Stepanchikova S.A., Kolonin G.R. Electronic spectra of neodymium, samarium, and holmium chloride complexes at temperatures up to 250^{O}C

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Abstract. Regularities, observed in the absorption spectra of acid chlorine-bearing solutions of 3-valent neodymium, samarium, and holmium ions at varying temperature within the concentration range of chlorine-ion from 0 to 5 mol/l, are used for determination of specie types and stability constant of monochloride complexes within the temperature range from 100 to 250^{O}C and infinite dilution.

There is only one study on the complex formation of REE at high temperatures [1]. In this study, stability and stoichiometry of chloride complexes of Nd(III) at temperatures 40-300^{O}C were determined from solubility of AgCl in solutions HCl+NaCl in the presence of Nd and regression of the results to obtain the first and the second constants of stability of Nd(III) chloride complexes.

An optical method of investigation of equilibria in chloride solutions is applied in the present study. The study of visible spectral transitions of 3-valent lanthanide ions showed that their forms, the position and intensities are related to temperature. The character of temperature dependence for the transitions, which are "super-sensitive" to ligand fields, differs form that of the "non-super-sensitive" transitions, which do not fulfill the selection rule for electrically quadruple transitions ($\Delta J \leq 2$, $\Delta L \leq 2$) [2]. Regularities, observed in the spectra of chloride Nd(III), Ho(III), and Sm(III) solutions at varying temperature and composition of a solution, were used for investigation of stability of their complexes.

Figure 1 shows an influence of temperature on the spectra of Nd^{3+} aqua-ion, produced by means of dissolution of Nd_2O_3 in the stoichiometric amount of perchloric acid. An increase of temperature is resulted in a significant decrease of intensities of all observed bands, where transitions with maxima at 17300, 17400, and 19100 cm^{-1} are "super-sensitive" (basic state is $^4I_{9/2}$). The unusual temperature dependence of spectroscopic properties of aqua-ions was explained by an influence of molecular interactions in a condensed substance. This influence results in difference of the measured values of the strength of the average light field form the strength of the microscopic field affecting a molecule. The microscopic field determines spectroscopic properties of the molecule and demonstrates a dependence of the adsorption coefficient on temperature for the spectral transitions inside the f-orbitals for the weak field of water molecules [3]. A value of this effect is defined by the dielectric permitivity of the substance and, respectively, can depend not only on temperature, but the concentration of solutions as well. Therefore, spectral measurements at constant temperature and in wide concentrational ranges without the additional refractometric measurements can result in significant experimental errors.

Figure 2 shows the spectra of a solution containing 0.1 mol/l $NdCl_3$ and 5 mol/l LiCl. Heating of the solution results in appearance of a line with a maximum at 17200 cm^{-1}, its subsequent growth and long-wave shift with a distinct isobestic point. In the region to the right form the super-sensitive line with the maximum at 19100cm^{-1}, new line appears and grows. Complexities at 28000 and 13000 cm^{-1} are also evident. An influence of the chloride-ion on intensities of the super-sensitive transitions is more notable for solutions containing 0.3 mol/l NaCl. However, in more concentrated solutions, both by $NdCl_3$ and NaCl, neither any new lines nor new isobestic points, corresponding to appearance of new aquatic species, were observed. This fact gave a preliminary idea that only two light-absorbing species, i.e. aqua-ion and monochloride complex $Nd_{aq}Cl^{2+}$, were present in the system. An increase of the intensity of the super-sensitive lines in lanthanides solutions in the presence of logands is considered to be related to the influence of oscillations of surrounding atoms [2]. Frequencies of normal oscillations involved in the electron transition depend on temperature and, along with the concentrational variations, can result in the increase of intensities of the spectral transitions. Thus, the temperature dependence of the absorption lines of aqua-ions in chloride solutions is opposite to the temperature dependence of the super-sensitive chloride complexes, which are used by us for quantitative estimations. Intensities of the lines of the super-sensitive complexes increase both with temperature and concentration of chloride-ion. A possible influence of intermolecular interactions in these regions is within the experimental errors.

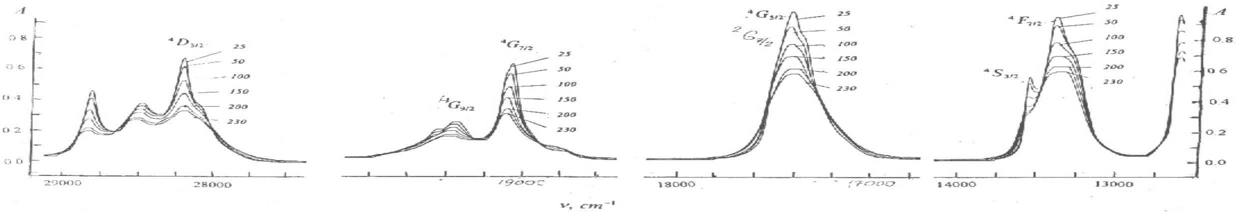

Fig. 1 Temperature influence on the absorption spectra of the solution containing 0.1 Mol/l of Nd_2O_3 and 0.4 mol/l of $HClO_4$. Temperature is shown at the curves

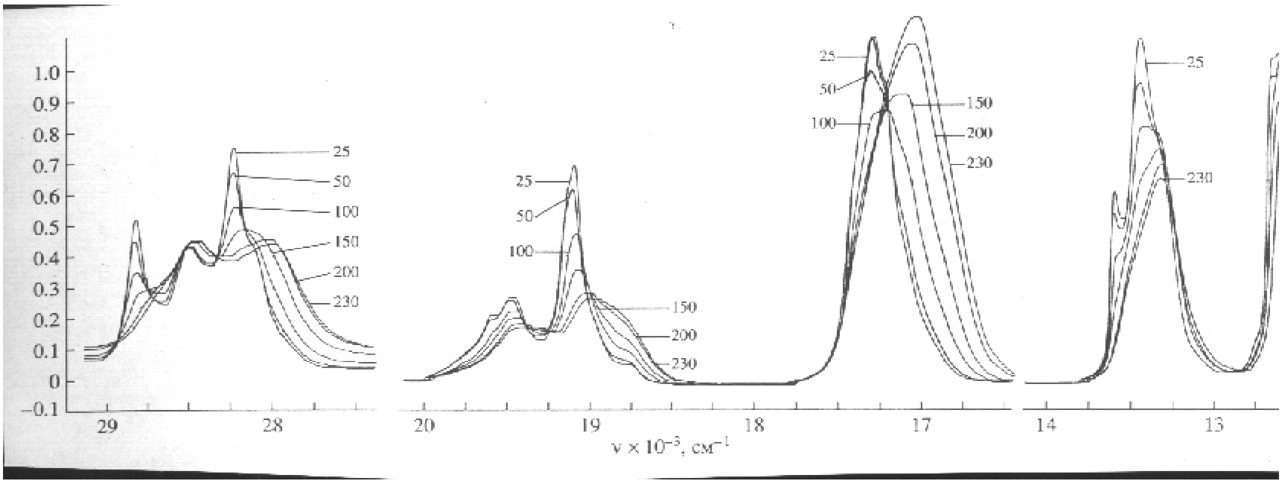

Fig. 2 Temperature influence on the absorption spectra of the solution containing 0.1 Mol/l of $NdCl_3$, 0.5 mol/l of $HClO_4$ and 5 mol/l of LiCl.

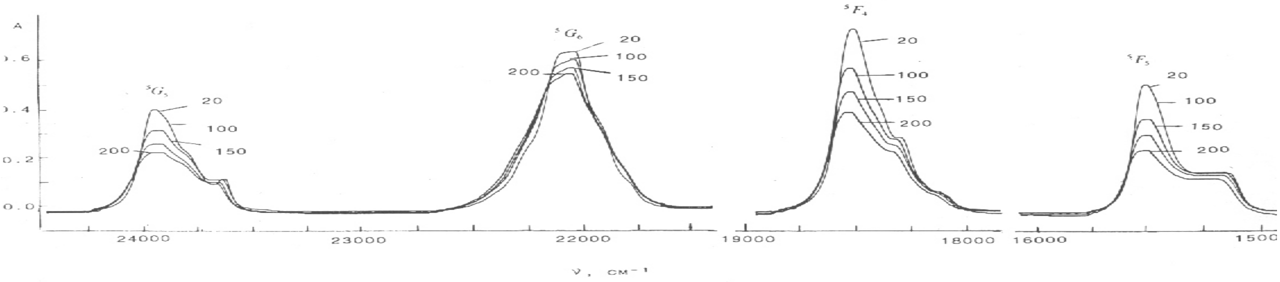

Fig. 3 Temperature influence on the absorption spectra of the solution containing 0.17 Mol/l of Ho_2O_3 and 0.8 mol/l of $HClO_4$..

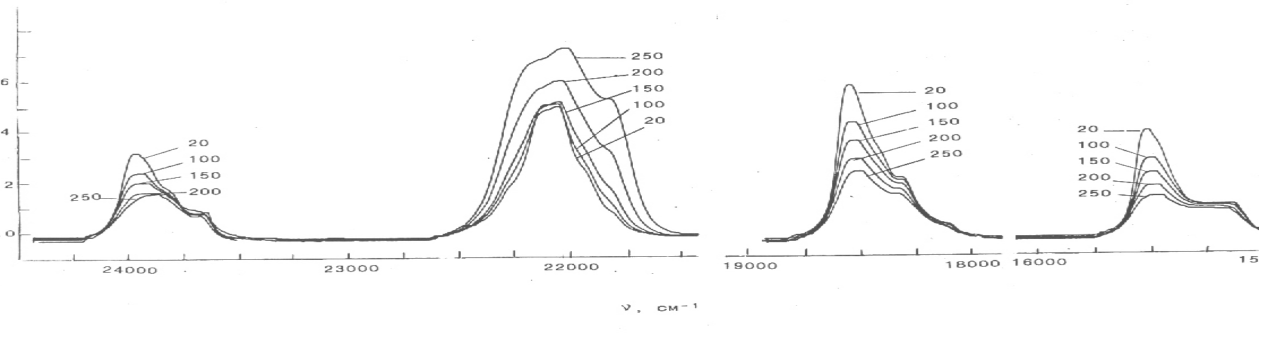

Fig. 4 Temperature influence on the absorption spectra of the solution containing 0.13 Mol/l of $HoCl_3$ and 0.5 mol/l of $HClO_4$.

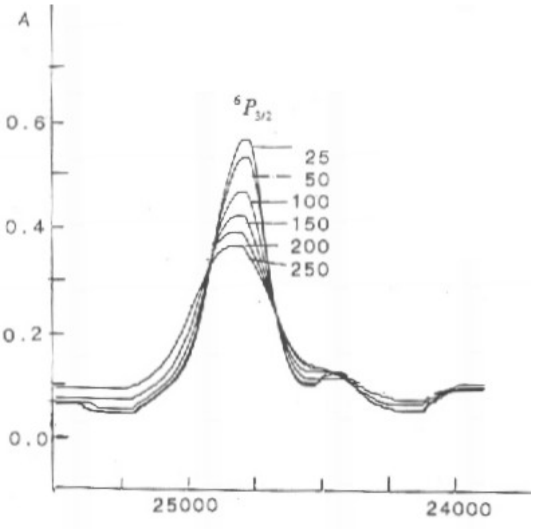

Fig. 5 Temperature influence on the absorption spectra of the solution containing 0.13 mol/l of Sm_2O_3 and 1 mol/l of $HClO_4$

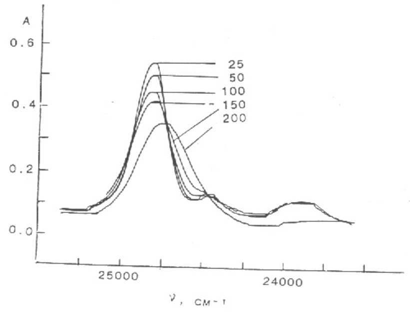

Fig. 6 Temperature influence on the absorption spectra of the solution containing 0.13 mol/l of Sm_2O_3, 1 mol/l of $HClO_4$ and 2.0 mol/l of NaCl.

Table 1. Logarithms of the stability constants (*β*) for Nd, Sm and Ho mono-chloride complexes, averaged by wave numbers, and their standard deviations (S)

t, ^{0}C	$NdCl^{2+}$		$SmCl^{2+}$		$HoCl^{2+}$	
	lg β	S lg β	lg β	S lg β	lg β	S lg β
100	1.429	0.013	1.456	0.034	2.137	0.054
150	1.670	0.006	1.784	0.070	2.218	0.036
175					2.303	0.036
200	1.973	0.010	1.960	0.075	2.338	0.029
225			2.208	0.083	2.421	0.019
250	2.456	0.018			2.656	0.016

In order to calculate the stability constants and the extinction coefficients of the mono-chloride complex and values of its molal exstinctions, determined in the given interval of wave numbers, we used spectral series of solutions of constant NaCl concentration 1.58 mol/l, and $NdCl_3$ concentration varying from 0.05-0.20 mol/l. Calculations were performed by means of linear regression using the iteration procedure. Calculations were carried out for 9 values of wave numbers within the interval 16600-17400 cm^{-1}. Table 1 shows the stability constants for temperatures 100-250^{O}C and infinite dilution, averaged by wave numbers.

Temperature influence on Ho^{3+}_{aq} spectra is expressed in significant decrease of strength of oscillators of the "non-super-sensitive" transitions at 24000, 18500 and 15500 cm^{-1} (basic state is $^5I_8$), and, in less degree, for super-sensitive transitions with general maximum at 22160 cm^{-1} (Fig. 3). Heating of $HoCl_3$ solutions up to 100^{O}C resulted in insignificant decrease of the absorption intensity in the super-sensitive region. Subsequent temperature increase resulted in the appearance of other system of lines in the same region. A basic maximum of this system was shifted into the long-wave region and continued to displace simultaneously with the increase of intensity (Fig. 4). The isobestic point did not appear. The spectra of the chloride complex could be distinguished from the spectra of the aqua-ion only by shape and inverse temperature dependence. An absence of the isobestic point and change in the shape of the absorption lines was explained by the additional Stark-splitting into the number of components, which resulted in the appearance of new lines [2]. Since the intensity of the lines of holmium mono-chloride, we did not use high concentrations of the chloride-ion. In order to calculate the stability constants and the extinction coefficients of species in equilibrium with holmium-bearing complexes, the spectral series of solutions with the increasing of $HoCl_3$ concentration and constant HCl concentration were used. Calculations performed by means of the above procedure for 8 values of wave numbers in the interval 21800-22400 cm^{-1} allowed estimation of the stability constants for $HoCl^{2+}$ and the experimental errors (sd) within 100-250^{O}C and infinite dilution.

Samarium aqua-ion has only one intense line in the visible region with maximum 24900 cm^{-1} ($^6H_{5/2} \rightarrow {}^6P_{3/2}$), which is useful for measurements (Fig. 5). Its temperature dependence generally repeats the temperature dependence of neodymium complexes. A presence of 2 mol/l of chloride-ion, added into the perchlorate solutions of samarium oxide, resulted in complexity in the long-wave portion of this line with the appearance of the single distinct isobestic point. It was evident at temperatures about $100^{O}C$ (Fig. 6). The mechanism of these changes is close to that for the neodymium complexes. Spectral series of solutions of Nd_2O_3 with concentrations from 0.4 to 1.7 mol/l were used for calculations. The averaged results are shown in Table 1.

A regular analysis and comparison of the obtained and approximated values of the stability constants with the data by [1] were carried out in [4]. The applied optical method allowed determination of a stoichiometry and the stability constants of mono-chloride complexes of some lanthanides and demonstrated a principal possibility of estimation of the relative stability of REE complex compounds in dependence on the atomic number regarding the metal-ligand interactions observed in the high-temperature spectra.

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