
Ultrasonic study of the complexation kinetics of aqueous yttrium nitrate solutions

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Ultrasound velocity dispersion measurements in aqueous yttrium nitrate solutions are analysed. A single relaxation and its concentration dependence has been determined. Data of ultrasound velocity dispersion are interpreted as being due to the process of association between the Y^{3+} and NO_3^{-} . Kinetic parameters for the formation of $[YNO_3]^{2+}$ complexes have been determined. The activation energy (the free enthalpy shift ΔH_2), the difference in enthalpy ΔH_0 and the change of molar volume during the association reaction ΔV were calculated.

Key words: ultrasound velocity dispersion, relaxation process, kinetic and thermodynamic parameters

INTRODUCTION

The inorganic complexation reaction of the type



can be discussed in terms of M^{z+} formation in inner or outer sphere complexes. In outer sphere complexes metal M^{z+} and ligand X^- (such as Cl^- , Br^- , ClO_4^- , SCN^- , NO_3^- , J^- , F^- and SO_4^{2-}) are separated by a layer of water molecules, but no hydration separating the cation and anion exists in inner sphere complexes.

Ultrasonic waves, *i. e.* the associated pressure and adiabatic temperature oscillations, disturb the equilibrium between solvent and solute molecules. These retarded equilibrium shifts between different molecular configurations or hydrated ions substitutions affect, in turn, the ultrasound velocity and absorption. Relaxation behaviour can be observed as well. In this way ultrasonic spectrometry permits to study complexation processes in solution and the extraction of specific relaxation parameters of a chemical equilibrium [1]. The existence of both outer and inner sphere complexes in polyvalent electrolytes including lanthanide salts systems has been observed in ultrasonic absorption measurements [2–6]. Chopin has summarized the data on the nitrates, concluding that the percentage of inner sphere complexes increases from the lighter to the heavier lanthanides [7]. In water, the ultrasonic relaxation technique can easily distinguish between the inner and the outer sphere ligands. Chloride, bromide, iodide

and perchlorate are the outer sphere in 0.2 mol/l solutions, whereas nitrate and sulphate are the inner sphere [8–10].

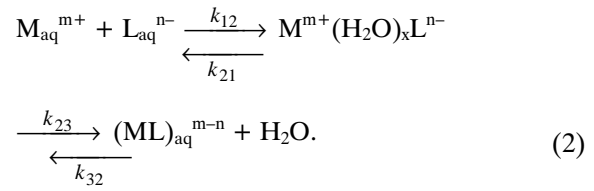
MATERIALS AND METHODS

In the present work we have investigated the relaxation process in aqueous yttrium nitrate solutions, some results on La^{3+} also have been included in order to compare the chemical behaviour of these early or pre-lanthanides (no *f* electrons) with the lanthanides (4*f*) in common systems [11]. The ultrasound velocity in aqueous $Y(NO_3)_3$ solutions was measured by an ultrasonic laser interferometer within the frequency range of 3 to 100 MHz [12–13], and ultrasound velocity dispersion was defined. All ultrasound velocity measurements at each frequency were made in tenfold. Measurement error at the medium ultrasonic frequencies was 0.001%. At low frequencies (<15MHz) experimentally determined diffraction corrections were introduced. The temperature was kept with an accuracy of ± 0.005 °C. The solutions were prepared by weighing bidistilled water and commercial salt $Y(NO_3)_3 \cdot 6H_2O$ without further purification. The concentration of cation was determined by EDTA titration, using Xylenol Orange as the end-point indicator. Each analysis, made in triplicate, gave a mean deviation less than 1% [14].

RESULTS AND DISCUSSION

A single relaxation was observed for investigated aqueous $Y(NO_3)_3$ solutions studied. Experimental re-

sults are listed in Table 1. Figure 1 shows dispersion curves at concentrations 0.1 mol/l, 0.2 mol/l and 0.3 mol/l. One can see that the ultrasound velocity at low frequencies c_0 ($f \ll f_R$), the relaxation frequency f_R and the velocity dispersion Δc increase with the electrolyte concentration C .



Concentration C , mol/l	Ultrasound velocity at low frequencies c_0 , m/s	Relaxation frequency f_R , MHz	Ultrasound velocity dispersion Δc , m/s
0.1	1490.46	63	0.66
0.2	1498.88	69	1.52
0.3	1507.70	72	3.90

We accept the modified two-step mechanism proposed by Eigen and Tamm for the studies of the complexation of many metal ions in water or mixed solvents [15]:

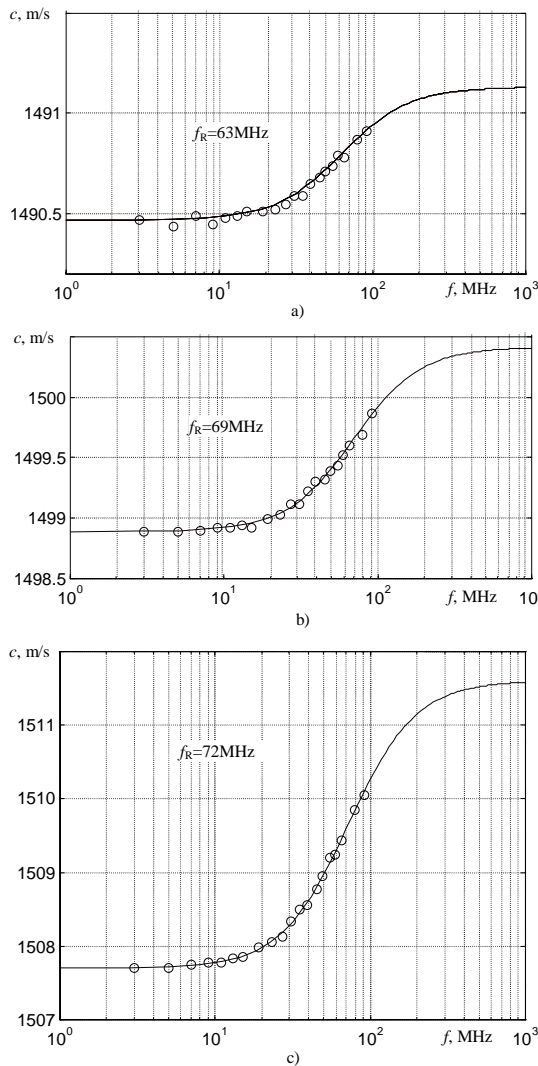


Fig. 1. Ultrasound velocity dispersion curves for $\text{Y}(\text{NO}_3)_3$ solutions in water at 20 °C: a) concentration $C = 0.1$ mol/l; b) $C = 0.2$ mol/l; c) $C = 0.3$ mol/l

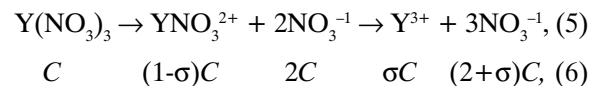
Step I represents a diffusion-controlled association of the two ions to form a solvent separated outer sphere complex coupled to solvent loss from the inner solvation shell of the ligand. Step II represents solvent loss from the cation solvation shell and the formation of inner sphere $[\text{ML}]^{m-n}$ complex. Here k_{12} , k_{23} are forward rate constants and k_{21} , k_{32} are reverse rate constants for reaction (2).

We have attributed the observed relaxation frequency to the second step of reaction (2). Relaxation frequency cannot be confined to step I as theoretically estimated rate constants, because a diffusion-controlled association would give about 10^9 – 10^{10} l/mol·s. Such a value predicts the relaxation frequency of an order of magnitude higher than that observed in this work. For a bimolecular second order reaction the correlation between the relaxation time τ and the forward and reverse rate constants k_f and k_R can be expressed as follows:

$$\tau^{-1} = 2\pi f_R = k_f \Theta + k_R, \tag{3}$$

$$k_f = \frac{k_{12} \cdot k_{23}}{k_{21} + k_{23}} k_R = \frac{k_{21} \cdot k_{32}}{k_{21} + k_{23}}. \tag{4}$$

The function Θ depends on the equilibrium activities of the free ions. The following dissociation scheme has been adopted:



where C is the analytic concentration of $\text{Y}(\text{NO}_3)_3$, σ is the ratio of the equilibrium concentration of Y^{3+} to the sum of the concentrations of Y^{3+} and YNO_3^{2+} , i.e., $\sigma = C_1 / (C_1 + C_2)$; C_1 is the concentration of Y^{3+} and C_2 is the concentration of YNO_3^{2+} . The function Θ for a 3–1 electrolyte is given by the following equation:

$$\Theta = \pi_f C [2(\sigma + 1) + (2 + \sigma) \partial \ln \pi_f / \partial \ln \sigma], \quad (7)$$

where π_f is the ratio of the activity coefficients of the ions:

$$\pi_f = \frac{\gamma_{Y^{3+}} \times \gamma_{NO_3^{-1}}}{\gamma_{YNO_3^{2+}}}. \quad (8)$$

To calculate γ_{ion} and hence π_f , the Davies equation must be used [16]:

$$-\lg \gamma_{ion} = Az_1^2 \left(\frac{\sqrt{I}}{1 + Ba\sqrt{I}} - 0.3I \right), \quad (9)$$

where $A = 0.509$, $B = 0.33 \times 10^8$, z_i is the charge of the ions, a is the closest approach of the ions, and I is the ionic strength.

$$I = 1/2 \sum C_i z_i^2 = 3(\sigma + 1)C. \quad (10)$$

There is no universally accepted opinion for the choice of the parameter a . Usually a is equal to the distance q in the Bjerrum model [1]:

$$a = q = |z_+ z_-| e^2 / 2DkT, \quad (11)$$

where e is the charge of the electron, D is the dielectric permeability of the medium, k is the Boltzmann's constant, T is the absolute temperature. For a 3-1 electrolyte, $q = 10.7 \cdot 10^{-10}$ at 25 °C.

In Table 2 the calculated values of σ , Θ and τ^{-1} for step II of reaction (2) at various concentrations of $Y(NO_3)_3$ solutions are listed.

Table 2. The values of σ , Θ and τ^{-1} for $Y(NO_3)_3$ solutions at 20 °C			
C, mol/l	σ	$\Theta \times 10^2$, mol/l	$\tau_{II}^{-1} \times 10^{-8}$, s $^{-1}$
0.1	0.47	8.07	3.96
0.2	0.41	13.01	4.27
0.3	0.29	15.00	4.52

In Fig. 2, the plot of τ_{II}^{-1} versus the calculated Θ is shown; the data for the forward and reverse rate constants k_f and k_R are determined as the slope and intercept of the plot:

$$k_f = 8.16 \times 10^8 \text{ (s} \cdot \text{mol/l)}^{-1}, \quad k_R = 3.28 \times 10^8 \text{ s}^{-1}.$$

So the kinetic association constant for the formation of $[YNO_3]^{2+}$ $K_0 = k_f/k_R = 2.49$ mol/l. Assuming the condition $k_{21} \gg k_{23}$, the rate constants k_f and k_R are equal:

$$k_f = k_{12}/k_{21} \times k_{23} = K_1 \times k_{23} \text{ and } k_R = k_{32}, \quad (12)$$

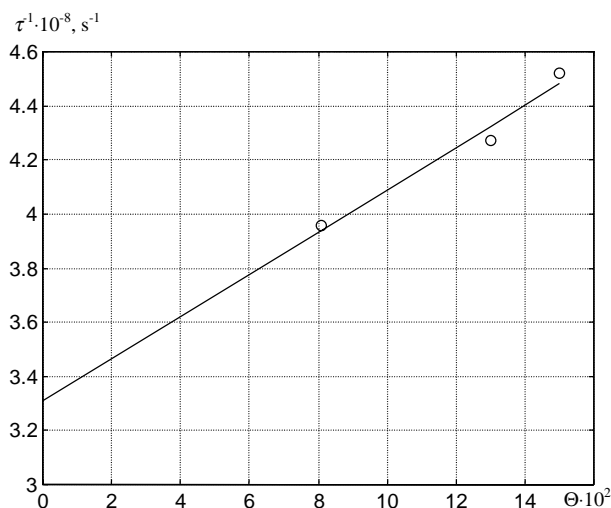


Fig. 2. τ^{-1} versus Θ for definition of the rate constants k_f and k_R

where K_1 is the equilibrium constant for step I of reaction (2) and $K_2 = k_{23}/k_{32}$ is the equilibrium constant for step II. The kinetic rate constants must be consistent with the Eigen association equilibrium relation [15]:

$$K_0 = K_1(1 + K_2). \quad (13)$$

From our value of K_0 , K_1 was chosen such as required by equation (13). Garnsey and Ebdon [17] by a graphical analysis found $K_1 = (4 \pm 2)$ for Gd^{3+} nitrate. Since gadolinium and yttrium have nearly the same ionic radius, electrostatics would predict that they have nearly the same formation constant. So the value of $K_1 = 2$ was taken by us and this would make $k_{23} = 4.08 \cdot 10^8 \text{ s}^{-1}$, $K_2 = k_{23}/k_{32} = 1.24 \text{ (mol/l)}^{-1}$.

Based on the numerical values of relaxation frequencies and on the ultrasound velocity dispersion at different concentrations and at various temperatures, we have calculated thermodynamic data of the relaxation process, as the activation energy E_a (the free enthalpy shift ΔH_2), the difference in enthalpy ΔH_0 and the molar volume shift ΔV during the reaction.

According to a two step mechanism, like the Eigen process the excess absorption per wavelength is given by equation [18]:

$$\mu_{\max}/C_A = \gamma(1-\gamma)(\Delta V_{II})^2 \pi / 2RT\beta_0, \quad (14)$$

where C_A is the equilibrium concentration of all associated species, $C_A = (1-\sigma)C$, γ is the degree of conversion of the second step of reaction (2) with $K_2 = 1-\gamma/\gamma$, ΔV_{II} is the change in volume per mole for step II, R is the gas constant, T is the absolute

temperature, and β_0 is the compressibility of the pure solvent. In the present work relaxation process in $Y(NO_3)_3$ is investigated by ultrasound velocity measurements; it is known that the excess absorption per wavelength is connected with the ultrasound velocity dispersion Δc by the following equation [1]:

$$(\infty\lambda)_{\max} = \mu_{\max} = \frac{\Delta c \cdot \pi}{c_{\infty}} \left(\frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \right)^{-1}, \quad (15)$$

where c_{∞} is the ultrasound velocity corresponding to very high frequencies $f \gg f_R$, $\omega = 2\pi f$.

Thus from equations (14) and (15) ΔV_{II} is obtained 8.7 cm³/mol. It can be seen that μ_{\max} as well Δc depend on K_1 through C_A , on K_2 through γ and on ΔV_{II}^2 . However, without knowing the precise values of K_1 and K_2 the magnitude of ΔV_{II} cannot be estimated with certainty. The change of molar volume ΔV_{II} also can be calculated from the theory for the relaxation of compressibility β_R [19]

$$\beta_R = \frac{\Delta V_R^2}{V_0 RT} \times \frac{1}{2(1 + \cos \Delta H_2 / RT)}, \quad (16)$$

where V_0 is the partial molar volume, ΔH_2 (the free enthalpy shift) is the activation energy E_a of the backward reaction. The activation energy E_a can be calculated using the theory of absolute reaction rates

$$f_R \cong k_i = \frac{kT}{h} \exp(-E_a / RT), \quad (17)$$

where k is the reaction rate constant, k is Boltzmann's constant, h is Planck's constant. The dependence of the relaxation frequency on temperature is shown in Fig. 3. The slope of $\lg(f_R/T)$ versus $1/T$ gives the activation energy: $E_a = -2.303Rtg\alpha = 10.3$ kJ/mol. $E_a = 6.5$ kJ/mol of the complexation reaction in $La(NO_3)_3$ solutions [11].

From our earlier experiments the partial molar volume $V_0 = 34.2$ cm³/mol [14]; $\beta_R = 44.047 \cdot 10^{-11}$ m²/N,

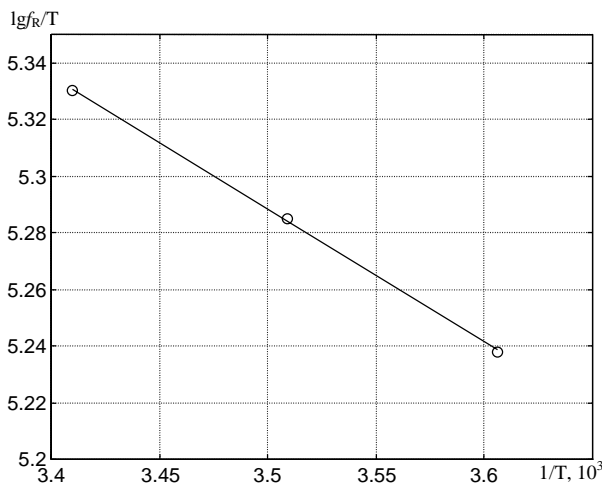


Fig. 3. Graphic determination of the activation energy E_a

thus from equation (16) $\Delta V_R = 12.1$ cm³/mol. This value is of the same order as that obtained from equation (15) and is the order of magnitude of the elimination of one molecule of water. The dissociation of a water molecule from the primary hydration shell is known to correspond to an increase in volume. The volume difference for the two coordinances, corresponding to the dissociation of one water molecule from $[Ce(H_2O)_9]^{3+}$ to form $[Ce(H_2O)_8]^{3+}$, has been calculated using a model developed by Swaddle [20]; this volume is +12.8 cm³/mol and agrees well with the reaction volume $\Delta V = 10.9$ cm³/mol determined experimentally by variable-pressure UV spectroscopy at 295 nm [21]. The formation of an inner sphere complex from oppositely charged ions involves an extensive break-up of the hydrate structures. The water molecules thus set free bring about a considerable part of the solution volume. The formation of an outer sphere complex is accompanied by a much less extensive dehydration, and hence by a much smaller increase in volume.

The difference in enthalpy ΔH_0 can be evaluated by a graphical method from the dependence of $\lg(T\mu_{\max}/c^2)$ versus $1/T$ [22] or in our case from ultrasound velocity dispersion measurements $\lg(T\Delta c\pi/c_{\infty} c_R^2)$ versus $1/T$, here $c_R = (c_{\infty} + c_0)/2$. The relaxation data of $Y(NO_3)_3$ solutions for the calculation of ΔH_0 are presented in Table 3.

Temperature T , °C	Relaxation frequency f_R , MHz	Ultrasound velocity dispersion Δc , m/s	Ultrasound velocity at high frequency C_{∞} , m/s
4.3	48	0.93	1435.07
12.0	55	0.75	1465.35
20.0	63	0.66	1491.12

The change in the internal energy ΔH_0 evaluated from the plots of $10 + \lg[T\Delta c\pi/c_{\infty} (c_R)^2]$ versus $1/T$ as shown in Fig. 4 is equal to 17.0 kJ/mol. In outer sphere complexation the primary hydration sphere is minimally perturbed, so no energy is required for dehydration and the difference in enthalpy $\Delta H_0 \approx 0$.

The equilibrium constant K_0 and the Gibbs free energy ΔG is connected by the equation

$$\Delta G = -2.303RT \lg K_0, \quad (18)$$

from here ΔG is estimated as 2.2 kJ/mol.

The entropy ΔS is defined by

$$-\Delta G = T\Delta S - \Delta H_0, \quad (19)$$

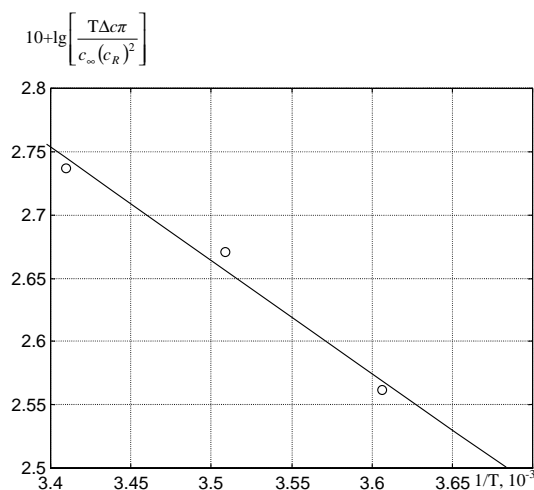


Fig. 4. Definition of the difference in enthalpy ΔH_0

so the experimental value ΔS was found to be 65.5 J/mol · K.

Table 4 lists the kinetic and thermodynamic parameters obtained from the studies of yttrium nitrate solutions.

Table 4. The kinetic and thermodynamic parameters for the formation of $[\text{YNO}_3]^{2+}$ complexes	
Parameter	Value
K_1 , l · mol ⁻¹	2.0
K_2	1.24
k_{23} , s ⁻¹	$4.08 \cdot 10^8$
k_{32} , s ⁻¹	$3.28 \cdot 10^8$
K_0 , l · mol ⁻¹	2.49
ΔV_2 , cm ³ · mol ⁻¹	8.7–12.1
E_A , kJ · mol ⁻¹	10.3
ΔH_0 , kJ · mol ⁻¹	17.0
ΔS , J · mol ⁻¹	65.5
$-\Delta G$, kJ · mol ⁻¹	2.2

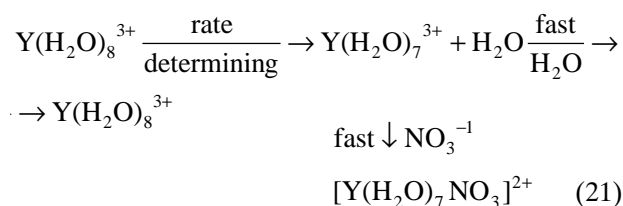
The free energy ΔG for the complexation reaction of lanthanide ions with various ligands can be expressed [8]:

$$\Delta G = \Delta G_R + \Delta G_H = \Delta H_R + \Delta H_H - T(\Delta S_R + \Delta S_H), \quad (20)$$

here R = cation – anion interaction, H = hydration changes upon complexation. In this equation $|\Delta H_H| > |\Delta H_R|$ and $|\Delta S_H| > |\Delta S_R|$. If the net hydration decreases upon complexation, both ΔH_H and ΔS_H would be positive; since positive values of ΔH and ΔS are observed for most reactions in aqueous solutions with simple ligands, the hydration terms are, indeed, larger than the reaction terms.

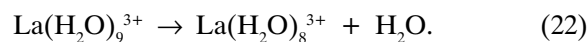
The experimental positive values of ΔH_0 and ΔS obtained in this work may be interpreted that hydration changes for complex formation in $\text{Y}(\text{NO}_3)_3$ solutions are larger than the yttrium–ligand interaction.

The rate constant k_{23} measured in this work by ultrasonic method corresponds closely with the rates for the exchange of labelled water molecules from the inner coordination spheres of the lanthanide(III) ions, determined by ¹⁷O-NMR relaxation and chemical shift measurements [23–24]. There is much evidence to support the theory that the removal of a water molecule from the primary hydration shell of a cation by the dissociative D or dissociative interchange I_d mechanism is the rate-determining process of step II of reaction (2) which would become:



with the assumption that Y(III) have the coordination number 8.

It is known that in aqueous solutions the coordination number is 9 for the light lanthanides in the La–Pm range [25], then for La^{3+} the rate-determining step is



The relaxation frequency f_R for $\text{Y}(\text{NO}_3)_3$ solutions is higher than for $\text{La}(\text{NO}_3)_3$ at the same concentrations [11]. The difference of f_R primarily reflects a difference in the k_{32} rate constants, so $k_{32} = 3.28 \cdot 10^8 \text{ s}^{-1}$ for $[\text{YNO}_3]^{2+}$ and $k_{32} = 1.76 \cdot 10^8 \text{ s}^{-1}$ for $[\text{LaNO}_3]^{2+}$ complexes. This is the anticipated result, since the activation energy E_a 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. This may reflect an increased rate constant k_{32} for a smaller Y(III) cation compared to La(III), e.g. $r_{\text{Y}^{3+}} = 1.06 \cdot 10^{-10} \text{ m}$, $r_{\text{La}^{3+}} = 1.22 \cdot 10^{-10} \text{ m}$. Assuming the ultrasound velocity dispersion Δc in $\text{Y}(\text{NO}_3)_3$ and $\text{La}(\text{NO}_3)_3$ solutions is caused by an association process, the magnitude of Δc may be the quantity of complexation, since the dispersion values are close, the amount of inner sphere complexes is approximately identical.

CONCLUSIONS

Rate constants and thermodynamic parameters for the formation of $[\text{YNO}_3]^{2+}$ complexes have been cal-

culated on the basis of relaxation data. The positive values of the entropy effect ΔS and the change in the internal energy ΔH_0 were interpreted in terms of dehydration during complexation. The obtained reaction volume ΔV_R indicates also the elimination of a water molecule from the primary hydration shell. The rate constant k_{23} measured in this work closely corresponds with the rates for the exchange of labelled water molecules from the first coordination sphere of the lanthanide (III) ions, determined by NMR measurements. Thus the dissociative substitution mechanism was proposed for the $[\text{YNO}_3]^{2+}$ complexes studied. We hope that ultrasound velocity dispersion measurements may contribute to a better knowledge of the fast reaction in solution.

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ULTRAGARSINIAI ITRIO NITRATO KOMPLEKSŲ KINETIKOS TYRIMAI

S a n t r a u k a

Analizuojami ultragarso greičio dispersijos matavimai vandeniniuose itrio nitrato tirpaluose. Aptiktas relaksacinis procesas apibūdinamas viena relaksacijos trukme. Ultragarso greičio dispersija interpretuojama Y^{3+} ir NO_3^- jonų asociacija, susidarant vidiniams kompleksams $[\text{YNO}_3]^{2+}$. Paskaičiuoti susidariusių kompleksų kinetiniai parametrai. Nustatyta aktyvacijos energija, entalpijos, entropijos ir tūrio pokyčiai asociacijos proceso metu.

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УЛЬТРАЗВУКОВЫЕ ИССЛЕДОВАНИЯ КИНЕТИКИ КОМПЛЕКСООБРАЗОВАНИЯ В ВОДНЫХ РАСТВОРАХ АЗОТНОКИСЛОГО ИТРИЯ

Р е з ю м е

Исследовалась дисперсия скорости ультразвука в водных растворах азотнокислого иттрия. Обнаружен релаксационный процесс с одним временем релаксации. Предполагается, что дисперсию скорости ультразвука вызывает ассоциация ионов Y^{3+} с NO_3^- с образованием внутрисферных комплексов $[\text{YNO}_3]^{2+}$. Расчитана энергия активации, определены изменения энтальпии и энтропии при реакции ассоциации.