208. The Reaction Volume for the Equilibrium between the Lanthanide(III) Ennea- and Octaaqua Ions as a Diagnostic Aid for their Water-Exchange Mechanisms

Preliminary Communication

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The equilibrium between $[Ce(H_2O)_9]^{3+}$ and $[Ce(H_2O)_8]^{3+}$ has been followed in aqueous solution at 298 K by variable-pressure UV spectroscopy at 295 nm. The derived volume of reaction for the dissociation of this enneaaqua ion is $\Delta V^0 = +10.9$ cm$^3 \cdot$ mol^{-1}. This value, together with the previously determined activation volume, $\Delta V^{\neq} = -6$ cm$^3 \cdot$ mol^{-1}, for H_2O exchange on $[Ln(H_2O)_8]^{3+}$ (Ln = Tb to Tm), allows the assignment of an associative interchange I_a mechanism on these octaaqua ions.

Advantage has recently been taken of available high-field NMR spectrometers (4.7 to 9.3 Tesla) to determine the very fast H_2O-exchange kinetics on six paramagnetic heavy lanthanide ions [1]. By combining measured ^{17}O-NMR chemical shifts, longitudinal and transverse relaxation rates, it was possible to show that the exchange rate constants k^{298} decrease regularly with the ionic radius from Tb^{3+} (5.0×10^8 s^{-1}) to Yb^{3+} (4.1×10^7 s^{-1}). Along the same lines as that used successfully to determine the solvent-exchange mechanisms on the first-row transition-metal series hexasolvato ions [2], the effect of pressure on the H_2O-exchange rates of the heavy lanthanides has been studied. The resulting $\Delta V^{\neq}$ values, close to – 6 cm$^3 \cdot$ mol^{-1}, indicate an associatively activated exchange mechanism [3]. However, for a more detailed mechanistic assignment, one should know the hydration number of the reacting ions, and to allow the distinction between I_a and A pathways, the $\Delta V^{\neq}_{\text{lim}}$ value for the limiting mechanism.

The coordination of Ln^{3+} ions in aqueous solution is certainly one of the most controversial questions of lanthanide chemistry [4]. Evidence has been accumulated recently for a hydration-number change from 9 to 8 in the middle of the lanthanide series [5]. The neutron-scattering first-order difference technique, pioneered by *Enderby* and *Neilson* [6] was applied to obtain specific information on the metal neighbourhood. Thanks to several technical improvements, it has been possible to work with reasonably dilute solutions (1 *m* or less) ensuring a complete hydration of the species in solution and also to avoid counterion coordination. A coordination number of eight (Dy: 7.9_5 and Yb: 7.8_4) was found for the two typical heavy lanthanide ions studied [7], corresponding most likely to dodecahedron or square-antiprism geometry.

The knowledge of the $\Delta V^{\neq}_{\text{lim}}$ value is linked to the availability of the reaction volumes ΔV^0 for the equilibria between ennea- and octaaqua ions for which no equilibrium studies exist to date. The electronic spectrum of Ce(III) [8] is simpler and more intense than the

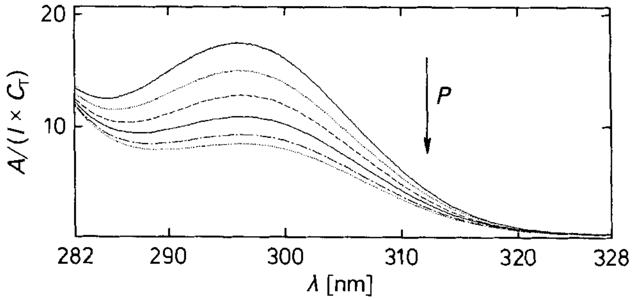

Fig. 1. *Pressure effect on the absorption spectra of a 0.0329* M *Ce(ClO$_4$)$_3$ and 0.100* M *HClO$_4$ aqueous solution at 298 K.* From top to bottom: P[MPa] = 2.2, 42.1, 80.5, 127.7, 170.8, and 200.4.

spectra of the other elements in the series [9]. In the solid state [10], the five UV absorption bands of $[Ce(H_2O)_9]^{3+}$ are assigned to 5d←4f transitions. They are due to the five *Kramers* doublets of the excited $^2D(5d^1)$ multiplet split by ligand-field interactions and spin-orbit couplings of the 5d electron in $[Ce(H_2O)_9]^{3+}$. However, in aqueous solution there is an extra week band at 295 nm ascribed to $[Ce(H_2O)_8]^{3+}$ [8]. Recently, *Kobayashi* and co-workers [11] have quantitatively interpreted the temperature dependence of these 5d←4f transitions in terms of *Reaction 1.* Their results, obtained between 5 and 55°, give

$$[Ce(H_2O)_9]^{3+} \rightleftarrows [Ce(H_2O)_8]^{3+} + H_2O \quad (1)$$

$K^{298} = 0.3$, $\Delta H^0 = +13$ kJ · mol^{-1} and $\Delta S^0 = +33$ J · K^{-1} · mol^{-1}. We have followed the decrease, with increasing pressure, of the absorption band due to $[Ce(H_2O)_8]^{3+}$ at 295 nm and 298 K *(Fig. 1)*. The molar absorptivity of the octaaqua ion ε_{295}, the equilibrium constant K, and the reaction volume ΔV^0 are related by *Eqns. 2–4,* where A_{295} is the

$$A_{295} = \varepsilon_{295} \times l \times [[Ce(H_2O)_8]^{3+}] \quad (2)$$

$$K = [[Ce(H_2O)_8]^{3+}]/(C_T - [[Ce(H_2O)_8]^{3+}]) \quad (3)$$

$$\ln K = \ln K_0 - (\Delta V^0 P/RT) \quad (4)$$

measured absorbance, l the optical pathlength, and C_T the total Ce(III) concentration. A multiparameter least-squares fitting procedure was applied to the experimental data, using *Eqns. 2–4,* leading to $\varepsilon_{295} = 99 \pm 2$M^{-1} · cm^{-1}, $K_0 = 0.21 \pm 0.03$, and $\Delta V^0 = +10.9 \pm 0.3$ cm^3 · mol^{-1}. The pressure variation of the equilibrium constants is illustrated in *Fig. 2.* The absolute partial molar volume of aqua ions in solution, in relation with their coordination number and their ionic radii, can be estimated using a semi-empirical model developed by *Swaddle* [12]. The volume difference for the two coordinances, corresponding to the dissociation of one water from $[Ce(H_2O)_9]^{3+}$ to form $[Ce(H_2O)_8]^{3+}$, has been calculated using cerium ionic radii from *Shannon* [13]. This volume is +12.8 cm^3 · mol^{-1} and agrees well with that determined experimentally. Further work is in progress to determine the thermodynamic parameters of the hydration equilibria for heavier lanthanide(III) ions for a deeper understanding of their aqueous behaviour and to obtain a more detailed picture of their H$_2$O-exchange mechanisms.

The activation volume $\Delta V^{\neq}_{\text{lim}}$ for a hypothetical limiting associative H$_2$O-exchange reaction on $[Ce(H_2O)_8]^{3+}$ should be close [2] to − 11 cm^3 · mol^{-1} according to the reaction

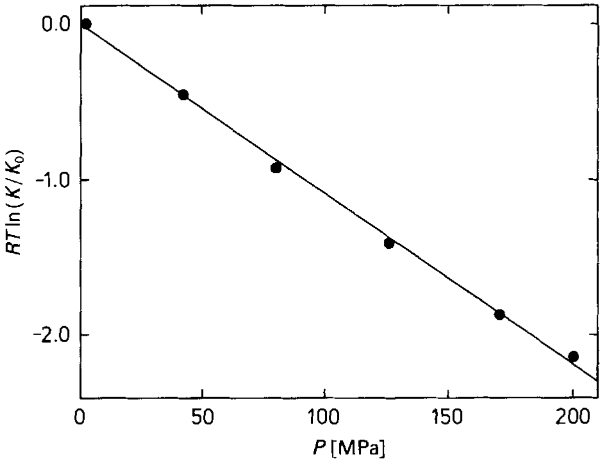

Fig. 2. *The normalised logarithm of the stability constant* K, *as a function of pressure for the reaction* $[Ce(H_2O)_9]^{3+} \rightleftarrows [Ce(H_2O)_8]^{3+} + H_2O$

volume measured for *Reaction 1*. The assumption that this reaction volume is similar along the lanthanide series, and the fact that the experimental activation volumes, – 6 $cm^3 \cdot mol^{-1}$, for the H_2O exchange on the ions $[Tb(H_2O)_8]^{3+}$ to $[Tm(H_2O)_8]^{3+}$ are clearly smaller, leads to the conclusion that the H_2O-exchange mechanisms on these octaaqua ions occurs most probably *via* a concerted I_a mechanism. The likely geometry for the ennea-coordinated transition state is a trigonal tricapped prism, since many hydrated salts of the lanthanides exhibit this structure in the solid state [5].

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Experimental. – Hydrated $Ce(ClO_4)_3$ was synthesized from Ce_2O_3 [3]. The spectrophotometric study was accomplished on a 0.0329 M $Ce(ClO_4)_3$ and 0.100 M $HClO_4$ aq. soln., with a *Perkin-Elmer Lambda 5* spectrophotometer equipped with a high-pressure optical cell (path-length: 2.1 cm) described in [14].

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