A Kinetic Investigation of Neodymium Sulphate Complexation in D_2O as a Test of the Eigen Mechanism

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Summary Since $NdSO_4^+$ formation was slowed by a factor of 2·3 in D_2O as compared with H_2O while the dissociation was accelerated, the Eigen complexation mechanism predicting cation–solvent exchange as the slow step, cannot be the controlling mechanism in lanthanoid complexation reactions.

IN recent years, complexation reactions of the lanthanoid(III) ions have been used as a probe for the solvated cations to investigate the possible existence of a solvation-number change occurring within the cationic series, based upon the assumption that the Eigen–Diebler multi-step complexation mechanism holds.[1,2] Step 12 involves the formation of a

$$M^{m+}(aq) + L^{n-}(aq) \underset{k_{31}}{\overset{k_{13}}{\rightleftharpoons}} M^{m+}(H_2O)_xL^{n-} \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} ML^{m-n}(aq) \quad (1)$$

Step 12 Step III

diffusion-controlled outer-sphere complex followed by ligand desolvation. Step III, the slow step, involves water loss from the solvation shell of the cation and rapid bond-formation between the cation and the ligand. Efforts to establish the validity of this mechanism for the rare earths have been limited to attempting to establish the independence of the complexation rate for each cation with different ligands[3–7] and to demonstrating the multi-step character of the complexation reactions.[8] The complexation between Nd^{III} and SO_4^{2-} was investigated in detail in D_2O and H_2O as a test to see if the slow step involves water loss from the inner solvation shell of the cation as the rate-determining process, as required by the Eigen mechanism.

The stock solutions were made by dissolving Nd_2O_3 in D_2O and D_2SO_4 or H_2O and H_2SO_4, respectively. The ultrasonic measurements were made using the techniques and equipment described earlier.[8] An excess of absorption was found in the frequency range 10—170 MHz for all of the solutions studied, and the data could only be explained on the assumption that at least two relaxations are present, with the relaxation frequencies attributed to Step 12 outside the experimental frequency range.

The relaxation time of the slow step, assumed to be Step III in the Eigen mechanism,[4–8] is given by

$$\tau_{III}^{-1} = 2\pi f_{R(III)} = k_{43} + k_{34}\phi\,(c) \quad (2)$$

The general form of ϕ (c) given by Tamm,[9] has been modified for lanthanoid systems. A restraint is placed on the possible values of k_{34} and k_{43} to the extent that $K_{III} = k_{34}/k_{43}$ must be consistent with the overall association constant, K_C, given by:

$$K_C = K_{12}\,(1 + K_{III}) \quad (3)$$

The rate constants were calculated through iterative methods using equations (2) and (3) with K_C in H_2O equal to 4367.[4] For solutions of equivalent concentrations, the high-frequency absorption data were identical in H_2O and D_2O, indicating that K_{12} is independent of these two solvents. In H_2O, $k_{34} = 1{\cdot}9 \times 10^8\ s^{-1}$, $k_{43} = 4{\cdot}8 \times 10^7\ s^{-1}$, and $K_{12} = 900$. In D_2O, the H_2O value of K_{12} was assumed, and $k_{34} = 0{\cdot}80 \times 10^8\ s^{-1}$, $k_{43} = 7{\cdot}1 \times 10^7\ s^{-1}$, and $K_C = 1920$. The rate constants in H_2O had an error of approximately $\pm 10\%$ and a somewhat greater error in D_2O due to the scatter caused by the presence of residual H_2O.

Since Step 12, postulated to involve sulphate desolvation, was unaffected by switching solvents, this indicated relatively weak sulphate–solvent interactions. However, for Step III, involving cation–solvent exchange, k_{34} decreased by a factor of 2·3 in D_2O as compared with H_2O, indicating hydrogen-bond breakage in the complexation

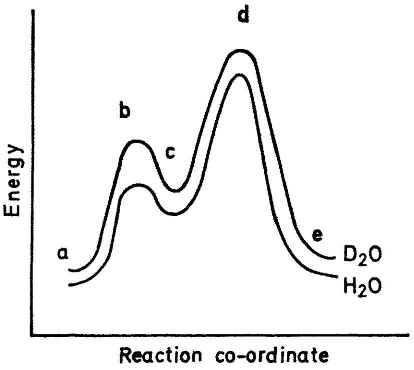

FIGURE *Free-Energy Diagram*: (a) solvent-separated outer-sphere complex; (b) activated complex for cation–solvent exchange; (c) complex with water lost; (d) activated complex for cation–ligand bond formation, resembling (e); (e) solvated inner-sphere complex.

step. Since the lanthanoid(III)–solvent interactions are known to extend beyond the primary solvation shell, with hydrogen bonding occurring between the solvated cation and the secondary solvation layer,[10] at least one hydrogen bond must be broken as a water molecule leaves the inner solvation shell of the cation. If bond formation between the solvated cation and the ligand is rapid compared to the solvent exchange rate, then a similar D_2O effect would be expected for the reverse step. However, the dissociation reaction was found to be even more rapid in D_2O than H_2O. Using the free-energy diagram in the Figure, the following mechanism is postulated. The first peak corresponds to a rapid cation–solvent exchange equilibrium, involving the breakage of at least one hydrogen bond in the activated complex. This is followed by the slower attachment of the ligand to the cation, which does not involve the breaking of hydrogen bonds in the activated complex, resulting in the same forward and reverse rates for this step in both solvents. k_{43} was larger in D_2O than H_2O, reflecting experimental error or small differences in the respective free energies of the solvated inner sphere complex and the activated complex in the two solvents. These results are consistent with those summarized elsewhere,[11] indicating that the suggested ligand-assisted complexation mechanism is the general one for lanthanoid complexation. Since the cation–solvent exchange is not the slow step in the complexation sequence, care must be exercised not to compare the magnitudes of k_{34} within the cationic series in an effort to establish the solvation number change, since k_{34} is not exclusively a function of the solvated cation.

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[1] H. Diebler and M. Eigen, *Z. phys. Chem. (Frankfurt)*, 1959, **20**, 299.
[2] M. Eigen and K. Tamm, *Z. Elektrochem.*, 1962, **66**, 93, 107.
[3] G. Geier, *Ber. Bunsenges. Phys. Chem.*, 1965, **69**, 617; H. B. Silber and J. H. Swinehart, *J. Phys. Chem.*, 1967, **71**, 4344; A. J. Graffeo and J. L. Bear, *Inorg. Nuclear Chem.*, 1968, **30**, 1577. H. B. Silber, R. D. Farina, and J. H. Swinehart, *Inorg. Chem.*, 1969, **8**, 819.
[4] D. P. Fay, D. Litchinsky, and N. Purdie, *J. Phys. Chem.*, 1969, **73**, 544.
[5] R. Garnsey and D. W. Ebdon, *J. Amer. Chem. Soc.*, 1969, **91**, 50.
[6] D. P. Fay and N. Purdie, *J. Phys. Chem.*, 1970, **74**, 1160.
[7] J. J. Grecsek, Ph.D. Thesis, Univ. of Maryland, College Park, 1970.
[8] H. B. Silber, J. J. Grecsek, G. Atkinson, and N. Scheinen, submitted to *Inorg. Chem.*
[9] K. Tamm, "Dispersion and Absorption of Sound by Molecular Processes," ed. D. Sette, Academic Press, New York, 1963, pp. 175—222.
[10] G. W. Brady, *J. Chem. Phys.*, 1960, **33**, 1079.
[11] K. Kustin and J. Swinehart in *Progr. Inorg. Chem.*, 1970, **13**, 107.