A Study of Ionic Association in Aqueous Lanthanide Nitrate Solutions by Ultrasonic Absorption Spectroscopy[1]

R. Garnsey[2a] and D. W. Ebdon[2b]

Contribution from the Department of Chemistry, University of Maryland, College Park, Maryland 20740. *Received June 10, 1968*

Abstract: Ultrasonic absorption measurements over a frequency range of 10–250 MHz are reported for some trivalent lanthanide nitrates, perchlorates, and chlorides in aqueous solution. Thermodynamic and kinetic parameters for the formation of MNO_3^{2+} complexes of neodymium and gadolinium have been determined. The approximations and assumptions made in this calculation are discussed. Changes in relaxation frequency with cation across the lanthanide series are discussed in terms of changes in cation coordination number.

Ultrasonic absorption measurements have been used extensively in the study of association behavior of bi-bivalent electrolytes and the results have been comprehensively reviewed.[3] The excess sound absorption in these solutions is attributed to a multistate association process. For magnesium sulfate Eigen and coworkers[4,5] have quantitatively interpreted the absorption in terms of a four-state association in which the solvated ions form solvent-separated ion pairs in which two intervening water molecules are successively replaced to form a contact ion pair.

The lanthanide nitrates show maxima in excess absorption per wavelength (μ) at frequencies between 10 and 100 MHz which are not observed for the chlorides or perchlorates. This considerable excess relaxational absorption is interpreted in terms of a three-state model illustrated in eq 1, where c = stoichiometric concentration and σ is the degree of dissociation.

$$\begin{array}{lccccccc}
 & & & \text{step I} & & \text{step II} & & \\
 & \text{solvated} & & & \text{solvent-} & & \text{contact} & \\
 & \text{ions} & & & \text{separated} & & \text{ion} & \\
 & & & & \text{ion pairs} & & \text{pairs} & \\
 & M^{3+} & + NO_3^- & \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} & \underbrace{M^{3+}\cdots NO_3^- \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} MNO_3^{2+}}_{} & & & (1) \\
\text{equil concn} & \sigma c & (2+\sigma)c & & (1-\sigma)c & & &
\end{array}$$

This is the simplest model consistent with the experimental data. The excess absorption can be represented to within experimental accuracy by a single relaxation process (one which may be characterized by a single time constant or relaxation time) and is attributed to step II. Evidence of the existence of lanthanide nitrate contact ion pairs has recently been published.[6] Lanthanide sulfates show a similar excess absorption which also has been interpreted in terms of contact ion pairing. The sulfate absorption is, however, considerably more complex, and quantitative interpretation is correspondingly less certain.

Provided that a relaxational absorption can be described by a single relaxation time (τ), only two parameters, μ_{max}, the maximum absorption per wavelength, and τ (or f_R the relaxation frequency), are necessary to completely specify behavior in the region of the relaxation. There is a fundamental difference between these two quantities; μ_{max} is related to thermodynamic quantities while f_R is determined by the kinetics of the system.

The variation of μ_{max} with concentration is used to determine $K_A\pi_f$, the apparent association constant for the over-all process shown in eq 1, at several concentrations, and K_A at zero ionic strength is estimated. To minimize the effect on μ_{max} of the anticipated but unknown variation of the activity coefficient product π_f with ionic strength, experiments were performed at constant stoichiometric cation concentration, varying the nitrate ion concentration by replacing it with perchlorate ion. The validity of this precedure is open to question, but it is our contention that errors so introduced are small, much smaller than those which would result from either ignoring variations in π_f or attempting to estimate variations from theoretical equations of the Debye–Hückel type.

The variation of τ with concentration is used to determine kinetic parameters of the system, in this instance k_{23} and k_{32}. The calculation requires a knowledge of the equilibrium concentrations of all species present and the concentration dependence of π_f. To perform similar calculations for the bi-bivalent salts,[7] it was necessary to use theoretical equations of the Debye-Hückel and Bjerrum type to estimate the required activity coefficients and association constants. Use of such equations may be justly criticized on two counts. First, there is the conceptual difficulty of employing equations which suppose the solvent to be a continuum to describe a process which recognizes the molecularity of the solvent. Second, the use of thermodynamic activity coefficients, which suppose the ion atmosphere to be in equilibrium, to describe ionic diffusion processes, which must occur at a rate comparable with the ion atmosphere relaxation,[8] is certainly invalid. Such equations may adequately describe diffusion-controlled association under certain limiting conditions, but they are not applicable to solutions of 3:1 electrolytes at the concentrations we are considering. We have used, instead, the results of our investigation

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[2] (a) Central Electricity Research Laboratories, Leatherhead, England; (b) Department of Chemistry, Eastern Illinois University, Charleston, Ill. 61920.

[3] J. Stuehr and E. Yeager, "Physical Acoustics," Vol. II, Part A, W. P. Mason, Ed., Academic Press, New York, N. Y., 1963, p 424.

[4] H. Diebler and M. Eigen, *Z. Physik. Chem.* (Frankfurt), 20, 299 (1959).

[5] M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 93, 107 (1962).

[6] I. Abrahamer and Y. Marcus, *Inorg. Chem.*, **6**, 2103 (1967).

[7] G. Atkinson and S. Petrucci, *J. Phys. Chem.*, 70, 3122 (1966).

[8] M. Eigen, *Discussions Faraday Soc.*, **24**, 25 (1957).

of μ_{max}. Thus a self-consistent analysis of the association behavior has been obtained from ultrasonic measurements without recourse to theoretical expressions or to results of independent experiments.

The uncertainties indicated above contribute to errors in the rate constants k_{23} and k_{32} which are difficult to determine quantitatively. The errors are unfortunately too large to permit meaningful comparisons to be made within the lanthanide series. The relaxation frequencies, however, do show a trend with cation across the lanthanide series, which is similar for both nitrates and sulfates. This trend is at least consistent with the supposition[9,10] that there is a change in average cation coordination across the lanthanide series.

Experimental Section

Apparatus. Ultrasonic absorption measurements were made at selected frequencies between 10 and 250 MHz using the pulse technique.[11] The procedure was similar to that used by other investigators.[7,12] The pulser-receiver was a Matec Model PR 201. The comparator and standard attenuator system was a Hewlett-Packard Model 608D. Frequencies were measured with a Gertsch frequency meter, Model FM 3.

The interferometer cell permitted a path-length change of up to 5 cm. The movable transducer and delay rod assembly could be replaced by a reflecting plate, permitting the cell to be used in a reflecting mode, thus doubling the variable path length. The cell was used in this mode for the low-frequency measurements on the more dilute solutions where the absorption is very low. The cell had double walls through which water was circulated from a thermostated tank. The temperature of the solution samples was maintained at 25 ± 0.05°.

The calibration of the apparatus was checked by determining the absorption of doubly distilled water over the entire frequency range. The values of α/f^2 (absorption coefficient over frequency squared) were constant over the frequency range to within $\pm 0.5 \times 10^{-17}$ cm^{-1} sec^2. The average value was 21.7×10^{-17} cm^{-1} sec^2. This value compares very well with the water value at 25° obtained by interpolation of Pinkerton's[11] data.

The sound velocity in gadolinium and neodymium nitrate solutions was precisely determined by the sing-around technique[13] in Dr. Litovitz's laboratory at the Catholic University of America. The velocity in the most concentrated solution was less than 0.2% above the pure water value. The velocity was therefore taken as constant and equal to 1500 m sec^{-1}.

Solutions. All solutions were made up with deionized, distilled water. Stock solutions were prepared at approximately the required concentration by weight. The solutions were analyzed to determine the cation concentration by an ion-exchange method.

Samples of the salt solutions were passed through columns containing Dowex 50 cation-exchange resin. The resulting acid solutions were titrated against standardized NaOH solution. Three samples were analyzed and a mean value was taken. The analysis was repeated if the three did not agree to within 0.5%. Solutions were then made up to the required concentration by accurate dilution.

Salts. The nitrates of La, Nd, Sm, Gd, and Er and the chlorides of Nd and Gd were obtained from American Potash and Chemical Corp., 99.9% pure, and used without further purification.

Solutions of the nitrates of Pr, Eu, Dy, and Yb and the perchlorates of Nd and Gd were prepared by dissolving the corresponding oxide (Bernard Ring, Inc., 99.9%) in a calculated amount of acid. Excess oxide was removed by filtration. The pH of all solutions was checked to ensure that they did not contain excess acid.

Results

Both the determination of the absorption parameters, μ_{max} and f_R, and their subsequent analysis depend on the assumption that step I is much faster than step II, that a single relaxation is observed, and that any excess absorption caused by step I is negligible. A theoretical estimation[14] of the rate constants for a diffusion-controlled association predicts f_R for step I between 500 and 1000 MHz, depending on choice of parameters. This is an order of magnitude higher than the relaxation process observed. To assess the second and third assumptions, the absorption data for gadolinium nitrate were fitted to eq 2 (where α = absorption coefficient, f = frequency, and f_R = relaxation frequency), which is a dispersion curve for a single relaxation process.[15]

$$\frac{\alpha}{f^2} = \frac{A}{1 + (f^2/f_R^{\,2})} + B \qquad (2)$$

The parameter A is expected to increase with concentration. B is expected to be constant and close to the value for pure water. Data at each concentration were fitted by the method of least squares to obtain the optimum set of values of A, B, and f_R. The values of B obtained were close to the water value but increased slightly with concentration. This is the anticipated behavior if step I causes a slight absorption. Differences between B and the pure water value were considered negligible, being always less than 1% of A. Analyses were carried out with B constant and equal to the pure water value of 21.7×10^{-17} cm^{-1} sec^{-2}.

The lanthanide nitrates hydrolyze slightly in water; consequently, the pH of the solutions varied between 4.5 and 5.2 over the concentration range investigated. To check the dependence of absorption on pH, the pH of a 0.2 M solution of neodymium nitrate was reduced to about 1 by the addition of $HClO_4$ and its absorption spectrum measured. No significant change was observed.

The excess absorption per wavelength is given by the equations

$$\mu = (\alpha_{solution} - \alpha_{solvent})u/f \qquad (3)$$

$$\mu = \frac{\pi\beta_R}{\beta_0}\,\frac{f/f_R}{1 + (f^2/f_R^{\,2})} \qquad (4)$$

where u = velocity of sound, β_R = relaxational contribution to the compressibility, and β_0 = compressibility of the pure solvent.

Figures 1 and 2 show plots of μ against f for neodymium and gadolinium nitrate solutions, respectively.[16] The full line is the single relaxation curve. Table I lists the values of μ_{max} and f_R.

The chlorides and perchlorates of neodymium and gadolinium showed no relaxational absorption in the frequency range studied. At comparatively high concentrations the α/f^2 values are higher than the pure water value, but no variation with frequency was observed. Table II shows the average α/f^2 values obtained at several concentrations.

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(9) T. Moeller, *et al.*, *Chem. Rev.*, **65**, 1 (1965); *J. Inorg. Nucl. Chem.*, **27**, 1477 (1965).

(10) F. H. Spedding, *et al.*, *J. Phys. Chem.*, 70, 2423, 2430, 2440, 2450 (1966); *J. Am. Chem. Soc.*, 76, 879, 882, 884 (1954).

(11) J. M. M. Pinkerton, *Proc. Phys. Soc.* (London), **B62**, 129, 286 (1949).

(12) N. Purdie and C. A. Vincent, *Trans. Faraday Soc.*, **63**, 2745 (1967).

(13) R. Garnsey, *et al.*, to be submitted for publication.

(14) M. Eigen and L. De Maeyer in "Technique of Organic Chemistry," Vol. VIII, Part 2, A. Weissberger, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p 1032.

(15) J. Lamb in ref 3, p 207.

(16) Tabulated experimental data available from authors on request.

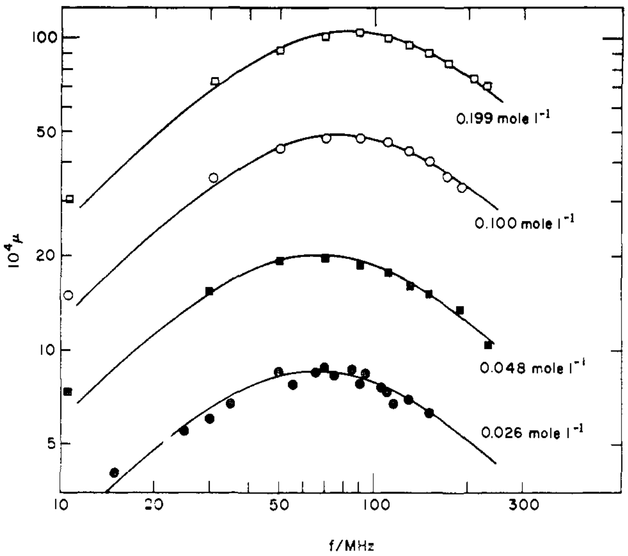

Figure 1. μ against f for $Nd(NO_3)_3$ solutions.

Table I. μ_{max} and f_R for Neodymium and Gadolinium Nitrate Solutions

	c, mole l.$^{-1}$	f_R, MHz	$10^4\mu_{max}$
$Nd(NO_3)_3$	0.026$_0$	66 ± 2	8.4
	0.048	67 ± 2	19.4
	0.100	78 ± 2	47.8
	0.199	82 ± 2	104
$Gd(NO_3)_3$	0.050	40 ± 2	6.0
	0.100	43 ± 2	14.1
	0.174	48 ± 2	27.3
	0.200	49 ± 2	31.5
	0.350	52 ± 2	61.5

Table II. $10^{17}\alpha/f^2$ (cm^{-1} sec^2) for Chlorides and Perchlorates

	Cl^-		ClO_4^-	
	0.2 M	0.4 M	0.2 M	0.4 M
Nd^{3+}	22.0	24.5	22.0	23.5
Gd^{3+}	24.5	27.5	23.0	26.0

Water value = 21.7

Analysis of μ_{max}. In aqueous solutions absorption resulting from the temperature wave associated with the sound wave is in general negligible[17] compared with that resulting from the pressure wave, and the following approximation for β_R may be made.

$$\beta_R = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S \approx -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{5}$$

From eq 4 and 5 the following expression for μ_{max} is obtained. For a discussion of approximations, see Tamm.[18]

$$\mu_{max}/C_A = \gamma(1 - \gamma)(\Delta V_{II})^2\frac{\pi}{2RT\beta_0} \tag{6}$$

C_A is the equilibrium concentration of all associated species and $(1 - \gamma)$ is the degree of reaction II. ΔV_{II} is the change in volume per mole for step II.

$$K_{II} = \frac{k_{23}}{k_{32}} = \frac{1 - \gamma}{\gamma} \tag{7}$$

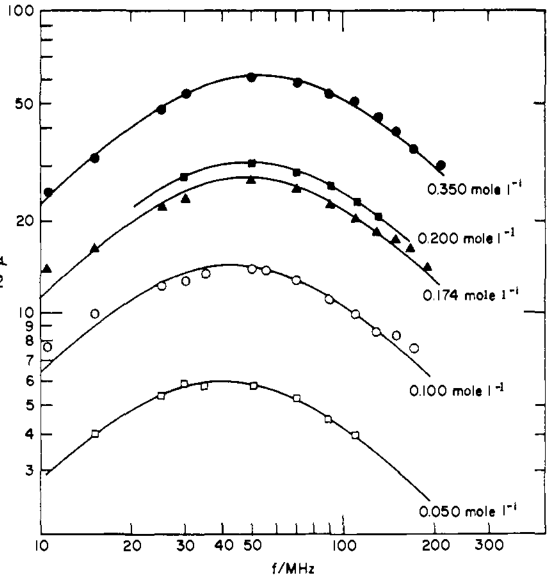

Figure 2. μ against f for $Gd(NO_3)_3$ solutions.

K_{II} is the equilibrium constant for step II. Provided step I is very much faster than step II, C_A is related to the stoichiometric concentration and the apparent association constant by the equations

$$C_A = (1 - \sigma)c \tag{8}$$

$$K_A\pi_f = \frac{1 - \sigma}{\sigma(2 + \sigma)c} \tag{9}$$

σ and hence C_A can only be evaluated as a function of c provided $K_A\pi_f$ is known as a function of c. If, however, experiments are performed in which the ratio (r) of nitrate to cation is varied while c and the ionic strength are retained constant, eq 9 becomes

$$K_A\pi_f c = (1 - \sigma)/\sigma(r - 1 + \sigma) \tag{10}$$

where $K_A\pi_f c$ is now constant for all r.

One condition which follows from eq 6 is that μ_{max}/C_A is a constant for all r. If, therefore, μ_{max} is determined for several values of r, both $K_A\pi_f$ and μ_{max}/C_A are determined as the values which fulfill this condition.

To achieve the above experimental conditions, mixtures of perchlorate and nitrate were prepared varying the ratio of nitrate to perchlorate while maintaining the cation concentration constant. This procedure is of course only valid provided that the perchlorate absorption is negligible and that replacement of nitrate by perchlorate does not significantly alter the conditions which determine $K_A\pi_f$. The first provision is certainly valid for the neodymium salts. It is not quite such a good approximation for gadolinium. The second can never be completely true, even if differences in specific interactions are ignored, since it requires two incompatible conditions: that the perchlorate is completely dissociated and that the ratio of dissociated-to-undissociated ions remain constant.

However, the reasonableness of the results suggests errors are small, or at least some cancellation occurs.

Table III lists μ_{max} for several values of r and the "best fit" values of μ_{max}/C_A and $K_A\pi_f$ for 0.2 M nitrate–perchlorate mixtures. For the neodymium solutions the table also illustrates the trend in μ_{max}/C_A for values

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[17] See ref 3, p 384.

[18] K. Tamm, "Dispersion and Absorption of Sound by Molecular Processes," D. Sette, Ed., Academic Press, New York, N. Y., 1963.

Table III. Variation of $\mu_{\max}$ with r and Dependence of $\mu_{\max}/C_A$ on $K_A\pi_f$ for 0.2 M Nitrate–Perchlorate Mixtures

	$Nd(NO_3)_r(ClO_4)_{3-r}$	$Nd(NO_3)_r(ClO_4)_{3-r}$ $10^3\mu_{\max}/C_A$, l. mole^{-1} $K_A\pi_f$ =			$Gd(NO_3)_r(ClO_4)_{3-r}$	$Gd(NO_3)_r(ClO_4)_{3-r}$ 10^3 $\mu_{\max}/C_A$, l. mole^{-1} $K_A\pi_f$ =
r	$10^4\mu_{\max}$	4.0	3.33^a	2.5	$10^4\mu_{\max}$	3.0^a
0.5	30.1	76.5	85.0	100.6		
1	53.2	77.5	85.2	99.4	15.8	26.6
2	85.0	78.8	85.2	97.0	25.3	26.5
3	104.0	79.7	84.9	94.5	31.5	26.6

^{a} Best fit.

of $K_A\pi_f$ above and below the best fit value. Having obtained a value for the constant $\mu_{\max}/C_A$, the C_A values for the pure nitrate solutions were calculated for various values of c from the corresponding $\mu_{\max}$ values. Then from eq 8 and 9 σ and $K_A\pi_f$ were calculated as a function of c. Table IV lists the values obtained. K_A was determined by extrapolation of a plot of ln $K_A\pi_f$ against the square root of the ionic strength. This plot was linear to within experimental accuracy for concentrations below 0.2 mole l^{-1}. A knowledge of $\mu_{\max}/C_A$ permits the minimum possible value of ΔV_{II} to be determined from eq 6 since $\gamma(1-\gamma)$ can never be greater than 0.25.

Table IV. $K_A\pi_f$ as a Function of Concentration

	c, mole l.$^{-1}$	σ	$K_A\pi_f$, l. mole^{-1}
$Nd(NO_3)_3$	0		17 ± 2^a
	0.0260	0.623	8.81
	0.048	0.521	7.63
	0.100	0.444	5.07
	0.199	0.387	3.33
$Gd(NO_3)_3$	0		15 ± 2^a
	0.050	0.587	6.40
	0.100	0.470	4.57
	0.174	0.411	3.41
	0.200	0.408	3.01
	0.350	0.339	2.38

^{a} Extrapolation.

Analysis of f_R. The relationship between relaxation times and the kinetic parameters for multistep processes has been discussed by several workers.[5,19,20] In general the individual steps are coupled; consequently relaxation times are not related in any simple way to individual reactions. However, for a two-step process in which step I is very much faster than II, the following relationships are obtained[18]

$$\tau_I^{-1} = k_{21} + k^0_{12}\theta(c) \tag{11}$$

$$\tau_{II}^{-1} = k_{32} + k_{23}\Phi(c) \tag{12}$$

where

$$\Phi(c) = k^0_{12}\theta(c)/[k_{21} + k^0_{12}\theta(c)]$$
$$= K_I\theta(c)/[1 + K_I\theta(c)] \tag{13}$$

and K_I is the association constant for step I. $\theta(c)$ depends on the equilibrium activities of the free ions.

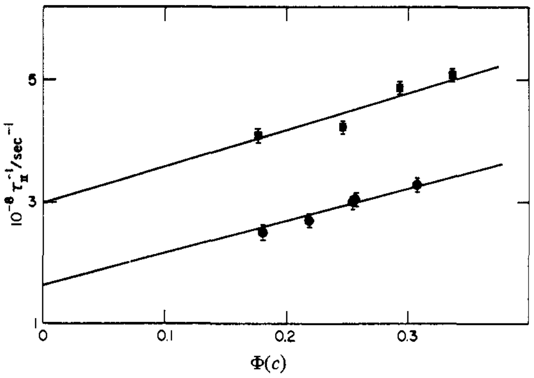

Figure 3. τ_{II}^{-1} against $\Phi(c)$: (■) $Nd(NO_3)_3$ taking K_{II} = 2, full line is $10^{-8}\tau_{II}^{-1} = 3 + 6\Phi(c)$; (●) $Gd(NO_3)_3$ taking K_{II} = 3, full line is $10^{-8}\tau_{II}^{-1} = 1.67 + 5\Phi(c)$.

For a 3:1 electrolyte it is given by the following equation

$$\theta(c) = \pi_f c\left[2 + 2\sigma + (2 + \sigma)\frac{\partial \ln \pi_f}{\partial \ln \sigma}\right] \tag{14}$$

As already indicated, the relaxation process corresponding to τ_I is not observed. If τ_{II} is measured as a function of concentration, k_{23} and k_{32} can be determined as the slope and intercept of a plot of τ_{II}^{-1} against $\Phi(c)$ provided $\theta(c)$ can be evaluated and K_I estimated. $\theta(c)$ was evaluated from the parameters listed in Table IV. Differentiation of eq 9 gives the expression

$$\left(\frac{\partial \ln \pi_f}{\partial \ln \sigma}\right)_c = \frac{1}{2}\frac{\sigma}{1 + \sigma}\ln \pi_f \tag{15}$$

which was used to evaluate the differential term. The uncertainty in this term is quite large, since evaluation of π_f at a given concentration involves the value of K_A obtained by extrapolation. However, the resulting error in $\Phi(c)$ is certainly no larger than would result either by ignoring this term or estimating its value from the Debye-Hückel theory.[21] K_I is related to K_A and the rate constants k_{32} and k_{23} by the equations

$$K_A = K_I(1 + K_{II}) \tag{16}$$

$$K_{II} = k_{23}/k_{32} \tag{17}$$

From our value of K_A, K_I was chosen such that the values of k_{23} and k_{32} obtained from the slope and intercept of a τ_{II}^{-1} against $\Phi(c)$ plot were consistent with eq 16 and 17. This procedure unfortunately does not produce a unique "best fit" of the experimental data. Figure 3 shows the plots of τ_{II}^{-1} against $\Phi(c)$. For the neodymium nitrate plot, K_I = 5.67 l. mole^{-1} corresponding to K_{II} = 2. These data could also have been fitted to within experimental uncertainty with K_{II} = 1 or 3. This uncertainty is, however, no larger than would result by estimating K_I from the Bjerrum theory and an arbitrary choice of the ion size parameter.[7]

From the value of K_{II} so obtained, γ can now be calculated from eq 7, and ΔV_{II} is evaluated from eq 6. Since the volume change for step I is assumed to be

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(19) G. W. Castellan, *Ber. Busenges. Physik. Chem.*, 67, 898 (1963).

(20) G. Schwarz, *Rev. Mod. Phys.*, 40, 206 (1968).

(21) Reference 3, p 388.

negligible, ΔV_A for the over-all association process may be calculated from the equation

$$\Delta V_A = \Delta V_I + \frac{K_{II}}{1 + K_{II}} \Delta V_{II} \tag{18}$$

Table V lists the thermodynamic and kinetic parameters obtained for the gadolinium and neodymium nitrates.

Table V. Thermodynamic and Kinetic Parameters for Formation of MNO_3^{2+} Complexes of Neodymium and Gadolinium at 25°

	$Nd(NO_3)_3$	$Gd(NO_3)_3$
K_I, l. mole^{-1}	6 ± 3	4 ± 2
K_{II}	2 ± 1	3 ± 1
K_A, l. mole^{-1}	17 ± 2	15 ± 2
k^0_{12}, sec^{-1} mole^{-1} [a]	4×10^{10}	4×10^{10}
k_{21}, sec^{-1}	7×10^9	1×10^{10}
k_{23}, sec^{-1} [b]	$(6 \pm 2) \times 10^8$	$(5 \pm 1.5) \times 10^8$
k_{32}, sec^{-1} [b]	$(3 \pm 0.5) \times 10^8$	$(1.7 \pm 0.2) \times 10^8$
ΔV_I, ml mole^{-1}	0	0
$\lvert\Delta V_{II}\rvert$, ml mole^{-1}	16.6	10.2
$\lvert\Delta V_A\rvert$, ml mole^{-1}	11	7.7

[a] Calculated from Debye equation (P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942)); Stokes–Einstein relationship used for ionic diffusion coefficients. [b] Error resulting from uncertainty in K_A and K_{II}.

The absorption spectra of lanthanum, praseodymium, samarium, europium, dysprosium, erbium, and ytterbium nitrates were determined at 0.2 mole l.$^{-1}$. The values of f_R and μ_{max} which were obtained are given in Table VI. The relaxation frequencies are plotted against cation atomic number in Figure 4 together with the values for the lanthanide sulfates obtained by Purdie and Vincent[12] and by Grecsek.[22]

Table VI. μ_{max} and f_R for 0.2 *M* Lanthanide Nitrate Solutions at 25°

Cation	f_R, MHz	$10^4\mu_{max}$	c, mole l.$^{-1}$
La	40 ± 2	49.5	0.200
Pr	68 ± 2	80.3	0.215
Nd	82 ± 2	104	0.199
Sm	80 ± 2	80.8	0.200
Eu	60 ± 2	41.5	0.189
Gd	52 ± 2	31.5	0.200
Dy[a]	37 ± 2	11.6	0.200
Er[a]	20 ± 2	12.5	0.209
Yb[a]	28 ± 3	14.5	0.200

[a] Background, *B*, taken as 23×10^{-17} cm^{-1} sec^2.

Discussion

Inorganic complexation reactions[23] of the type

$$M^{z+}(H_2O)_n + X^-(aq) \rightleftharpoons [MX(H_2O)_m]^{z-1} \tag{19}$$

still seem to be discussed in terms of whether M forms an inner- or outer-sphere complex with X. These terms can only refer to limiting cases of association behavior in solution. If inner sphere refers to complexes in which X occupies a position in the first coordination sphere of M and outer sphere to those in which X is in the second or some other coordination sphere, then in general both such complexes are present in solution. It is therefore necessary to specify the ratio of the two and the ratio of associated species to unassociated ions in any discussion of the reaction.

The existence of an ultrasonic absorption for dilute lanthanide nitrate and sulfate[12] solutions indicates that the ratio of "inner" to "outer" sphere complex is close to unity. The absence of an equivalent absorption for the corresponding chloride and perchlorate solutions suggests that for these solutions the concentration of inner-sphere lanthanide complexes is very low. There are, however, other possible explanations for very low absorbance; for example, the volume change for the reaction (see eq 6) may be small. Obviously corresponding absorptions would not have been observed if they occur at frequencies below the range investigated. This possibility is, however, considered unlikely since it would imply that lanthanide complexes with chloride and perchlorate are more stable than those with nitrate or sulfate.

The values of the apparent association constants obtained for gadolinium and neodymium nitrate are considered reasonable. They compare very well with the corresponding quantities for some other lanthanide nitrates obtained by a solvent extraction technique.[24]

The rate constant k_{23} is interpreted as the rate of exchange of a water molecule in the first coordination sphere of the cation with a ligand in the second coordination sphere. k_{32} is the rate for the reverse process. Investigations[25] of numerous related systems indicate that the rate-determining step for k_{23} is the loss of water from the first coordination sphere. For a given cation k_{23} is therefore expected to be approximately, though not necessarily completely, independent of the ligand. For the gadolinium salts the value we obtain for the water–nitrate exchange rate, 5×10^8 sec^{-1}, is comparable with the water–murexide rate, 1×10^8 sec^{-1} l. mole^{-1}, obtained by Geier,[26] using a "temperature-jump" technique, and with the water–water exchange rate, 9×10^8 sec^{-1} (assuming a coordination number of 9), obtained by Marianelli,[27] using an nmr–esr technique. Considering the differences in the experimental techniques and the naiveté of the model, the differences in these results are, perhaps, not surprising. A more sophisticated comparison of ligand–water exchange rates with water–water exchange rates should include a statistical correction factor, or some other correction for the competition between ligand and water for the vacated site in the first coordination sphere of the cation. Comparison of k_{23} with Geier's $\vec{k}$ should not be pressed too far, but we believe the difference between them would be even less if his $\vec{k}$ values were corrected for activity terms (π_f). In the method used low concentrations of lanthanide murexide were investigated in a swamping (0.1 *M* KNO_3) electrolyte medium, and in the calculations activity terms were ignored. Although a swamping medium may ensure that π_f does not vary significantly with murexide concentration, its value may not be assumed to be unity. It will be considerably less. Correction for this would give higher values for $\vec{k}$. Geier also chose to ignore the

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(22) J. J. Grecsek, M.S. Thesis, University of Maryland, 1966.

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slight differences in the rate constants which were observed when the swamping medium was changed from nitrate to chloride, a difference this investigation suggests should be observed since, at the concentration investigated, the nitrate ion could well be effectively competing with the murexide for the lanthanide ion.

The limiting process determining k_{32} is presumably the loss of the ligand from the first coordination sphere of the cation. k_{32} will therefore be dependent on the nature of the ligand. If k_{23} is assumed to be independent of the ligand, it follows from eq 17 that k_{32} is inversely proportional to the ratio of inner- to outer-sphere complex. Thus k_{32} is an indication of a ligand's ability to compete with the solvent for a given cation.

Both k_{23} and k_{32} should be dependent on the nature of the cation. Geier[26] has discussed changes in $\vec{k}$ (related to k_{23}) for the lanthanide cations and also some other tri- and bivalent cations. Unfortunately, the ultrasonic technique does not yield k_{23} and k_{32} values with sufficient precision to warrant a discussion of changes of these separate quantities with cations in the lanthanide series.[28] However, the relaxation frequencies (f_R) which are related to a sum of these rates

$$2\pi f_R = k_{32} + k_{23}\Phi(c) \qquad (20)$$

do show a characteristic variation with lanthanide cation which is indicated in Figure 4. It is therefore of interest to consider the parameters which influence f_R and to attempt to interpret the variation in terms of a variation in cation property. $\Phi(c)$ in eq 20 cannot in general be precisely determined; it depends on the concentration. But for the lanthanide salts this variation with c is small. Its magnitude depends to some extent on the nature of the cation, for example, on the charge type and the ionic radii to the extent that these influence the degree of ionic association. It will also depend on the extent to which this particular reaction is coupled with other reactions occurring in the solution. However, at constant concentration, $\Phi(c)$ may be assumed constant for closely related cations such as the lanthanides. f_R will thus vary as the weighted sum of k_{23} and k_{32}.

Figure 4 illustrates how f_R first increases then decreases across the lanthanide series. This behavior, like the behavior of the thermodynamic properties[9,10] of lanthanide salts, cannot be explained simply in terms of changes in cation size, supposing the solvent to be a continuum. The high electric field strength at the surface of the cation must greatly influence the solvent molecules, or the solvent structure, in the immediate vicinity of the ion. It is the changes in this solvent structure, resulting from the variation in cation size, and to a lesser extent the influence of 4f orbitals, which are primarily responsible for the differences in behavior exhibited by the various lanthanide cations. In the absence of a complete understanding of the structure of water and how it is influenced by the presence of ions, it is convenient to regard such structural changes as changes in average cation coordination number. A plausible explanation of the variation of several properties of lanthanide salts is possible supposing that there is a change in average cation coordination number across the series.[9,10]

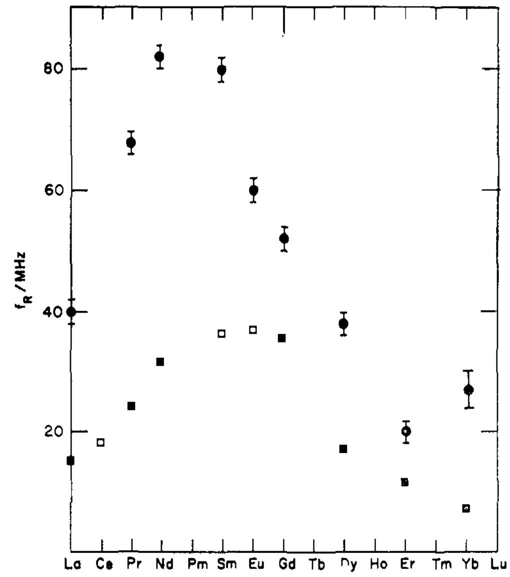

Figure 4. Relaxation frequency against cation atomic number: (□) sulfates, Purdie and Vincent,[12] $c \approx 0.05$ mole l.$^{-1}$; (■) sulfates, Grecsek,[22] $c \approx 0.05$ mole l.$^{-1}$; (●) nitrates, this work, $c = 0.2$ mole l.$^{-1}$

The variation of f_R is consistent with this supposition if in addition it be assumed that for cations toward the center of the series, where two (or more) coordination numbers become equally probable, the change from one coordination number to another occurs more readily. The rate constants k_{23} and k_{32} refer to the forward and backward rates for the exchange of anion and water between the first and second coordination spheres of the cation. It is not unreasonable to suppose that the transition state for such a process will involve a coordination number change in both coordination spheres. Consequently an increase in both k_{23} and k_{32}, and hence f_R, is anticipated if a change in coordination number occurs more readily. The smooth variation of f_R across the series suggests that this change in average coordination number occurs gradually.

The f_R values for the nitrates are consistently higher than those for the corresponding sulfates. The difference primarily reflects a difference in the k_{32} rate constant. This is the anticipated result since the activation energy for this reaction, the release of the anion from the first coordination sphere of the cation, might reasonably be expected to be related to the coulombic interaction between anion and cation.

The μ_{max} values for the nitrates, Table VI, show an interesting trend across the lanthanide series. From eq 6 it can be seen that μ_{max} depends on K_I through C_A, on K_{II} through γ, and on $(\Delta V_{II})^2$. Inspection of the results for the neodymium and gadolinium salts suggests that differences in μ_{max} at constant stoichiometric concentration primarily reflect differences in ΔV_{II}. However, without precise values of both K_I and K_{II} the magnitude of ΔV_{II} cannot be estimated with certainty and the experiment of course gives no indication of

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[28] Purdie and Vincent[12] tabulate rate constants which are equivalent to k_{23} and k_{32} which they obtained from ultrasonic measurements and an analysis involving a four-state model. However, since several of the assumptions implicit in their analysis are not valid for their system, we feel that these rate constants should be regarded with skepticism. One assumption which is particularly poor is that $k_{12},k_{21} \gg k_{23},k_{32} \gg k_{34},k_{43}$, where the k's refer to the forward and back rate constants for the three consecutive reactions postulated.

the sign of ΔV_{II}. Without such information further speculation concerning the significance of the trend would be premature.

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The Kinetics of Oxidation of Copper(I) by Molecular Oxygen in Perchloric Acid–Acetonitrile Solutions[1a]

Robert D. Gray[1b]

Contribution from the Department of Chemistry and the Institute of Molecular Biophysics, The Florida State University, Tallahassee, Florida 32306.

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Abstract: Spectrophotometric and polarographic methods were used to study the oxidation of Cu(I) by dissolved O_2 in $HClO_4$–CH_3CN solutions of ionic strength 0.1 *M*. The reaction follows the rate law $-d[Cu(CH_3CN)_2^+]/dt = d[Cu^{2+}]/dt = k_c[Cu(CH_3CN)_2^+][O_2][H^+]/[CH_3CN]^2$, where $k_c = 6.9 \pm 0.3 \times 10^7\ M^{-2}\ sec^{-1}$ at 30°. The activation energy for the process is 8.4 ± 0.4 kcal/mole in the temperature range 9.8–48°. The data are interpreted in terms of a bimolecular reaction between a hypothetical CuO_2^+ complex and H^+ in the rate-limiting step of a sequence which involves the prior rapid dissociation of the $Cu(CH_3CN)_2^+$ complex followed by the formation of the oxygenated intermediate. The stoichiometry of the reaction indicates that under the reported conditions Cu(I) reacts more slowly with H_2O_2 than with O_2. A small amount of the Cu(I) ion can be detected at the conclusion of O_2 uptake, at which time the addition of a complexing agent preferential for Cu(I) results in the relatively slow formation of the Cu(I) complex in a pH-dependent reaction. Although the reaction sequence implies the participation of free-radical oxygen intermediates, attempts to obtain evidence for the appearance of these reactive species by the ability of the reaction mixture to hydroxylate benzoic acid were unsuccessful. In addition the ultraviolet spectra for the acetonitrile and aquo complex ions of Cu(I) were obtained; attempts to detect the CuO_2^+ intermediate spectroscopically failed.

The addition of copper ion to apoproteins to form copper enzymes and proteins is a reaction of importance in the study of the biosynthesis and the reconstitution of copper proteins. While virtually nothing is known about the biosynthesis of copper proteins, exploratory work is available on the reconstitution of several copper proteins,[2] particularly hemocyanin, ceruloplasmin, and cytochrome *c* oxidase. For these and several other copper proteins, the prosthetic copper can be removed to form a copper-free apoprotein. Restoration of the prosthetic copper to form biologically functional molecules in general requires the participation of Cu(I). A recent paper by Hemmerich[3] describing the properties of the water-soluble compound $Cu(CH_3CN)_4ClO_4$ prompted us to use this substance as a source of univalent copper in studying the reconstitution of apoceruloplasmin. It became apparent during the course of our study,[4] and it was also recently reported by Nair and Mason[2c] in the reconstitution of apocytochrome *c* oxidase, that the added Cu(I) is oxidized by dissolved O_2 in a reaction which is rapid compared to the apparent velocity of the reconstitution reactions.

In addition, the importance of Cu(II) as a catalyst in oxidation–reduction reactions involving molecular oxygen is well known in both enzymic[5] and nonenzymic[6] systems. The mechanism of catalytic action is generally attributed to the rapid regeneration of Cu(II) by the facile oxidation of Cu(I) by O_2. However, the rapidity of the oxygenation of Cu(I), the paucity of soluble Cu(I) salts, and the competing disproportionation reaction of Cu(I) have made difficult a quantitative study of the kinetics of the oxidation of Cu(I) by O_2.

Wieland and Franke[7] in 1929 observed that the ratio of the velocity of oxidation of CuCl by O_2 to the velocity of its oxidation by H_2O_2 is a function of pH, where higher acidity favors an increase in the magnitude of the ratio. Nord[8] found that in 0.04–0.4 *M* HCl, the velocity of the oxidation of $CuCl_2^-$ by O_2 depends on $[H^+]$ and is limited by the rate of diffusion of O_2 from

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