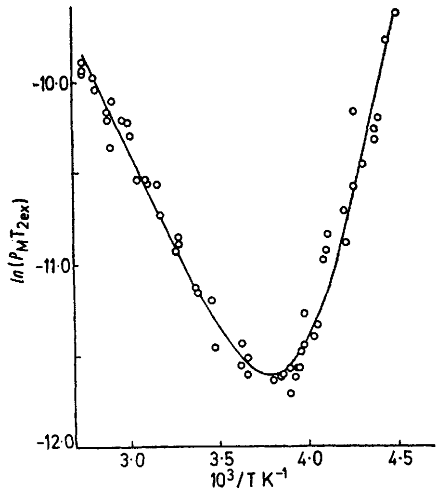

FIGURE. *Curve fit of equation* (1) *to* T_{2ex} *datum points.*

chloric acid reference solution and the tetrachlorogallate(III) ion solution, τ_M is the mean life time of a chloride ligand in tetrachlorogallate(III) ion, τ_C is the correlation time for the quadrupole induced relaxation process, P_M is the mole fraction of complexed chloride ion, and the other symbols have their usual meaning.[1,5] The T_{2ex} data derived from solutions, in which the tetrachlorogallate(III) ion concentrations were 0·30, 0·20, and 0·10 M and the total chloride concentration was adjusted to 11·00 M with concentrated hydrochloric acid, are shown in the figure. At lower temperatures the term τ_M/P_M, which characterises the chloride chemical exchange process, predominantly determines the magnitude of T_{2ex}, whereas at higher temperatures the term $\hbar^2(e^2Qq)^{-2}/(P_M A \tau_C)$ which typifies the ^{35}Cl relaxation process predominates. The solid curve in the figure represents the best fit of equation (1) to the T_{2ex} data.

The rate of chloride exchange is given by: rate = $4\,k_{298}[\mathrm{GaCl_4^-}]$ where $k_{298} = \tau_M^{-1} = (1{\cdot}8 \pm 0{\cdot}2) \times 10^6\,\mathrm{s^{-1}}$ and $\Delta H^\ddagger = 30{\cdot}1 \pm 1{\cdot}5$ kJ mol^{-1} and $\Delta S^\ddagger = -24 \pm 6$ J mol^{-1} K^{-1}. At 298 K a τ_C value of $(1{\cdot}6 \pm 0{\cdot}2) \times 10^{-11}$ s is obtained when $e^2Qq\,h^{-1}$ is equated to 32·2 MHz, the value obtained[6] for $\mathrm{Ga^+.GaCl_4^-}$. The "activation energy", E_a, for τ_C is $17{\cdot}6 \pm 1{\cdot}5$ k J mol^{-1} which is greater than that reported for pure carbon tetrachloride and titanium(IV) chloride.[7] This E_a value is similar to that reported[8] for other metal complexes in solution and may reflect a modification of the tumbling process for tetrachlorogallate(III) ion as a result of solvation.

No ^{35}Cl relaxation is observed under similar conditions for the tetrachloroaluminate(III) system in the temperature range 220·5 to 361·5 K consistent with an upper limit of $k_{361{\cdot}5} \leqslant 10^4\,\mathrm{s^{-1}}$. This is also consistent with the observed relative labilities of other ligands co-ordinated to aluminium (III) and gallium(III).[9]

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