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Application of Correlation Analysis to Description of Stability of Complex Compounds of Lanthanoid Ions with H_3Nta and H_6Ntph in Aqueous Solution

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Abstract—A series of correlations of logarithms of stability constants of the lanthanoid ion complexes with nitrilotriacetic and nitrilotrimethylenephosphonic acids of different composition with fundamental characteristics of the central ion is analyzed. A four-parameter equation gives the best agreement with the experimental data. The equation is used for estimation of stability of nonstudied complexes of ions Pm^{3+}, Eu^{3+}, Ho^{3+}, Tm^{3+}.

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There are numerous correlations in the literature [1–5] connecting physical and thermodynamic properties of lanthanoids with various characteristics of the central ion: the number of *f*-electrons in the Ln^{3+} ion shell (N_f), the size of the ion, quantum numbers of the ground state S, L, or just the serial number N of the ion in the sequence of lanthanoids. As to the number of various correlations including those for complex compounds, the f-elements are leaders among other elements.

Earlier [6, 7], using the method of potentiometric titration, we have measured the stability constants for complexes of various composition of 11 lanthanoids (Ln^{3+}) with nitrilotriacetic (NTA, H_3Nta) and nitrilotrimethylenephosphonic (NTP, H_6Ntph) acid.

As seen from Figs. 1 and 2, the stability of complexes in the series of lanthanides changed nonmonotonously. When the dependence log β vs. N_f (or the serial number of Ln, or ionic radius) is nonmonotonous, a linear dependence can be obtained when considering the properties of ions Ln^{3+} and their complexes (log β) as a function of the orbital quantum number L of the ground state of ion Ln^{3+}. The set of points fall on the lines which form a "turned on a side *W*." It was mentioned in the literature [8] that the points, plotted as a function of "*n*," which is proportional to the serial number of ion Ln^{3+}, are much better described by straight lines. The value of *n* is equal to 0, 2, 4, 6 for the first quarters (tetrads) for each half-period, and to 6, 4, 2, 0 for the second

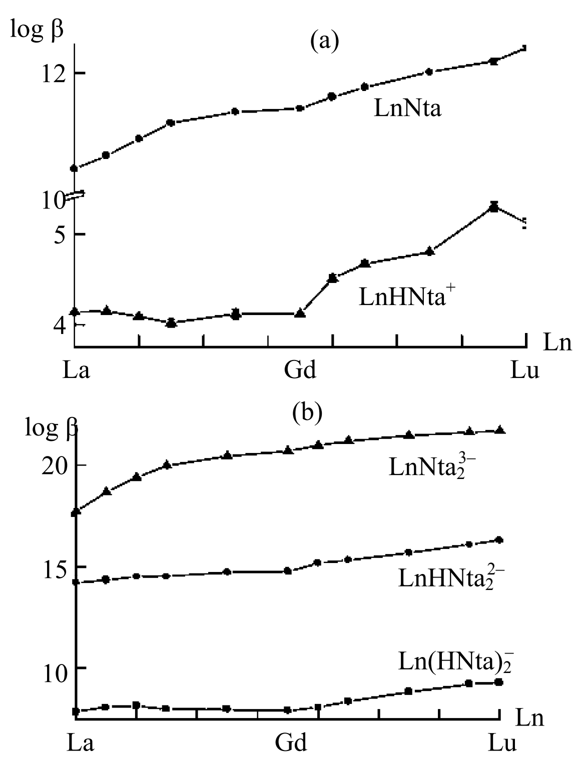

Fig. 1. Variation of log β of nitrilotriacetate complexes in the series of lanthanides.

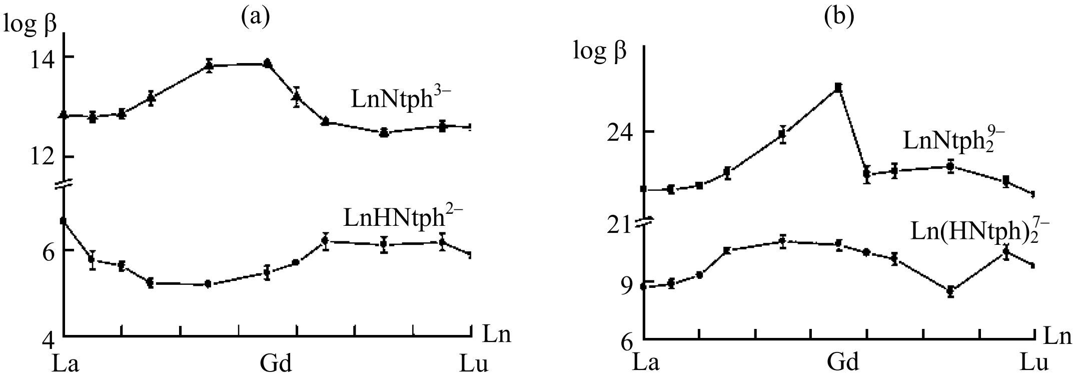

Fig. 2. Variation of log β of nitrilotrimethylenephosphonate complexes in the series of lanthanides.

quarters of the half-period. The presence of three points on the line allows to predict the numerical values for the forth point using the corresponding correlation equation. In this method the following correlation equation is used:

$$\log \beta_i = w_i n + k_i, \quad (1)$$

where w_i and k_i are coefficients characterizing the slope of the line and the intersects on the ordinate axis. The *W*–type plot for complexes of the LnNta composition is shown in Fig. 3. It is seen that the points in quarter-periods fit well the straight lines (coefficient of correlation $r > 0.99$).

A satisfactory *W*–type plot is obtained also for LnNta_2^{3-} complexes ($r > 0.99$). For other studied Ln complexes with NTA and NTP, satisfactory correlation coefficients were obtained only for some tetrads, and deviations of the experimental values from the log β_i values calculated from Eq. (1) reached one logarithmic unit.

Therefore, there are two necessary conditions for the prediction of complex stability from the *W*–plots: the presence of three of four possible values, that is, twelve experimental values of log β_i of the fifteen possible, and a high coefficient of linear correlation between log β_i and *n*. These conditions are by no means always fulfilled, thus in general such an approach is not reliable. In more complex correlation equations the fundamental characteristics of lanthanoids are used.

It is known that there is a relation between different properties of ions Ln^{3+} and their compounds (including the values log β) with the number of *f*-electrons in the shell of the lanthanoid ion, quantum numbers S, L of the ground state. For log β, the three-parameter [Eq. (4)] and four-parameter [Eq. (5)] equations were suggested in the literature:

$$\log \beta(\mathrm{LnLig}) = \log \beta(\mathrm{LaLig}) + a\mathrm{N_f} + b\mathrm{S} + c_1\mathrm{L}(c_2\mathrm{L}), \quad (2)$$

$$\log \beta(\mathrm{LnLig}) = \log \beta(\mathrm{LaLig}) + a\mathrm{N_f} + b\mathrm{S} + c_1(c_2)\mathrm{L}_1 + d_1(d_2, d_3, d_4)\mathrm{L}_2, \quad (3)$$

where *a, b, c_i, d_i* are correlation coefficients calculated from the experimental data.

The analysis of the results of treatment of the experimental data has shown that Eq. (2) much better describes the character of variation of stability of the Ln complexes with NTA than Eq. (1). Deviations of the experimental values log β from the calculated from Eq. (2) do not exceed 0.17 log units. For complexes with NTP of the LnNtph^{3-} and $\mathrm{LnHNtph}^{2-}$ composition the deviations reach 0.36 log units.

It was assumed that the character of variation of the complex stability in the series of lanthanoids can be described with smaller deviations by the use of Eq. (3). Correlation coefficients of Eq. (3) calculated for log β

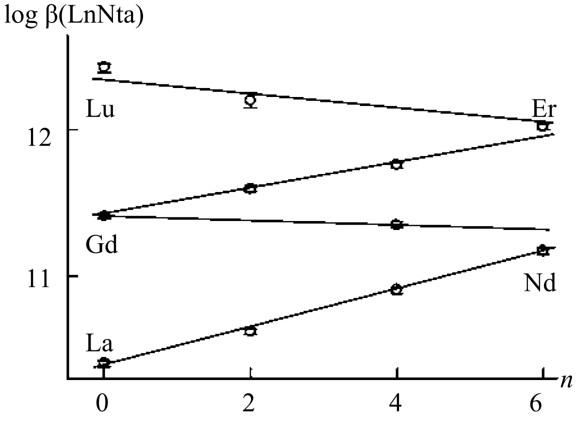

Fig. 3. Dependence of log β(LnNta) on the number *n*.

Table 1. Correlation coefficients for Eq. (3)

Complex	log β(LaLig)	*a*	*b*	c_1	c_2	d_1	d_2	d_3	d_4
$LnHNta^+$	4.14±0.02	0.070	–0.146	–0.019	0.018	0.040	0.069	0.201	0.287
LnNta	10.40±0.02	0.144	0	0.056	0.005	–0.025	0.004	0.037	–0.087
$Ln(Hnta)_2^-$	7.89±0.03	0.101	–0.194	0.016	0.021	0.179	0.004	–0.041	0.067
$LnHNta_2^{2-}$	14.18±0.04	0.151	–0.141	0.015	0.007	0.055	0.070	0.151	0.017
$LnNta_2^{3-}$	17.71±0.02	0.283	0.283	0.163	0.032	0.190	–0.043	0.076	0.016
LnNtph	12.84±0.06	–0.018	0.330	–0.017	–0.109	–0.180	0.322	–0.316	0.067

of complexes $LnHNta^+$, LnNta, $LnHNta_2^{2-}$, $Ln(HNta)_2^-$, $LnNta_2^{3-}$ and $LnNtph^{3-}$ are given in Table 1.

The results of treatment of the data using Eq. (3) have shown that deviations of the calculated values of log β from the experimental for complexes LnNta, $LnNta_2^{3-}$, $LnHNta_2^{2-}$, $Ln(HNta)_2^-$, $LnNtph^{3-}$ do not exceed 0.05 log. unit, that is, Eq. (3) describes the character of variation of log β in the series of lanthanoids within the statistical error of determination of log β. Equation (3) allows the estimation of the stability constants for complex ions of lanthanoids for which they were not determined experimentally. The values of log β for complexes Nta^{3-} and $Ntph^{6-}$ with nonstudied lanthanoids as predicted by correlation Eq. (3) are given in Table 2.

Therefore, analysis of correlation equations describing variation of complex stability in the series of lanthanoids has shown that the most reliable results are obtained by the four-parameter Eq. (3) regardless of whether there is a clearly expresses tetrad effect or not. For calculation of the coefficients of Eq. (3), the experimental values of log β for complexes of nine lanthanoids are needed. Correlation Eqs. (1) and (2) require larger array of experimental data.

Table 2. Predicted values of log β for complexes of Pm, Eu, Ho, Tm

Complex	Ln^{3+}			
	Pm	Eu	Ho	Tm
LnNta	11.31	11.38	11.88	12.07
$LnHNta^+$	4.02	4.15	4.66	5.19
$Ln(HNta)_2^-$	8.00	7.95	8.64	9.06
$LnHNta_2^{2-}$	14.59	14.76	15.45	15.89
$LnNta_2^{3-}$	20.38	20.54	21.30	21.53
$LnNtph^{3-}$	13.33	14.01	12.66	12.58

EXPERIMENTAL

The EMF of the chain with transfer, including a glass and silver chloride electrodes, was measured by the compensatory method. All measurements were performed at 25ºC and ionic strength $I = 0.1$ (KNO_3). The experimental data of the potentiometric measurements were treated by the use of the PHMETR program [11] based on minimization of the likelihood function $F = \Sigma(p_cH_{exp} - p_cH_{calcd})^2$, where p_cH_{exp} and p_cH_{calcd} are the experimental values and those calculated from the model, respectively. In Figs. 1, 2 the obtained logarithms of the equilibrium constants (log β) are given for the following reactions:

$$Ln^{3+} + H_iL^{i-n} = LnH_iL^{3+i-n}, \tag{4}$$

$$Ln^{3+} + 2H_iL^{i-n} = Ln(H_iL)_2^{3+2(i-n)}, \tag{5}$$

where L = Nta^{3-}, Ntf^{6-}.

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