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Investigation of the optical and ultrasonic properties of praseodymium and cerium chlorides in nonaqueous solutions

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Abstract

The excitation, emission and absorption spectra of anhydrous and hydrated chlorides in anhydrous alcohols (C_2H_5OH and n-C_3H_7OH) were investigated at 300 and 77 K with the aim of explaining the spectroscopic properties (emission and absorption) of Ce^{3+} and Pr^{3+} in non-aqueous systems. Ultrasonic velocities and densities were measured and adiabatic compressibility coefficients were calculated to explain the structure of the solvates forming in solution. The role of the type of solvent on the symmetry and stoichiometry of the solvates is discussed on the basis of intensity analysis and energy and splitting of f–d and f–f transitions and correlated with our previous ultrasonic and optical results. The effect of concentration and energy excitation on the structure and splitting of the bands observed in the excitation and emission spectra was examined. The results are interpreted in terms of chemical relaxation in solution and coordination of chloride anions.

Keywords: Solvation; Praseodymium chloride; Cerium chloride; Ethanol; n-Propanol; Non-aqueous solutions; Spectroscopy; Sound velocity; Compressibility; Solvation numbers

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1. Introduction

Recently, we reported the results of a spectroscopic investigation of lanthanide chlorides in non-aqueous solutions [1,2], as well as the optical properties of silica sol-gel glasses obtained, among others, by the alcoholic method [3,4]. It was shown that the optical properties of active ions in a gel depend on its structure, which can be modified by the type of precursor salt, the solvent, and the type of silan [5,6]. However, the emission properties of these systems also depend on the equilibria between different oxidation states of the metal ions (M^{3+}/M^{4+}). These equilibria are controlled by the concentrations of ions in solution [7,8]. The results presented are a consequence of the earlier research. The goal was to focus on the role of the solvent in the creation of the metal centres and to find the best conditions for strong emission. Additionally, ultrasonic measurements were applied, since they are useful in the investigation of the solvation processes, as well as of the relaxation processes in solution.

2. Experimental

Hydrated and anhydrous cerium and praseodymium chlorides were obtained by modification of the method for the corresponding perchlorates [9]. The presence of water was controlled using IR spectra. Purification of the solvents was as described previously [10]. Absorption spectra were measured at room temperature using a Cary-Varian 5 spectrophotometer. Emission and excitation spectra were measured at 77 and 293 K with a SPF 500 spectrofluorimeter. Details of the acoustic measurements can be found in Refs. [11,12].

3. Results and discussion

Four systems are the subject of this paper: cerium and praseodymium chlorides in anhydrous ethanol and n-propanol solutions. This choice was motivated by the possibility of correlating the results for f–d and/or C-T transition intensities and energies with the data for f–f transitions. In fact, the C-T state can also play a significant role in the emission of Ce(III). Moreover, two types of transitions can be detected in praseodymium spectra (f–d

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and f–f), which allows us to make a comparison with the data for cerium systems.

3.1. Solutions of cerium chloride

Absorption spectra of anhydrous and hydrated $CeCl_3$ in C_2H_5OH and n-C_3H_7OH solutions are shown in Fig. 1. The spectra contain transitions from $^2F_{5/2}$ ground state multiplets of cerium(III) ions to the excited 5d levels. The absorption spectrum in the UV region is composed of five bands with different half-band widths and intensities. The first band, located at 310 nm, is more intense than the others, also having a larger half-width.

Deconvolution of the spectra into components using the Gauss–Lorentz functions leads to the intensity calculation results shown in Table 1. Note that the energy of all the bands (with the exception of the system $CeCl_3$(anhydr.)+ ethanol) is similar to that reported earlier for solutions in methanol and iso-propanol [2]. The spectrum of anhydrous $CeCl_3$ in ethanol is shifted by about 8 nm.

Since cerium(III) has only one optically active electron, two levels in the 4f configuration of the free ion, the $^2F_{5/2}$ ground state and the $^2F_{7/2}$ excited state are separated by $\cong 2200\ cm^{-1}$. In the 5d configuration it also has two levels: $^2D_{3/2}$ and $^2D_{5/2}$, and the O_h symmetry splits them into three components; at lower symmetry, degeneration of these levels is removed. The crystal field splits these levels into two and three components; thus, one can expect five transitions from the $^2F_{5/2}$ ground state of Ce^{3+} to the excited states only if the experiment is performed at low temperature. However, the absorption spectra of our solutions were recorded at room temperature (ca. 293 K), where all the Stark components of the $^2F_{5/2}$ term can be populated. On the other hand, since splitting of the $^2F_{5/2}$ ground state by CF is less than that of d orbitals, the shape of the spectra is mainly governed by the CF effect on the 5d configuration (Figs. 2 and 3).

The above finds confirmation in the emission spectra, where the emission band obtained at 293 K is composed of two transitions (split by $\cong 2000\ cm^{-1}$) which are further split into two components located at energies $\cong 338$ nm and 362.5 nm at 77 K. The energy of separation of these bands is $1950\ cm^{-1}$ and corresponds to two ^2F terms of the Ce(III) ion. Thus, either the first broad bands in the absorption are composed of transitions of different components of the ground state multiplet and vibronic components, or they are composed of transitions originating from two or more different species existing in solution. The latter assumption would be acceptable only if sufficiently strong differences in the CF effect were observed for these species.

Our further studies of the absorption spectra at low

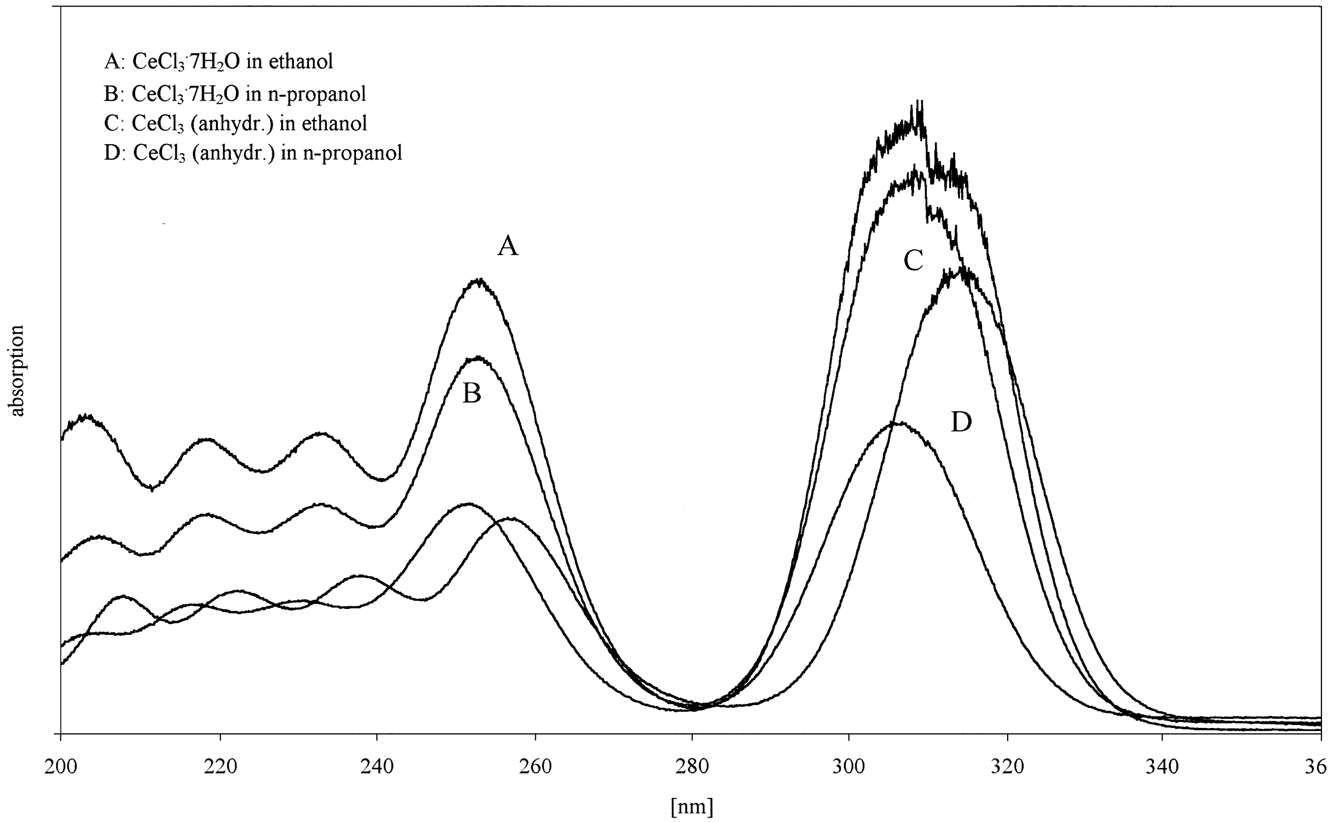

Fig. 1. Absorption spectra of cerium chlorides (hydrated and anhydrous) in ethanol and n-propanol. The curves were normalized to a similar scale and the absorption (*Y*-axis) is given.

Table 1
Intensity analysis of f–d and f–f transitions in the cerium and praseodymium systems investigated[a]

	4f–5d										$P_\Sigma \times 10^5$	
	1		2		3		4		5			
	λ (nm)	$P \times 10^5$	λ (nm)	$P \times 10^5$	λ (nm)	$P \times 10^5$	λ (nm)	$P \times 10^5$	λ (nm)	$P \times 10^5$		
$CeCl_3 \cdot 7H_2O + C_2H_5OH$ ($c = 0.11$ M)	203	384	219	269	233	252	253	544	309	614	2063	
$CeCl_3 + C_2H_5OH$ ($c = 0.052$ M)	208	215	223	228	238	278	257	441	314	813	1975	
$CeCl_3 \cdot 7H_2O + n\text{-}C_3H_7OH$ ($c = 0.084$ M)	205	254	218	255	233	252	253	562	308	664	1885	
$CeCl_3 + n\text{-}C_3H_7OH$ ($c = 0.046$ M)	203	168	217	240	231	276	251	632	307	631	1948	
	4f–5d		4f–4f									
			$^3P_2$		$^1I_6$ $^3P_1$		$^3P_0$		$^1D_2$		$^1G_4$	
	λ (nm)	$P \times 10^5$	λ (nm)	$P \times 10^8$	λ (nm)	$P \times 10^8$	λ (nm)	$P \times 10^8$	λ (nm)	$P \times 10^8$	λ (nm)	$P \times 10^8$
$PrCl_3 \cdot 6H_2O + C_2H_5OH$ ($c = 0.094$ M)	224	1089	446	1255	471	623	483	360	595	286	1007 1029	41.0
$PrCl_3 + C_2H_5OH$ ($c = 0.053$ M)	228	1498	447	1106	472	580	484	362	595	250	1001 1030	41.4
$PrCl_3 \cdot 6H_2O + n\text{-}C_3H_7OH$ ($c = 0.080$ M)	223	1100	446	1279	471	632	483	364	594	284	1009 1028	36.8
$PrCl_3 + n\text{-}C_3H_7OH$ ($c = 0.045$ M)	221	956	447	1344	470	627	482	337	594	298	1009 1026	40.2

[a] Oscillator strengths for separated components were obtained after resolving the bands using the Gauss function. P_Σ, is ''total'' oscillator strength calculated from the area under the full experimental band.

temperature (77 K or lower) in frozen solutions can explain this problem. In our earlier papers one finds confirmation of phonon-assisted lines in the low-temperature spectra of lanthanide solutions in halogeno derivatives of alcohols [13,14].

Note also the minor changes of the energy and intensity of the two bands observed in the emission spectra of $CeCl_3$ in ethanol of concentrations 10^{-1} and 10^{-3} M, since the CF effect is smaller for components which correspond to the 4f configuration. Thus, the number of innersphere Cl^- does not affect these bands and is less than for d-configuration transitions (Fig. 4).

It is also worth noting that, in fact, the differences between the spectra for ethanol and n-propanol are not significant, confirming the similar structures of the solvates forming in solution, and the drastic differences observed for the iso-propanolic systems examined recently [2] arise from steric factors. Moreover, we could not detect any trace of Ce^{4+} in any solvent, even after 10 h. The dependencies of the Ce^{3+}/Ce^{4+} equilibria on time and temperature will be the subject of a future communication.

The subtle differences observed for anhydrous $CeCl_3$ in C_2H_5OH most probably result from an equilibrium between two (or more) forms created in the system, for instance $CeCl_2(C_2H_5OH)_7 \leftrightarrows CeCl_3(C_2H_5OH)_6$. The latter form seems to dominate at higher concentrations. The existence of these forms finds confirmation in the analysis of C-T bands of $EuCl_3$ spectra in C_2H_5OH solution, as well as from conductivity measurements of this system [15]. The creation of somewhat different solvates in ethanolic solutions also manifests itself in changes of the intensities of long-wave bands (see Table 1).

The above interpretation does not contradict the results of emission and excitation experiments. The emission bands are temperature-controlled and shift towards higher energies with decreasing temperature. Moreover, splitting of these bands allows us to observe two ^2F_J levels of Ce(III) and to determine the splitting between them to be 1950 cm^{-1}.

The excitation spectra split into at least five components. Note that the first bands of these spectra, corresponding to the broad band located at 320 nm in the absorption spectrum, are split into two components for anhydrous $CeCl_3$ in C_2H_5OH and for $CeCl_3 \cdot 7H_2O$ in $n\text{-}C_3H_7OH$.

Two components are also observed in the room temperature spectra of anhydrous $CeCl_3$ in ethanol and n-propanol. Consequently, additional components of the $4f^{n-1}5d$ transition should reflect different complexes created in solution.

Ultrasonic measurements detect the rearrangement of chloro complexes in the concentration range 0.01–0.06 M of anhydrous $CeCl_3$ and $PrCl_3$ in C_2H_5OH. The solvation

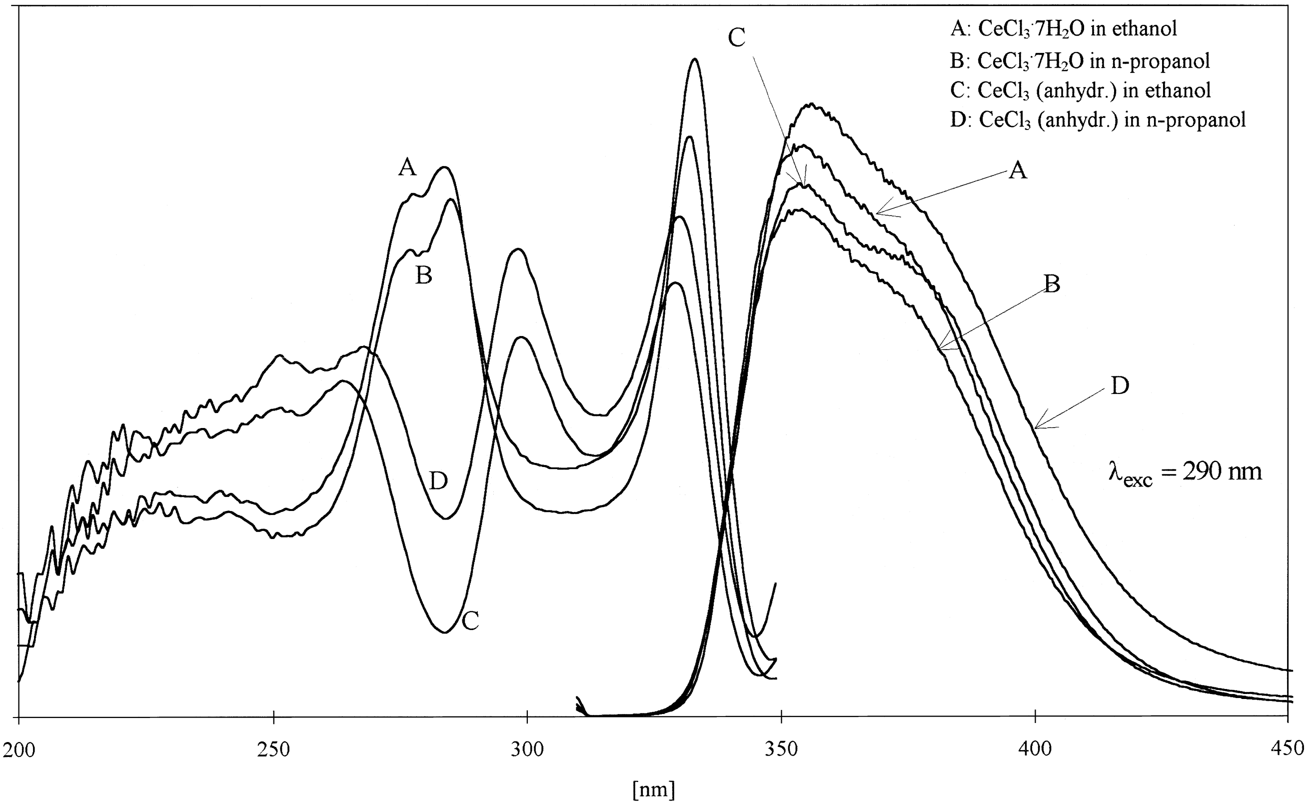

Fig. 2. Excitation (left) and emission (right) spectra of cerium chlorides (hydrated and anhydrous) in ethanol and n-propanol; room temperature. *Y*-axis scale is arbitrary (see Fig. 1).

numbers (S_N) change significantly faster compared with the respective hydrated solutes: for hydrated salts, $S_N \sim 10$ for low, and ~9 for higher concentrations of the hydrated chlorides under test, compared with 8 and 6, respectively, for the anhydrous chlorides. Thus, the change of S_N with increasing salt content is about 1 for hydrated and about 2 for anhydrous solutes. In the case of n-propanol solvent, for all the salts tested, the solvation number decreases with increasing electrolyte content, confirming that the formation of trichloro complexes dominates at higher concentration. Detailed results of ultrasonic measurements, not being within the scope of this journal, will be the subject of a future paper.

The minor Stokes shifts, $\cong 2000$ cm^{-1} (1815 cm^{-1} for hydrated and 2020 cm^{-1} for anhydrous salts at 293 K, and 1157 and 1089 cm^{-1} at 77 K, respectively), observed in emission and excitation spectra demonstrate the rather low covalency of the systems under investigation.

Splitting of $^2D_{3/2}$ and $^2D_{5/2}$ into the maximum number of components indicates lower than O_h symmetry of the lanthanide centres. Analysis of the possible symmetry for C.N. = 9, as determined from the C-T states in the respective Eu(III) systems and remembering that there are two or three chloride ions in the inner sphere of metal ions, makes it reasonable to assume C_{3v} and/or C_{2v} symmetries of the solvates formed.

3.2. Praseodymium chloride solutions

Here, one broad band is observed in the UV region of the absorption spectra. It is located at 225 nm and corresponds to the 4f–5d transition (Fig. 5).

Moreover, transitions from the $^3H_4$ ground state multiplet to the ^3P_J, $^1D_2$ and $^1G_4$ levels are observed. Intensities of the f–f transitions are less sensitive to the changes of equilibria between different chloro complexes in solution than those of f–d transitions. The most sensitive are the $^3H_4 \rightarrow {}^3P_2$ and $^1D_2$ transitions obeying the selection rule $\Delta J = 2$ (Fig. 6).

More information can be obtained from analysis of the splitting and intensity of f–d bands. Similarly to cerium systems, the band of anhydrous $PrCl_3$ in C_2H_5OH is shifted by 4 nm towards lower energy, thus indicating subtle differences in formation of chloro complexes. In fact, the position of the broad f–d band is the same as in the systems investigated recently [2], and it is shifted by almost 80 nm from the first band of the respective cerium sample.

Table 1 shows the results of oscillator strength calculations for f–d and f–f transitions. It is worth noting that the intensities of the f–d bands in Pr(III) spectra are larger than those of the first bands of cerium systems. Finally, similar changes of energies of bands of anhydrous $PrCl_3$ in

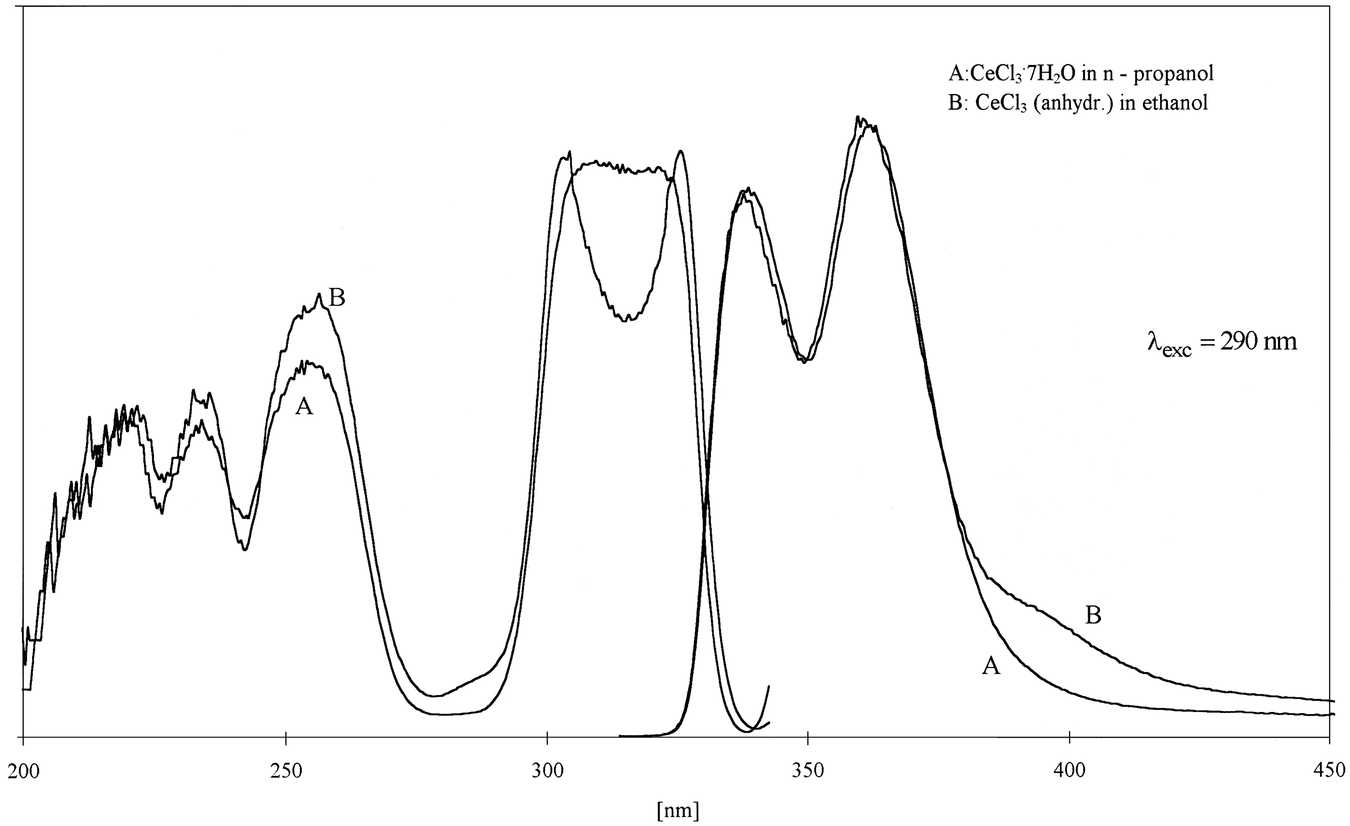

Fig. 3. Excitation (left) and emission (right) spectra of cerium chloride in alcohols recorded at 77 K. *Y*-axis scale is arbitrary (see Fig. 1).

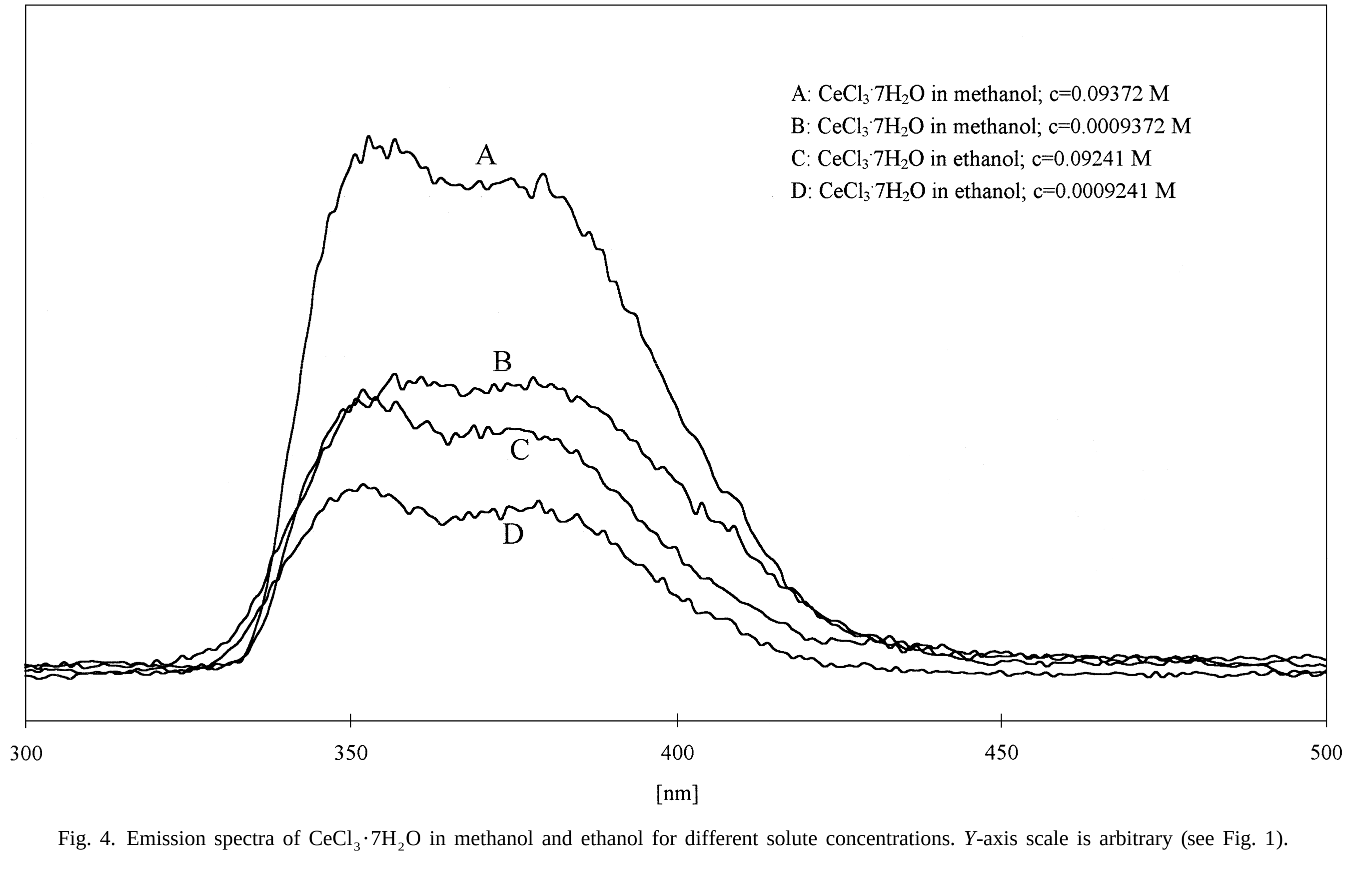

Fig. 4. Emission spectra of $CeCl_3 \cdot 7H_2O$ in methanol and ethanol for different solute concentrations. *Y*-axis scale is arbitrary (see Fig. 1).

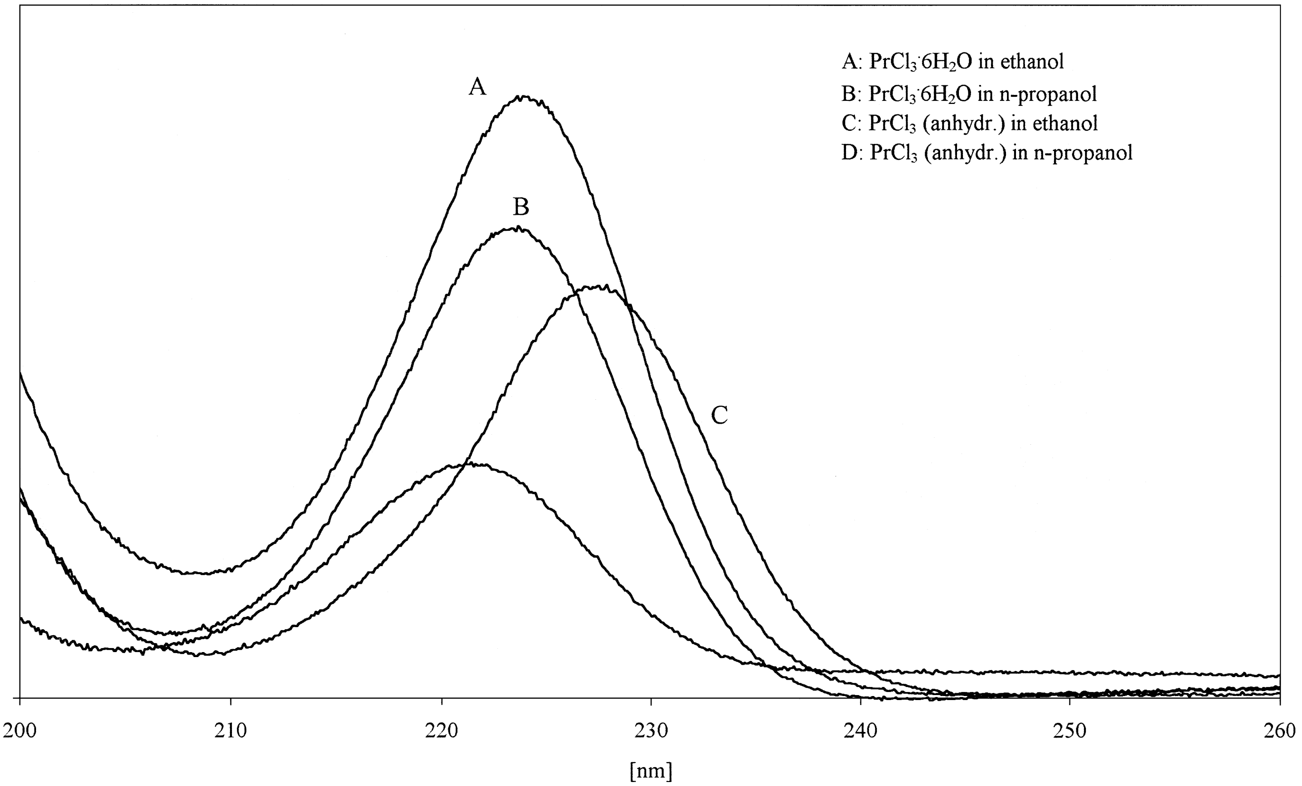

Fig. 5. Absorption spectra of praseodymium chlorides (hydrated and anhydrous) in ethanol and n-propanol (the region of f–d transitions). *Y*-axis scale is arbitrary (see Fig. 1).

ethanolic solution were also detected in the range of f–f transitions.

4. Conclusions

1. Analysis of the energy, splitting and intensity of f–d and f–f bands shows that the former better reflect the equilibria in the systems under investigation.
2. Essential differences in Stokes shifts were detected in the spectra of anhydrous cerium solutions.
3. The UV region (200–350 nm) in the absorption and excitation spectra is composed of five components ($^5D_{3/2}$, $^5D_{5/2}$, splitting levels), indicating a low symmetry (C_{2v}, C_{3v}) of the metal centres.
4. Splitting given by the crystal field demonstrates the existence of equilibria of centres of different symmetries.
5. Acoustic investigation (to be presented in detail in a future publication) indicates the presence of equilibria of different chloro complexes, seen as the gradual change of solvation number with concentration, thus confirming the spectroscopic results.

Acknowledgements

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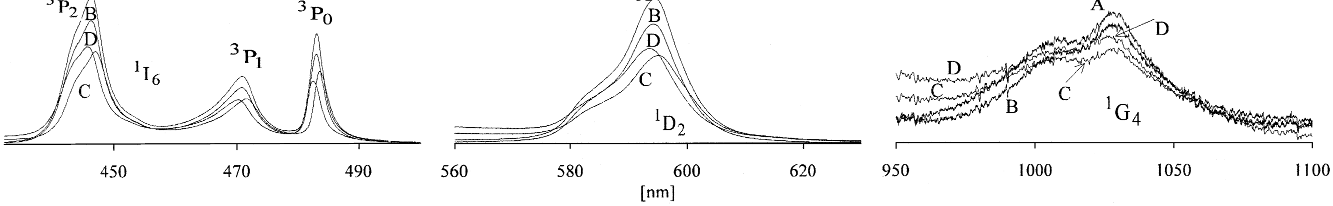

Fig. 6. Absorption spectra of praseodymium chlorides (hydrated and anhydrous) in ethanol and n-propanol (the region of f–f transitions): (A) $PrCl_3 \cdot 7H_2O$ in ethanol, (B) $PrCl_3 \cdot 7H_2O$ in n-propanol, (C) $PrCl_3$ (anhydrous) in ethanol, (D) $PrCl_3$ (anhydrous) in n-propanol. *Y*-axis scale is arbitrary (see Fig. 1).

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