Complex formation between Ce(III) and NO_3^- or SO_4^{-2} in aqueous salt solutions

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Introduction

The association reaction between lanthanide (III) ions and various ligands has been investigated by different authors using diverse techniques [1-5]. There are disagreements concerning formation predominantly outer sphere or inner sphere complexes by simple ligands such as Cl^-, Br^-, ClO_3^-, SCN^-, NO_3^-, F^- and SO_4^{-2}. In outer sphere the complexes of metal and ligand are separated by one or more water molecules but no hydration separating the cation and anion exists in inner sphere complexes. The existence of both outer and inner sphere complexes in lanthanide salts systems has been observed in ultrasonic experiments [6].

The aim of this paper was to determine the rates of complexation of Ce^{3+} with NO_3^- or SO_4^{-2} from ultrasound velocity dispersion measurements. The ultrasound velocity in aqueous $Ce(NO_3)_3$ and $Ce_2(SO_4)_3$ solutions has been measured by the ultrasonic laser interferometer within the frequency range of 3-200 MHz [7]. The solutions were prepared in deminerallized water of hydrated salts. The concentration of Ce^{3+} was determined by an analysis of the aqueous solutions using the cation exchange technique and titration with standard base.

Results and discussion

A single relaxation was observed for $Ce(NO_3)_3$ and $Ce_2(SO_4)_3$ solutions. Figure 1 shows dispersion curves for tested solutions. As seen, ultrasound velocity at low frequencies c_o, the relaxation frequency f_R and the velocity dispersion Δc increase with an electrolyte concentration C. Experimental results are listed in Table 1.

Table 1. **Relaxation parameters of $Ce(NO_3)_3$ and $Ce_2(SO_4)_3$ solutions at the temperature 20°C**

Electrolyte	C,mole/l	c_o, m/s	f_R,MHz	Δc, m/s
Ce(NO₃)₃	0.043	1483.76	41.0	0.54
	0.088	1485.01	43.0	1.50
	0.180	1487.70	44.5	3.50
Ce₂(SO₄)₃	0.005	1482.46	12.2	0.74
	0.010	1482.65	15.8	1.30
	0.020	1483.00	20.0	2.60

For the studies of the complexation for many metal ions in aqueous solutions the modified two-step mechanism is accepted:
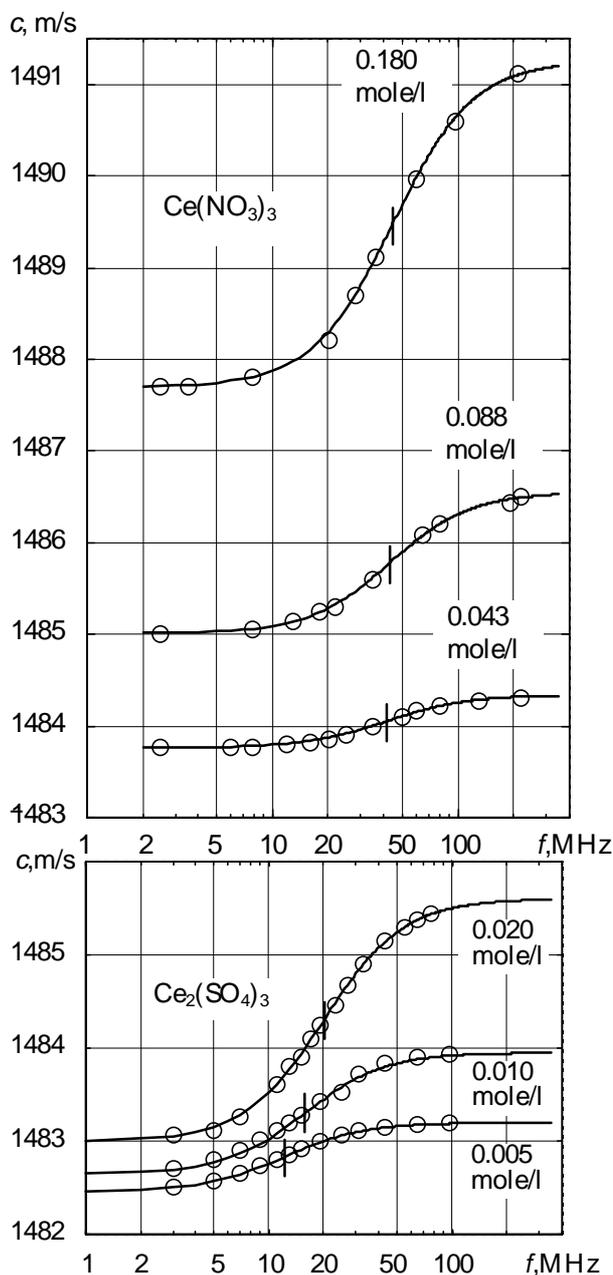
Fig.1.**Dispersion curves for Ce(NO₃)₃ and Ce₂(SO₄)₃ solutions**

step I

$$M_{aq}^{m+} + L_{aq}^{n-} \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} M^{m+}(H_2O)_x L^{n-}$$

$$\underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} (ML^{m-n})_{aq} + H_2O \qquad (1)$$
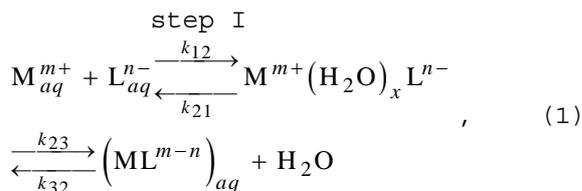
step II

where the solvated cation M_{aq}^{m+} may form with the anion L_{aq}^{n-} both outer sphere $M^{m+}(H_2O)_x L^{n-}$ and inner sphere $(ML^{m-n})_{aq}$ complexes. Here k_{12}, k_{23} are forward rate constants and k_{21}, k_{32} are reverse rate constants for a reaction (1). Ultrasound velocity dispersion is considered to be due to the process of association of Ce^{3+} with NO_3^- or SO_4^{-2} and formation of inner sphere complexes $[CeNO_3^{+2}]_{aq}$ or $[CeSO_4^+]_{aq.}$. For a bimolecular second order reaction the correlation between relaxation time τ and forward and reverse rate constants k_f and k_R can be expressed as follows:

$$\tau^{-1} = 2\pi f_R = k_f \theta + k_R, \qquad (2)$$

where $k_f = \dfrac{k_{12} \cdot k_{23}}{k_{21} + k_{23}}$, $k_R = \dfrac{k_{21} \cdot k_{32}}{k_{21} + k_{23}}$. (3)

The function θ depends on the equilibrium activities of the free ions. For a 3:1 electrolyte it is given by the following equation:

$$\theta = \pi_f \cdot C \left[2(1+\sigma) + (2+\sigma) \frac{\partial \ln \pi_f}{\partial \ln \sigma} \right], \qquad (4)$$

and for a 3-2 electrolyte is given by:

$$\theta = \pi_f \cdot C \left[(5-4\sigma) + (3-2\sigma) \frac{\partial \ln \pi_f}{\partial \ln \sigma} \right], \qquad (5)$$

where σ is the degree of dissociation, π_f is the ratio of the activity coefficients of the ions:

$$\pi_f = \frac{\gamma_{M^{m+}} \gamma_{L^{n-1}}}{\gamma_{ML^{m-n}}}. \qquad (6)$$

In order to calculate γ_i and hence π_f the Davies equation must be used [8]:

$$-\lg \gamma_i = A z_i^2 \left(\frac{\sqrt{J}}{1 + B a \sqrt{J}} - 0.3J \right), \qquad (7)$$

where A=0.509, B=0.33×10⁸, z_i is the charge of the ions, a is the distance of closest approach of the ions and J is the ionic strength.

For the solutions of Ce(NO₃)₃ and Ce₂(SO₄)₃ J is expressed accordingly as:

$$J_1 = 3(\sigma + 1)C, \quad J_2 = 3C + 12(1-\sigma)C. \qquad (8)$$

There is no universally accepted opinion for the choise of the parameter

a. Usually a is equal to a distance q in the Bjerrum model:

$$a = q = \frac{|z_+ \cdot z_-| e^2}{2DkT}, \qquad (9)$$

where e is the charge of the electron, D is the dielectric permeability of the medium, k is the Baltzmann constant, T is the absolute temperature.

In table 2 the values of σ, θ and τ_{II}^{-1} for the step II at various concentrations for Ce(NO₃)₃ and Ce₂(SO₄)₃ are listed.

Table 2. **The values of σ, θ and τ_{II}^{-1} for tested solutions**

Electrolyte	C, mole/l	σ	$\theta 10^2$, mole/l	$\tau_{II}^{-1} \cdot 10^{-8}$, s⁻¹
Ce(NO₃)₃	0.043	0.706	6.22	2.58
	0.088		7.58	2.70
	0.180	0.544	8.23	2.80
		0.420		
Ce₂(SO₄)₃	0.005	0.605	0.365	0.76
	0.010		0.555	0.94
	0.020	0.540	1.058	1.25
		0.435		

If τ_{II} is measured as a function of concentration rate, constants k_f and k_R can be determined as the slope and intercept of a plot of τ_{II}^{-1} against θ. For Ce(NO₃)₃: k_f=10.0·10⁸ (s·mole/l)⁻¹, k_R=1.92·10⁸ s⁻¹; for Ce₂(SO₄)₃: k_f=0.72·10¹⁰ (s·mole/l)⁻¹, k_R=0.50·10⁸ s⁻¹

In order to determine the dependence of complexation rates on the nature of anion it is necessary to calculate the rate constant k_{23}. It is interpreted as the rate of exchange of a water molecule in the first coordination sphere of the Ce^{3+} with the anion NO_3^- or SO_4^{-2} in the second coordination sphere. Constant k_{32} is the rate for the reverse process.

Assuming the condition $k_{21} \gg k_{23}$ rate constants k_f and k_R are equal

$$k_f = \frac{k_{12}}{k_{21}} k_{23} = K_1 k_{23} \text{ and } k_R = k_{32}, \qquad (10)$$

where K_1 is the equilibrium constant for the step I of the reaction (1).

The rate constants k_{12} and k_{21} are calculated theoretically according to the Smoluchowsky-Debye and the Eigen equations for the diffusion - controlled reactions [9]:

$$k_{12} = \frac{4\pi N(z_+ z_-) e^2 (d_+ + d_-)}{1000 DkT \left\{ \left[\exp \frac{(z_+ z_-) e^2}{DakT} \right] - 1 \right\}}, \qquad (11)$$

$$k_{21} = \frac{3(z_+ z_-)e^2(d_+ d_-)}{Da^3 kT\left[1 - \exp\dfrac{-(z_+ z_-)e^2}{DakT}\right]}, \qquad (12)$$

where N is the Avogadro's constant, d_+ and d_- are the diffusial coefficients of cation and anion respectively.

The rate constants for $Ce_{(III)}$ complexes are presented in Table 3.

It is evident that k_{23} is of the same order of magnitude for NO_3^- and SO_4^{-2} anions. Therefore, the

Table 3. **Kinetic parameters for formation of complexes**

Rate constants	Electrolyte	
	$Ce(NO_3)_3$	$Ce_2(SO_4)_3$
$k_{12}\cdot 10^{-10}$, $(s\cdot mole/l)^{-1}$	1.8	3.7
$k_{21}\cdot 10^{-8}$, s^{-1}	8.4	1.7
$k_{23}\cdot 10^{-7}$, $(s\cdot mole/l)^{-1}$	1.5	4.1
$k_{32}\cdot 10^{-8}$, s^{-1}	2.0	0.52

dissociative mechanism of the reaction (1) may be accepted. The ultrasound velocity dependence on concentration of the solutions $Ce_2(SO_4)_3$ is given in Figure 2.
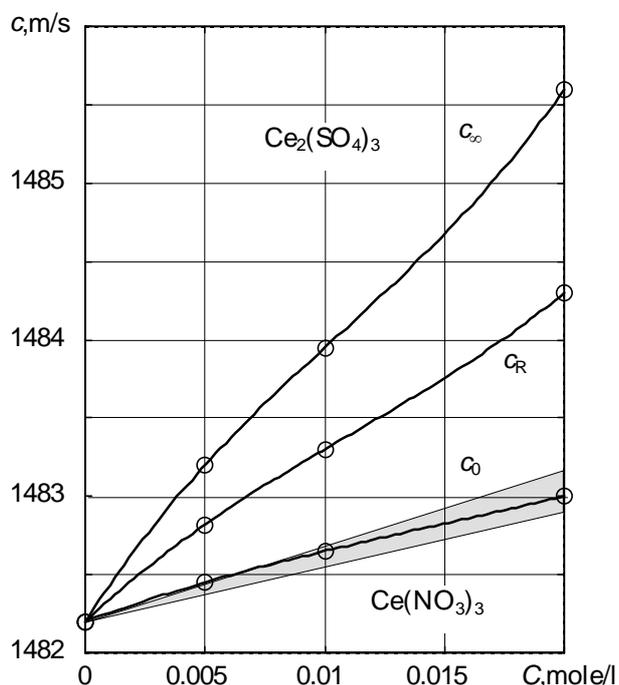
Fig.2.**Ultrasound velocity dependence on concentration in $Ce_2(SO_4)_3$ and $Ce(NO_3)_3$ solutions at 20°C**

From data of the curves it is possible to determine the value of dispersion Δc at any concentration and also the ultrasound velocity c_R at the

relaxation frequency f_R. As seen, the magnitude of ultrasound dispersion for $Ce(NO_3)_3$ is much smaller (shaded area) than that of $Ce_2(SO_4)_3$ solutions. Using the interpretation that the dispersion in $Ce_2(SO_4)_3$ and $Ce(NO_3)_3$ solutions is caused by an association process, the an magnitude of an ultrasound dispersion may be the quantity of complexation. The lanthanide nitrates are known to form predominantly outer sphere complexes with some inner sphere substitution occurring only at high concentrations [5]. The lanthanide sulphates on the other hand form predominantly inner sphere complexes. The magnitude of the dispersion in the $Ce_2(SO_4)_3$ solutions increases with concentration of the cation and with the amount of inner complexes. In order to produce an appreciable concentration of inner complexes in the $Ce(NO_3)_3$ solutions for a similar dispersion and relaxation a tenfold higher concentrations of the nitrates must be used.

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Ce(III) ir NO_3^- arba SO_4^{-2} kompleksø susidarymas vandeniniuose druskø tirpaluose

Reziumë

Tyrinëta ultragarso greièio dispersija vandeniniuose $Ce(NO_3)_3$ ir $Ce_2(SO_4)_3$ tirpaluose. Padaryta iðvada, kad ultragarso greièio dispersijà sukelia Ce(III) ir anionø NO_3^- arba SO_4^{-2} asociacija, atsirandanti susidarant $\left[CeNO_3^{+2}\right]_{aq}$ ir $\left[CeSO_4^+\right]_{aq}$ kompleksams. Apskaièiuotos kompleksø susidarymo greièio

konstantos. Palyginti tyrinėtø tirpalø relaksaciniai parametrai. Sulfatø tirpaluose ultragarso greièio dispersija, esant tai paèiai katijono koncentracijai, yra eile didesnë negu nitratø tirpaluose. Daroma iðvada, kad sulfatø tirpaluose esama gerokai daugiau vidiniø kompleksø.