Thermodynamics of Mn(II) and La(III) sulphate complexes in aqueous solutions

B. Voleišienė[1], D. Rutkūnienė[2]

Kaunas University of Technology,

[1]*Prof. K. Baršauskas Ultrasound Research Institute,* [2]*Department of Physics*

Introduction

In recent years lanthanide (III) ions are often used as structural probes in biological systems in order to obtain some information on the binding sites of "vitality" elements such as Ca, Mg, Mn, Fe, Mo, V and others that are formed in coordinated complexes of humane organism. Two-metal ions model (Mg^{2+}-La^{3+}) was proposed at a constant concentration of Mg^{2+}ion with La^{3+} as a competing metal ion in the ribozyme cleavage reaction [1]; this mechanism may be also applied to many phosphoryl transfer reactions catalyzed by polymerases and related enzymes in the processes of gene expression and their regulation. Rare earth elements have also been widely used as the micro-fertilizer for improving the growth and quality of crops in China [2]. It has been verified that a suitable amount of lanthanide ions can improve the photosynthesis of plants. The replacements of magnesium in chlorophyll by light rare earth elements, such as La^{3+}, $Sm^{3+}$and Dy^{3+}have been reported by several researchers [2].

Comparing the ionic radius of Mn^{2+} and La^{3+} and on the similarity of their chemical properties the knowledge of the structural properties as well as kinetical and thermodynamical processes occurring in aqueous solutions of sulphates of these elements is very important for understanding many phenomena in physical chemistry, biochemistry, also for chemical engineering and process control.

The aim of this paper was to determine the thermodynamic parameters of complexes of Mn(II) and La(III) with SO_4^{-2} on the basis of ultrasound velocity dispersion measurements data.

Results and discussion

In our earlier studies [3, 4], ultrasound velocity dispersion was investigated in aqueous solutions of $MnSO_4$ and $La_2(SO_4)_3$ sulphates at different concentrations and at various temperatures. A single relaxation was observed for investigated solutions. No concentration dependence of relaxation frequency f_R was observed in the case of both systems, but f_R increases with the increase of the temperature. Experimental results for tested solutions are listed in Table 1.

We have calculated thermodynamic data of the relaxation process based on the numerical values of relaxation frequencies and on the ultrasound velocity dispersion at different temperatures. According to the variation of $\tau^{-1}=2\pi f_R =k_f +k_R$ with temperature T it may be written as

$$\frac{d\ln(\tau^{-1}/T)}{d(1/T)} = \frac{\Delta H_2}{R} + \frac{d\ln(1+K)}{d(1+K)},$$

$$\frac{dK}{d(1/T)} = -\frac{\Delta H_2}{R} - \frac{K}{1+K}\frac{\Delta H_0}{R}, \qquad (1)$$

where $(K/1+K)(\Delta H_0/R$ is small with respect to $\Delta H_2/R$, then Eq.1 reduces to

$$\frac{d\ln(\tau^{-1}/T)}{d(1/T)} = -\frac{\Delta H_2}{R} \qquad (2)$$

Table 1. **Relaxation parameters of MnSO₄ solutions at the concentration 0.55 mol/l and of La₂(SO₄)₃ solutions at the concentration of 0.01 mol/l for different temperatures**

Investigated solutions	Temperature t, ^{0}C	Relaxation frequency f_R, MHz	Ultrasound velocity dispersion c_∞-c_0, m/s	Ultrasound velocity at high frequencies c_∞, m/s	Ultrasound velocity at the relaxation frequency c_R, m/s
MnSO₄	10	2.7	2.4	1507.2	1506.0
	16	2.9	2.5	1526.6	1525.6
	20	4.5	2.8	1538.0	1536.8
	30	5.0	3.1	1559.8	1558.5
La₂(SO₄)₃	20	13.5	1.10	1483.9	1483.3
	30	17	1.06	1510.5	1509.9
	40	23	0.97	1530.0	1529.5

and a plot of $\ln(\tau^{-1}/T)$ versus $1/T$ shall give $-\Delta H_2/R$ as the slope and $[\ln(k/h)]+(\Delta S/R)$ as the intercept (where k_f and k_R are the rate constants for the forward and reverse processes, $K = k_f/ k_R$ is the equilibrium constant, k – Boltzmann's constant, h – Planck's constant, T is the absolute temperature, R is the gas constant, $-\Delta H_2$ -the free enthalpy shift is the activation energy E_a of the backward reaction, ΔH_0 is the difference in enthalpy).

Fig. 1 reports the plot of $\ln((\tau^{-1}/T)$ versus $1/T$ for $MnSO_4$ solutions and Fig. 2 for $Ln_2(SO_4)_3$ solutions respectively. The slope of $\ln(f_R/ T)$ versus $1/ T$ gives the activation energy: $E_a = 23$ kJ/mol of the relaxation process in $MnSO_4$ solutions and $E_a = 19$ kJ/mol for $Ln_2(SO_4)_3$ solutions. The entropy ΔS is calculated from the intercept: ΔS=-115.2 J·K^{-1}·mol^{-1} for $MnSO_4$ and ΔS=-103,4 J· K^{-1}·mol^{-1} for $Ln_2(SO_4)_3$. These values at T=293 K give in turn ΔG=42.8 kJ·mol^{-1} for $MnSO_4$ and ΔG=24.0 kJ·mol^{-1}for $Ln_2(SO_4)_3$ complexation reaction.
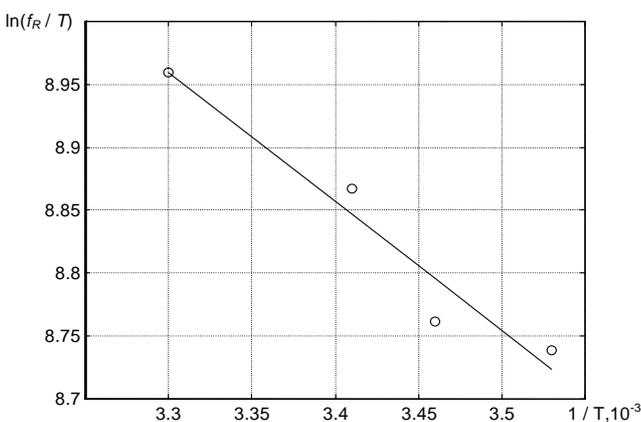

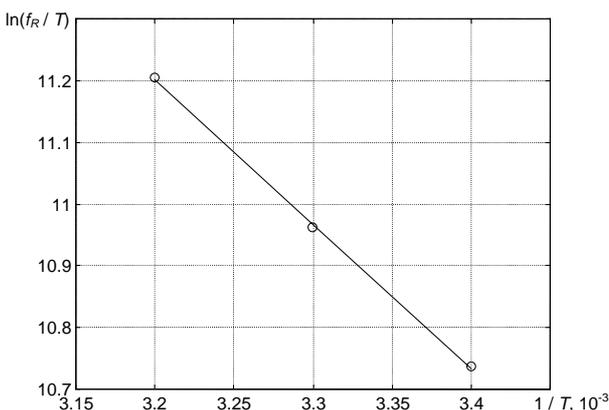Fig. 1. **Variation of $\ln(f_R / T)$ versus $1 / T$ for MnSO$_4$ solution**

Fig. 2. **Variation of $\ln(f_R / T)$ versus $1 / T$ for La$_2$(SO$_4$)$_3$ solution**

The difference in enthalpy ΔH_0 can be evaluated by the graphical method from the dependence of $\lg(T \mu_{max}/c^2)$ versus $1/T$ [5] or in our case from ultrasound velocity dispersion measurements $\lg(T \Delta c \pi /c_\infty \times c_R^2)$ versus $1/T$, because it is known that the excess absorption per

wavelength is related to the ultrasound velocity dispersion Δc by the following equation [6]:

$$(\alpha\lambda)_{max} = \mu_{max} = \Delta c \pi / c_\infty \times (\omega^2\tau^2/1+(\omega^2\tau^2)^{-1}, \qquad (3)$$

where c_∞ is the ultrasound velocity corresponding to very high frequencies $f>>f_R,$

$$\omega = 2 \pi f, c_R = (c_\infty + c_0)/2.$$

The change in the internal energy ΔH_0 evaluated from the plots of $10 + \lg(T \Delta c \pi /c_\infty \times c_R^2)$ versus $1/T$ as shown in Fig. 3 is equal to 9.1 kJ/mol of the complexation reaction in $MnSO_4$ solutions and $\Delta H_0 = -6.25$ kJ/mol in the case of $Ln_2(SO_4)_3$ solutions (Fig. 4).
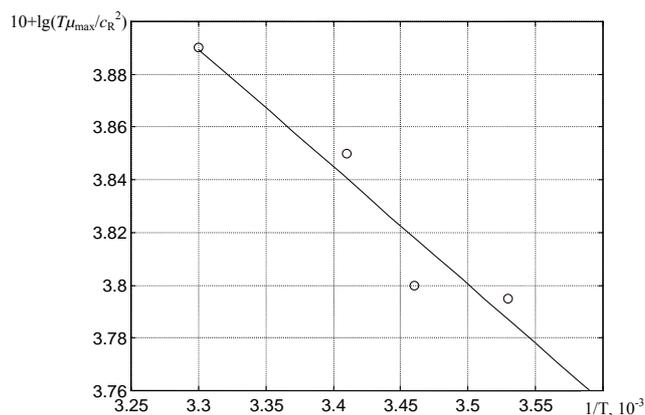

Fig. 3. **Graphic determination of the change in the internal energy ΔH_0 of the relaxation process in MnSO$_4$ solution**
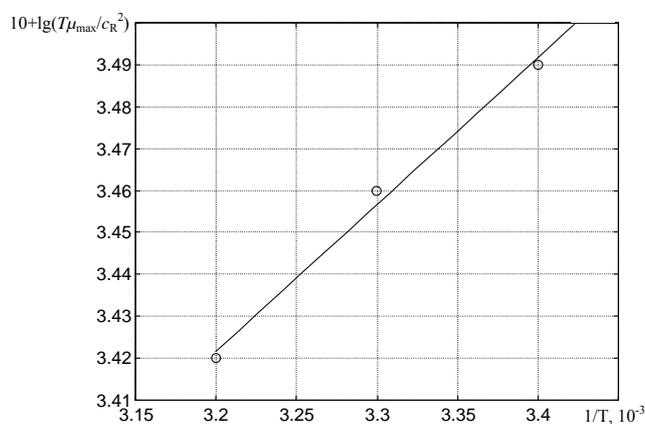

Fig. 4. D**efinition of the difference in enthalpy ΔH_0 for complexation reaction in Ln$_2$(SO$_4$)$_3$ solutions**

Table 2 lists the thermodynamic parameters obtained from the studies solutions.

The free energy ΔG of the complexation reaction for the same ligand and the different cation can be expressed [7]:

$$\Delta G = \Delta G_R + \Delta G_H =$$
$$= \Delta H_R + \Delta H_H - T(\Delta S_R + \Delta S_H), \qquad (4)$$

where R denotes cation – anion interaction, H denotes hydration changes upon complexation.

Table 2. **The thermodynamic parameters for complex formation of Mn^{2+} and La^{3+} sulphates**

Parameters	Complexes of Mn^{2+}	Complexes of La^{3+}
E_a (kJ·mol^{-1})	23.0	19.0
ΔH_0 (kJ·mol^{-1})	9.1	-6.25
ΔS (J·K^{-1}·mol^{-1})	-115.2	-103.4
ΔG (kJ·mol^{-1})	42.8	24.0

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 reaction in aqueous solutions with simple ligands, the hydration terms are, indeed, larger than the reaction terms. Moreover, if the hydration terms cancel, then
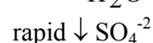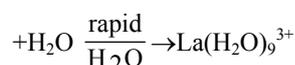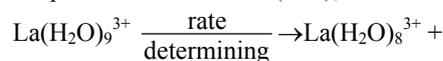
$$\Delta H_H \approx T\Delta S_H; \; \Delta G_H \approx 0.$$

As a result, $\Delta G \approx \Delta G_R$, i.e., the free energy of complexation is reflective from the cation – ligand interaction.

Ultrasound velocity dispersion is considered to be due to the process of association of Mn^{2+} and La^{3+} ions with SO_4^{-2} and formation of inner sphere complexes according to 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 [8]. In outer sphere complexation the primary hydration sphere of ions are minimally perturbed, so the difference in enthalpy ΔH_0 must be ≈ 0. In general, the values of enthalpy of complexation for the same ligand depend on interactions between Me – H_2O and Me – L (Me – metal ion, L – ligand). The positive value of enthalpy of complex formation in $MnSO_4$ solutions is offered as a possible explanation in terms of the hydratational changes. It agrees with the water exchange reaction between the first and the second coordination shell around Mn^{2+} ion in aqueous solutions. Water exchange process on $[Mn(H_2O)_6]^{2+}$ is characterized by positive enthalpy $\Delta H^{\#}$ value and negative sign of the volume of activation $\Delta V^{\#} = -5.4$ cm^3·mol^{-1} [9]. This indicates an associative activation mode and a concerted I_a mechanism is proposed according to Langford and Gray classification of reaction mechanisms [10]. Both bond making and bond breaking are involved in the rate – determining reaction for interchange mechanism I. A ligand (e.g. a co–ordinating solvent molecule) rapidly diffuses into the outer-sphere of the complex, followed by an interchange with the leaving ligand. For associative interchange I_a mechanism bond making dominates over bond breaking.

The experimental negative value of enthalpy obtained in this work for complex formation in $La_2(SO_4)_3$ solutions may be interpreted so that the lanthanum-ligand interaction is larger than the hydratational changes. As it is known, the chemical bond of complex formation depends on the ionic potential z/r (z is the valency of metal, r is the radius of the cation). Ionic radii in aqueous solutions are following: $r_{Mn}^{2+} = 83$ pm and $r_{La}^{3+} = 122$ pm [11]; so the ionic potential of lanthanum is larger and cation-ligand interaction is stronger.

Now it is well established from neutron scattering, X-ray scattering, density and spectrophotometric techniques [12] that the lighter ions of lanthanide (La^{3+} - Nd^{3+}) predominate in nine-coordinate species. Then the rate-determining step for complex formation in $La_2(SO_4)_3$ solution is proposed:

$$La(H_2O)_9^{3+} \xrightarrow[\text{determining}]{\text{rate}} La(H_2O)_8^{3+} +$$

$$+H_2O \xrightarrow[H_2O]{\text{rapid}} La(H_2O)_9^{3+}$$

rapid $\downarrow SO_4^{-2}$

$$[La(H_2O)_8SO_4]^+ \qquad\qquad (5)$$

The relaxation frequency is independent of concentration for both studied solutions. Therefore $\tau^{-1} = 2\pi f_R = k_f + k_R$ gives:
$MnSO_4$, t = 20^0 C, $k_f + k_R = 2.8\cdot10^7$ s^{-1},
$La_2(SO_4)_3$, t = 20^0 C, $k_f + k_R = 8.5 \; 10^7$ s^{-1}.

The relaxation frequency f_R primarily reflects on the rate of constant k_R. The water exchange rates are closely correlated with the rate k_I of the interchange between an inner sphere water molecule and SO_4^{-1} ion from the outer sphere coordination. The dissociation of a water molecule from the primary hydration shell for the water exchange on $[Nd(H_2O)_9]^{3+}$ [12] corresponds to an increase in volume, this pathway is classified as a dissociative interchange I_d mechanism. Water exchange on the ion La^{3+} occurs most probably by a I_d mechanism if this reaction volume is similar for the all light lanthanide ions.

The activation energy E_a of the backward reaction of complexation, e.g. the release of the ligand from the first coordination sphere of the cation in $MnSO_4$ solutions is larger than E_a in $La_2(SO_4)_3$ solutions. It may be explained by the difference in the coordinated numbers of the cation. The Mn^{2+} ion in water solutions exists as hexaaqua species and confirms the fact that the hydration process has an electrostatic character the ion-solvent interactions is stronger for $[Mn(H_2O)_6]^{2+}$ compare to $[La(H_2O)_9]^{3+}$ species.

Using the interpretation that the ultrasound velocity dispersion Δc in $MnSO_4$ and $La_2(SO_4)_3$ is caused by an association process, the magnitude of Δc may be the quantity of complexation. As seen from Table 1, the dispersion values are close for studied solutions but the concentration of $MnSO_4$ solutions is approximately 55 times larger. Thus, the amount of inner sphere complexes in $MnSO_4$ solutions is very insignificant, therefore the our determined rate constant is closely correlated with water exchange rate constant on $[Mn(H_2O)_6]^{2+}$ which is equal so $2.1\cdot10^7$ s^{-1} [12].

Conclusions

The thermodynamic parameters for the formation of inner sphere complexes in $MnSO_4$ and $La_2(SO_4)_3$ solutions have been calculated on the basis of relaxation data. The positive value in the internal energy ΔH_0 in $MnSO_4$ solution is interpreted in terms of the hydrational changes during the association process and negative value ΔH_0 for the $[LaSO_4]_{aq}^{+1}$ complexes is proposed with dominant the

lanthanum-ligand interaction. The amount of inner sphere complexes in $MnSO_4$ solution is very insignificant occurring only at high concentrations. In the rate determining reaction for complex formation different mechanisms for individual cations are proposed, e.g. the associative interchange I_a for Mn(II) and the dissociative interchange I_d for La(III) sulphates.

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Mn(II) ir La(III) kompleksų vandeniniuose sulfatų tirpaluose termodinaminiai parametrai

Reziumė

Remiantis relaksacinių parametrų temperatūrinėmis priklausomybėmis apskaičiuoti vandeniniuose sulfatų tirpaluose esančių Mn(II) ir La(III) kompleksų su vidine koordinacine sfera termodinaminiai parametrai. Aktyvacijos energija E_a apibūdina kompleksų susidarymo reakcijos atgalinį procesą, t.y. vandens molekulių grįžimą į katijono koordinacinę sferą. Susidarant mangano sulfatiniams kompleksams, E_a = 23 kJ/moliui, o susidarant lantano sulfato kompleksams, E_a = 19 kJ/moliui. Nevienoda E_a aiškinama skirtingu Mn^{2+} ir La^{3+} katijonų koordinaciniu skaičiumi, kadangi lantano koordinacinis skaičius yra 9, taigi katijonas ir vandens molekulės sąveikauja silpniau. Nustatėme, kad, susidarant mangano kompleksams, entalpijos pokytis ΔH_0 = 9,1 kJ/moliui, o susidarant lantano sulfatui ΔH_0 yra neigiamas ir lygus–6,25 kJ/moliui.Teigiamas ΔH_0 dydis mangano kompleksų susidarymo reakcijoje leidžia teigti, kad vyksta dehidratacija. Susidarant lantano kompleksams, lemiamą įtaką ΔH_0 turi ne hidratacijos sumažėjimas, bet katijono ir anijono sąveika. Abiejų tyrinėtų tirpalų reakcijų entropija yra neigiama.