Intensity Analysis and Luminescence Spectra of Non-Aqueous Solutions of Europium Compounds

Janina Legendziewicz, Grażyna Oczko,
Institute of Chemistry, University of Wrocław, Wrocław, Poland
and Wiesław Stręk
Institute for Low Temperature and Structure Research, Polish Academy of Sciences, Wrocław, Poland

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The oscillator strengths of the f-f transitions as well the fluorescence spectra for europium perchlorate, chloride and nitrate in mono- and disubstituted amides have been measured. The Judd-Ofelt parameters are calculated. The formation of inner-sphere europium complexes is discussed on the basis of intensity analysis of the absorption and luminescence spectra. In mono- and disubstituted amides solutions the f-f transitions of Eu^{+3} have been analysed and the three τ_λ parameters fitted with satisfactory accuracy. Among all f-f transitions the hypersensitive ones in absorption $^7F_0 \rightarrow {}^5D_0$ and fluorescence $^5D_0 \rightarrow {}^7F_2$ varied most markedly. From an analysis of the data it was concluded that only $Eu(NO_3)_3$ and $EuCl_3$ in DMF form inner-sphere complexes. At low concentration of $EuCl_3$ in DMF the predominant form is $[EuCl(DMF)_{y-1}]^{+2}$, whereas at high concentration the predominant form is $[EuCl_2(DMF)_{y-2}]^{+1}$. The intensity of the hypersensitive bands decreases with increasing $EuCl_3$ concentration, contrary to the common opinion that complexation increases the intensity of hypersensitive bands.

Introduction

In recent years considerable effort has been made to elucidate the nature of the interaction between lanthanide compounds and solvents, especially the formation of Ln(III) first coordination spheres. Nd, Ho and Er compounds in non-aqueous solutions have been investigated by us [1–6] for the influence of the solvents on the intensity of f-f transitions and the possible mechanism of hypersensitive transitions.

In the present paper the intensity of the absorption and fluorescence spectra of europium salts in mono- and disubstituted amides is analysed, and on the basis of the results the solvatation and complexation processes of Eu^{+3} ion in non-aqueous solutions are discussed.

Experimental

The absorption spectra (range 16000–28000 cm^{-1}) of solutions of europium perchlorate, chloride and nitrate in mono- and disubstituted amides (N-methylformamid = MFA, N,N-dimethylformamide = DMF), and in H_2O were measured on a "Cary 14" spectrophotometer in the concentration range $\sim 0.09 \div 0.9$ M at 25 °C. The oscillator strengths were determined for all bands in the mentioned spectral range using an ICH30 integrating programme.

The salts were synthetized by the method described in [1, 2, 5]. The lanthanide ion concentrations were determined gravimetrically [7] and complexometrically [8]. The solvents had been freshly purified before each measurement, and their purity was checked by refractive index and molar conductivity measurements. The n_D^{25} and $\varkappa^{25}$ values for DMF and MFA were 1.4320 and 1.4319, and 2.9×10^{-7} ohm^{-1} cm^{-1} and 5×10^{-6} ohm^{-1} cm^{-1}, respectively. The refractive indices of the solutions at 25 °C and different concentrations were: $Eu(ClO_4)_3$ in H_2O: 1.3340 (0.11871 M), 1.3623 (0.68203 M); $Eu(ClO_4)_3$ in MFA: 1.4360 (0.10029 M), 1.4452 (0.60332 M); $Eu(ClO_4)_3$ in DMF: 1.4355 (0.11933 M), 1.4448 (0.34377 M); $EuCl_3$ in H_2O: 1.3745 (0.95014 M); $EuCl_3$ in DMF: 1.4720 (0.95014 M), 1.4360 (0.0995 M); $EuCl_3$ in MFA: 1.4352 (0.10739 M), 1.4660 (0.97085 M); $Eu(NO_3)_3$ in H_2O: 1.3749 (0.9962 M); $Eu(NO_3)_3$ in DMF: 1.4740 (0.9962 M), 1.4360 (0.12347 M); $Eu(NO_3)_3$ in MFA: 1.4370 (0.12773 M), 1.4687 (0.9771 M).

The fluorescence spectra of the Eu^{+3} solutions were excited by a HBO200 lamp with UG-1 and

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Reprint requests to Dr. J. Legendziewicz, Institute of Chemistry, 14 Joliot-Curie Street, 50-383 Wrocław, Poland.

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UG-11 glass filters and recorded by a GDM 1000 grating monochromator (C. Zeiss, Jena) coupled with a cooled photomultiplier M10 FD9 (C. Zeiss, Jena).

The relative intensities of the $^5D_0 \rightarrow {}^7F_{1,2,4}$ transitions were measured planimetrically because the response of the monochromator in the measured range is almost constant.

Ultrasonic absorption measurements on the DMF solutions were carried out on an interferometer made in the Institute for Basic Problems of Technology, Polish Academy of Sciences.

Results and Discussion

The majority of the f-f transitions observed in the absorption spectra of lanthanide ions are of the electric dipole type. According to Judd-Ofelt [9] the oscillator strength is given by

$$P = \varkappa \frac{8\pi^2 m c \sigma}{3h(2J+1)} \sum_{\lambda=2,4,6} \Omega_\lambda \langle \psi J \| U^{(\lambda)} \| \psi' J' \rangle^2, \quad (1)$$

where σ is the wavenumber of the $\psi_J \rightarrow \psi'_{J'}$ transition, $U^{(\lambda)}$ is the unit tensor operator of the order $\lambda = 2, 4, 6$, $\varkappa = (n^2+2)^2/9\,n$, where n is the refractive index. The squares of the matrix elements of $U^{(\lambda)}$ were tabulated by Carnall [9].

The absorption spectra of the Eu^{+3} compounds in MFA and DMF are presented in Figures 1–3. The transitions were identified on the basis of the spectrum of the Eu^{+3} aquoion [10] and of the "Spectra of the Rare Earths" by Eljashevich [11].

In $Eu(ClO_4)_3$ solutions $c \sim 0.4$ M for DMF and $c \sim 0.7$ M for MFA and H_2O the $^7F_0 \rightarrow {}^5D_0$ transitions were observed for DMF and MFA only, the $^7F_1 \rightarrow {}^5D_0$ transitions in all three cases and the $^7F_2 \rightarrow {}^5D_0$ transitions again for DMF and MFA solutions only. The absorption bands observed for those three transitions for $Eu(NO_3)_3$ in MFA $c \sim 0.97$ M are split; the half-width of the band deriving from the $^7F_0 \rightarrow {}^5D_0$ transition exceeds remarkably that observed for analogous solutions of $Eu(NO_3)_3$ in DMF and of the other europium salts in DMF or MFA.

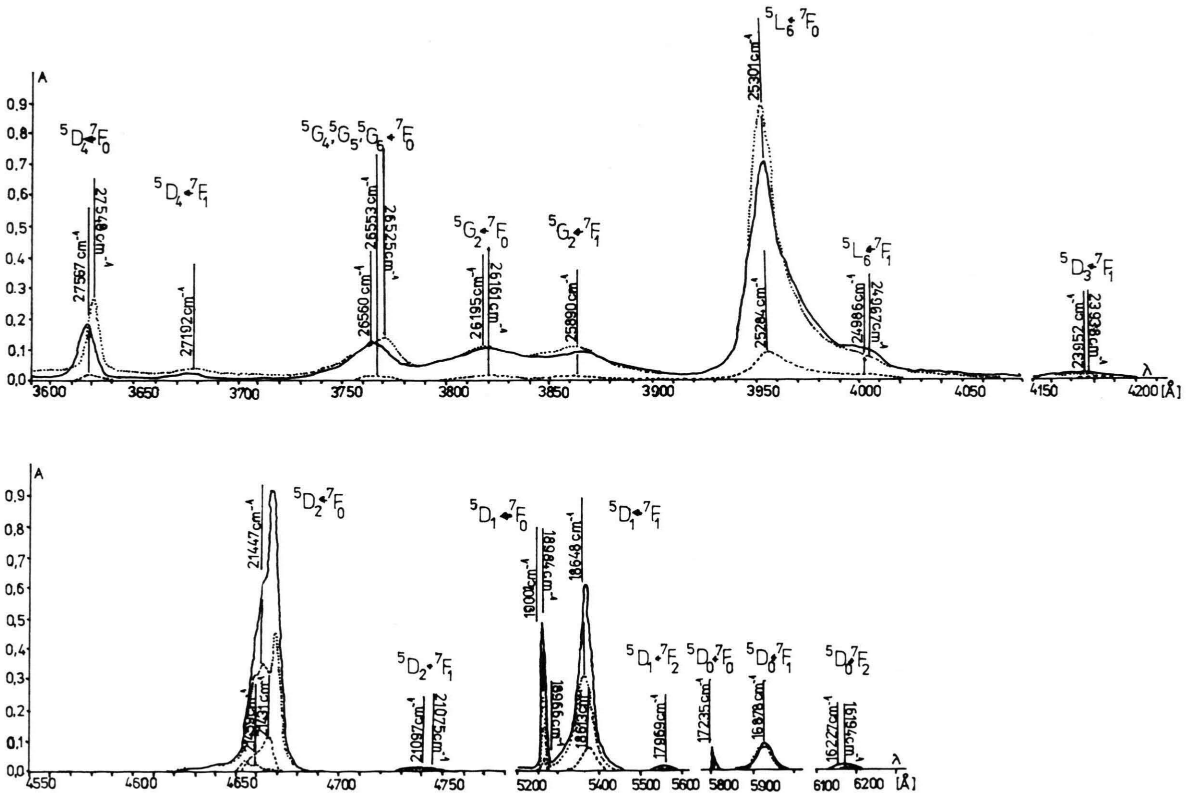

Fig. 1. Absorption spectrum of $Eu(NO_3)_3$ in DMF (0.996 M) ——, (0.123 M) – – –, in MFA (0.977 M) ···, (0.128 M) –·–·– only $^7F_0 \rightarrow {}^5D_2$. Above $d = 0.2$ cm, below $d = 1$ cm and $d = 5$ cm.

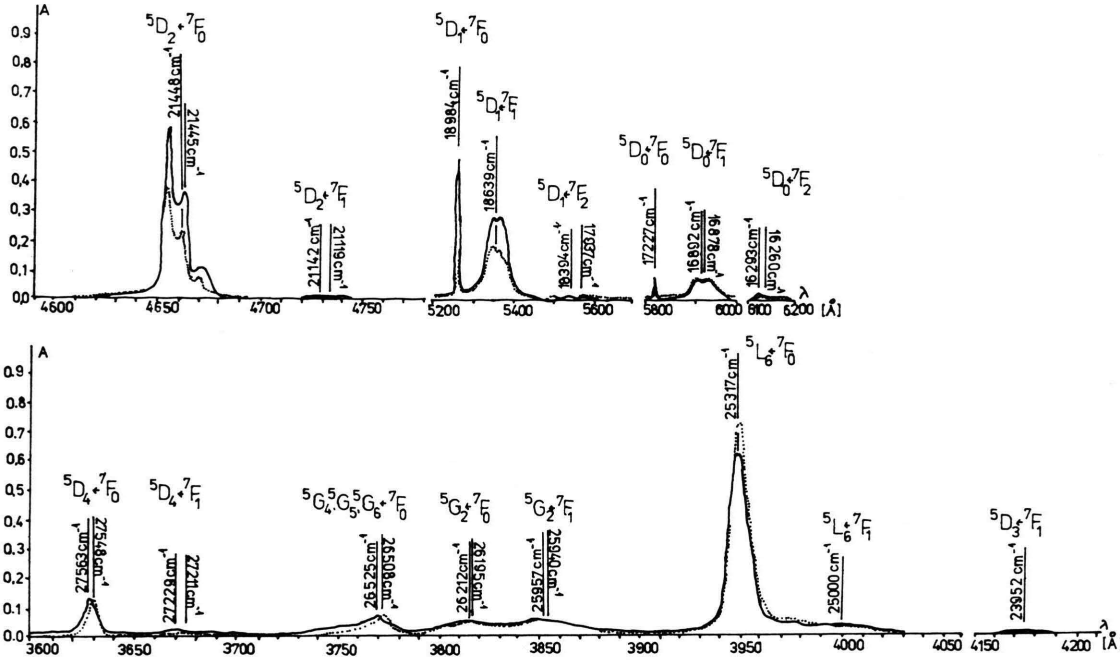

Fig. 2. Absorption spectrum of $EuCl_3$ in DMF (0.950 M) ——, in MFA (0.971 M) ···. Above $d = 1$ cm and $d = 5$ cm, below $d = 0.1$ cm.

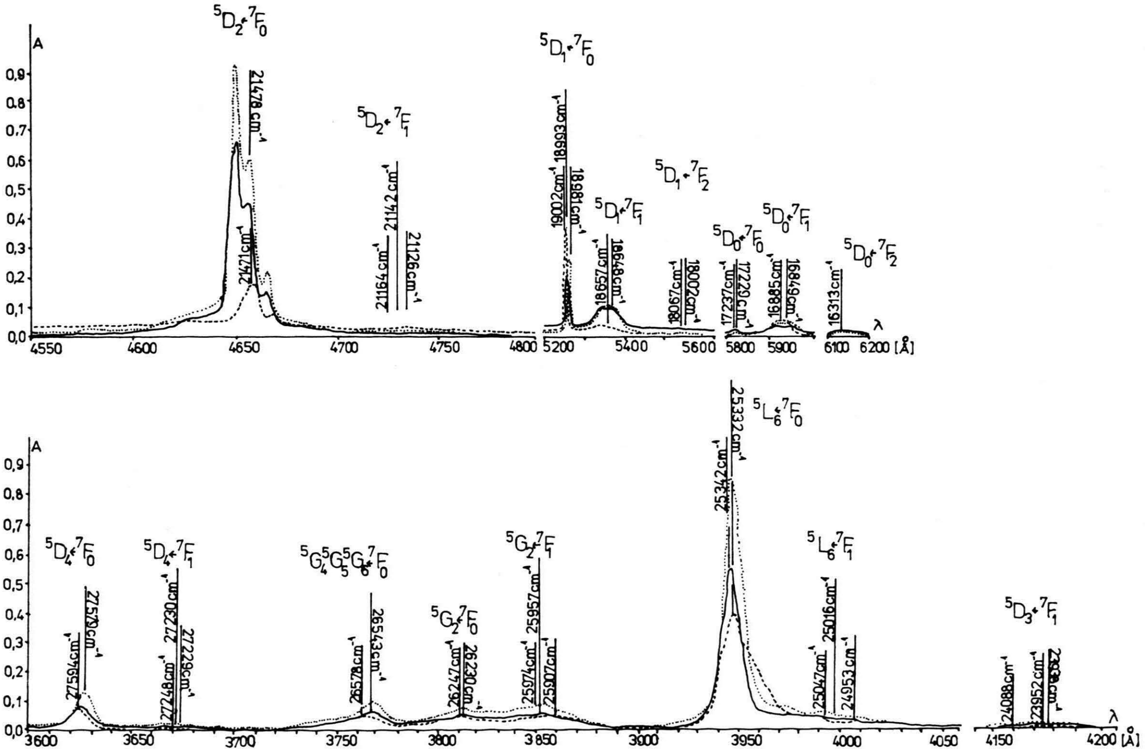

Fig. 3. Absorption spectrum of $Eu(ClO_4)_3$ in DMF (0.344 M) ——, in MFA (0.603 M) ···, in H_2O (0.682 M) - - -. Above $d = 5$ cm, below $d = 0.2$ cm.

Table 1. The experimental ($P_{\mathrm{exp}} \times 10^8$) and calculated ($P_{\mathrm{cal}} \times 10^8$) oscillator strengths and rms deviations $S = \left[\frac{\Sigma(\Delta P)^2}{i-3}\right]^{1/2}$ for $Eu(NO_3)_3$ and $EuCl_3$ in DMF and MFA. Transitions used in the calculation of τ_λ parameters and S values are marked with asterisk.

Compound	$Eu(NO_3)_3$								$EuCl_3$							
Solvent	DMF				MFA				DMF				MFA			
C [M/l]	0.99620		0.12347		0.97710		0.12773		0.95014		0.09950		0.97085		0.10739	
TERM / $P \times 10^8$	$P_{\mathrm{exp.}}$	$P_{\mathrm{cal.}}$	$P_{\mathrm{exp.}}$	$P_{\mathrm{cal.}}$	$P_{\mathrm{exp.}}$	$P_{\mathrm{cal.}}$	$P_{\mathrm{exp.}}$	$P_{\mathrm{cal.}}$	$P_{\mathrm{exp.}}$	$P_{\mathrm{cal.}}$	$P_{\mathrm{exp.}}$	$P_{\mathrm{cal.}}$	$P_{\mathrm{exp.}}$	$P_{\mathrm{cal.}}$	$P_{\mathrm{exp.}}$	$P_{\mathrm{cal.}}$
$^5D_0 \leftarrow {}^7F_2$	0.32	–	–	–	0.24	–	–	–	0.24	–	–	–	0.11	–	–	–
$^5D_0 \leftarrow {}^7F_1$	1.30	–	–	–	1.32	–	–	–	1.56	–	–	–	1.31	–	–	–
$^5D_0 \leftarrow {}^7F_0$	0.20	–	–	–	0.11	–	–	–	0.25	–	–	–	0.14	–	–	–
$^5D_1 \leftarrow {}^7F_2$	0.28	–	–	–	0.19	–	–	–	0.22	–	–	–	0.32	–	–	–
$^5D_1 \leftarrow {}^7F_1$	8.34	–	8.71	–	5.40	–	3.36	–	5.17	–	7.19	–	3.61	–	3.08	–
$^5D_1 \leftarrow {}^7F_0$	1.62	–	1.66	–	1.64	–	1.59	–	1.63	–	1.59	–	1.54	–	1.24	–
$^5D_2 \leftarrow {}^7F_1$	1.10	–	1.47	–	0.85	–	0.57	–	0.81	–	0.42	–	0.65	–	0.88	–
$^5D_2 \leftarrow {}^7F_0^*$	24.12	24.12	26.15	26.15	15.47	15.47	10.54	10.54	15.92	15.92	21.24	21.24	10.72	10.72	8.90	8.90
$^5D_3 \leftarrow {}^7F_1$	8.31	–	12.09	–	8.88	–	8.07	–	6.52	–	8.81	–	7.57	–	7.86	–
$^5L_6 \leftarrow {}^7F_1$	54.87	–	63.82	–	47.70	–	41.97	–	24.15	–	24.84	–	37.01	–	32.91	–
$^5L_6 \leftarrow {}^7F_0^*$	234.38	229.51	255.42	250.29	258.20	252.15	290.02	281.97	245.19	238.94	202.33	193.48	280.49	272.39	293.81	285.68
$^5G_2 \leftarrow {}^7F_1$	56.96	–	60.74	–	59.42	–	67.28	–	52.17	–	45.40	–	65.76	–	70.98	–
$^5G_2 \leftarrow {}^7F_0$	64.04	–	66.25	–	54.26	–	52.63	–	45.57	–	33.55	–	46.56	–	48.97	–
$({}^5G_4, {}^5G_5, {}^5G_6) \leftarrow {}^7F_0^*$	52.36	71.29	55.32	75.25	53.34	76.86	52.76	84.09	52.28	76.60	34.08	68.56	47.84	79.41	55.44	87.11
$^5D_4 \leftarrow {}^7F_1$	6.18	–	4.20	–	6.14	–	5.43	–	9.46	–	10.02	–	8.73	–	12.23	–
$^5D_4 \leftarrow {}^7F_0^*$	31.54	19.93	29.89	17.68	34.09	19.68	38.25	19.06	39.76	24.87	51.94	30.81	34.82	15.49	41.80	22.40
$S \times 10^8$		2.27		2.39		2.82		3.76		2.92		4.14		3.79		3.80

Table 2. $P_{exp} \times 10^8$ and $P_{cal} \times 10^8$ values and rms deviation S for $Eu(ClO_4)_3$ in DMF, MFA and H_2O. Asterisk denotation as in Table 1.

Compound	$Eu(ClO_4)_3$												
Solvent	DMF					MFA				H_2O			
C [M/l]	0.34377		0.11933			0.60332		0.10029		0.68203		0.11871	
TERM / $P \times 10^8$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^5D_0 - {}^7F_2$	0.10	–	–	–	–	0.04	–	–	–	–	–	–	–
$^5D_0 - {}^7F_1$	1.41	–	–	–	–	1.22	–	–	–	1.04	–	–	–
$^5D_0 - {}^7F_0$	0.09	–	–	–	–	0.04	–	–	–	–	–	–	–
$^5D_1 - {}^7F_2$	0.14	–	–	–	–	0.18	–	–	–	0.06	–	–	–
$^5D_1 - {}^7F_1$	4.06	–	3.61	–	–	3.20	–	4.37	–	0.53	–	–	–
$^5D_1 - {}^7F_0$	1.67	–	1.22	–	–	1.55	–	1.87	–	1.36	–	1.37	–
$^5D_2 - {}^7F_1$	0.78	–	–	–	–	0.66	–	–	–	0.20	–	–	–
$^5D_2 - {}^7F_0^*$	12.96	12.96	10.40	10.40	32.24[a]	9.51	9.51	9.66	9.66	2.33	2.33	2.00	2.00
$^5D_3 - {}^7F_1$	8.29	–	8.43	–	–	13.02	–	13.06	–	3.20	–	1.52	–
$^5L_6 - {}^7F_1$	53.43	–	39.92	–	–	40.86	–	32.10	–	22.13	–	22.69	–
$^5L_6 - {}^7F_0^*$	333.20	324.59	304.81	296.98	296.98[a]	286.17	279.39	280.89	275.03	178.78	174.81	180.00	176.16
$^5G_2 - {}^7F_1$	92.09	–	70.65	–	–	70.15	–	67.59	–	37.64	–	39.79	–
$^5G_2 - {}^7F_0$	63.36	–	53.37	–	29.52[a]	56.39	–	56.93	–	29.96	–	30.68	–
$(^5G_4, {}^5G_5, {}^5G_6) - {}^7F_0^*$	66.51	100.06	59.83	90.32	90.32[a]	57.65	84.04	65.00	87.80	35.45	50.88	36.44	51.39
$^5D_4 - {}^7F_1$	11.44	–	10.22	–	–	7.04	–	12.78	–	2.62	–	3.51	–
$^5D_4 - {}^7F_0^*$	47.83	27.30	41.63	22.96	22.96[a]	36.20	20.04	41.97	28.01	19.13	9.66	19.10	9.94
$S \times 10^8$	4.03		3.66		3.45[a]	3.17		2.74		1.86		1.79	

[a] P_{cal} values calculated from the $^7F_0 \rightarrow {}^5G_2$ transition.

Table 3. τ_λ parameters for $Eu(NO_3)_3$, $EuCl_3$ and $Eu(ClO_4)_3$ in DMF and MFA, and of $Eu(ClO_4)_3$ in H_2O. The τ_λ^* have been calculated after elimination of the refraction coefficient.

	$Eu(NO_3)_3$				$EuCl_3$			
	DMF		MFA		DMF		MFA	
	0.99620	0.12347	0.97710	0.12773	0.95014	0.09950	0.97085	0.10739
$\tau_2 \times 10^9$	14.06±13.25	15.25±13.96	9.02±16.46	6.14±21.91	9.28±17.02	12.37±24.12	6.25±22.08	5.18±22.13
$\tau_4 \times 10^9$	6.57± 6.45	5.83± 6.70	6.49± 8.02	6.26±10.63	8.20± 8.28	10.17±11.75	5.11±10.76	7.39±10.78
$\tau_6 \times 10^9$	5.85± 0.57	6.39± 0.60	6.43± 0.70	7.16± 0.93	6.09± 0.73	4.92± 1.03	6.94± 0.94	7.28± 0.95
$\tau_2^* \times 10^9$	13.10±12.35	14.20±13.00	8.48±15.39	5.71±20.39	8.66±15.88	11.52±22.46	5.86±20.70	4.83±20.62
$\tau_4^* \times 10^9$	6.12± 6.01	5.43± 6.32	6.07± 7.50	5.83± 9.89	7.65± 7.73	9.47±10.94	4.79±10.09	6.89±10.05
$\tau_6^* \times 10^9$	5.45± 0.53	5.95± 0.56	6.01± 0.65	6.66± 0.87	5.68± 0.68	4.58± 0.96	6.51± 0.88	6.78± 0.89

	$Eu(ClO_4)_3$					
	DMF		MFA		H_2O	
	0.34377	0.11933	0.60332	0.10029	0.68203	0.11871
$\tau_2 \times 10^9$	7.54±23.43	6.06±21.31	5.53±18.44	5.63±15.93	1.36±10.80	1.16±10.44
$\tau_4 \times 10^9$	8.99±11.41	7.57±10.38	6.61± 8.98	9.23± 7.76	3.18± 5.25	3.27± 5.08
$\tau_6 \times 10^9$	8.26± 1.00	7.57± 0.91	7.11± 0.79	7.00± 0.68	4.45± 0.46	4.48± 0.45
$\tau_2^* \times 10^9$	7.04±21.89	5.65±19.85	5.20±17.35	5.24±14.84		
$\tau_4^* \times 10^9$	8.40±10.66	7.05± 9.67	6.22± 8.45	8.60± 7.23		
$\tau_6^* \times 10^9$	7.72± 0.93	7.05± 0.85	6.69± 0.74	6.52± 0.63		

Equation (1) is the basis for the intensity analysis of the f-f transitions. The Ω_λ parameters are treated as the phenomenological parameters determined from the experimental data. The comparison of data calculated from the absorption spectra might be facilitated by replacement of the parameter in (1) by τ_λ, where

$$\tau_\lambda = (2J+1)\, c\, T_\lambda\,,$$

$$\Omega_\lambda = (8\pi^2 m\, c\, \varkappa/3\, h)^{-1} \sqrt{\tau_\lambda}$$
$$= (1.085 \cdot 10^{11} \varkappa)^{-1} \sqrt{\tau_\lambda} \quad [12]$$

The observed intensities for the europium compounds are by two orders of magnitude lower than those for the other lanthanide ions. The error in the calculated intensities exceeds that reported for the other lanthanide ions [1–6] but is comparable with data for the europium aquoion [9].

The τ_λ parameters are listed in Table 3. The error in the determination of the τ_λ parameters also exceeds that calculated for non-aqueous solutions of the other lanthanide salts. It is due to the small number of bands (four) used for the evaluation of the parameters (Table 1, 2, 3). Among the τ_λ parameters, τ_2 increases most compared with the aquoion (Table 3). That enhancement may be attributed to the strong increase of the hypersensitive band $^7F_0 \rightarrow {}^5D_2$.

According to Mason et al. [13] the polarizability of the ligands is responsible for the enhancement of the hypersensitive transitions. An analysis of these transitions may give information about the structural properties of lanthanide systems.

Tables 1 and 2 indicate that the intensities of all transitions observed for $Eu(ClO_4)_3$, $EuCl_3$ and $Eu(NO_3)_3$ at low concentrations in monosubstituted amides are almost the same. This confirmes our earlier suggestion [3] concerning the appearance of homogeneous solvates for $LnCl_3$, $Ln(NO_3)_3$ and $Ln(ClO_4)_3$ in monosubstituted amides.

The great differences in oscillator strenghts for the chlorides and nitrates may be due to the formation of inner-sphere complexes of the form $[LnX(DMF)_{y-1}]^{+2}$ with $X = NO_3^-, Cl^-$.

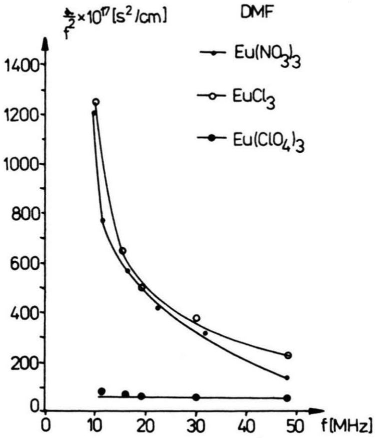

Fig. 4. Ultrasonic absorption for $Eu(NO_3)_3$ (0.386 M), $EuCl_3$ (0.428 M) and $Eu(ClO_4)_3$ (0.199 M) in DMF at 25 °C.

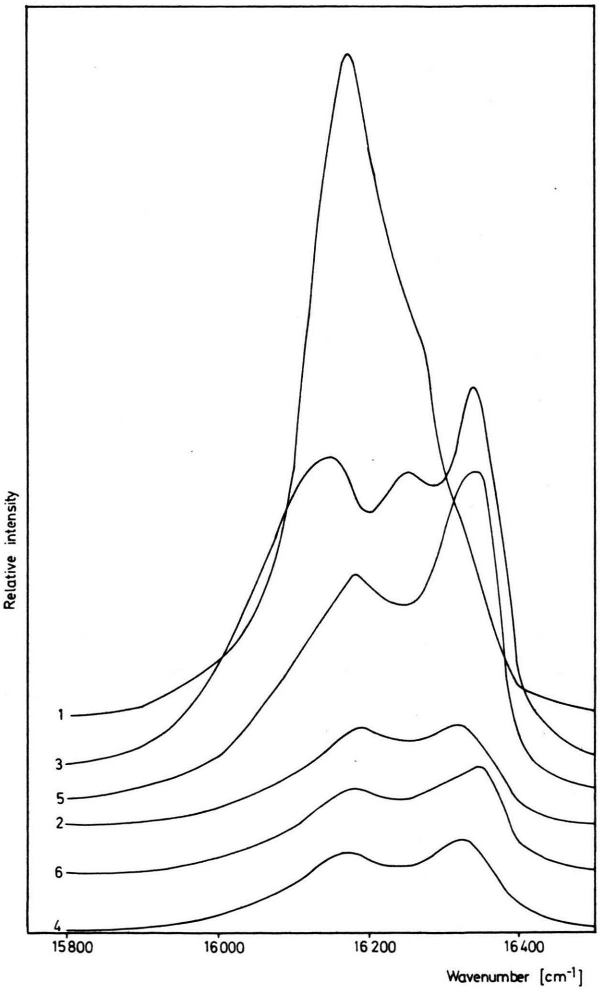

Fig. 5. The hypersensitive transition $^5D_0 \rightarrow {}^7F_2$ for Eu salts. 1: $Eu(NO_3)_3$ in DMF (0.0869 M), 2: in MFA (0.0786 M), 3: $EuCl_3$ in DMF (0.0975 M), 4: in MFA (0.0994 M), 5: $Eu(ClO_4)_3$ in DMF (0.0972 M), 6: in MFA (0.0987 M).

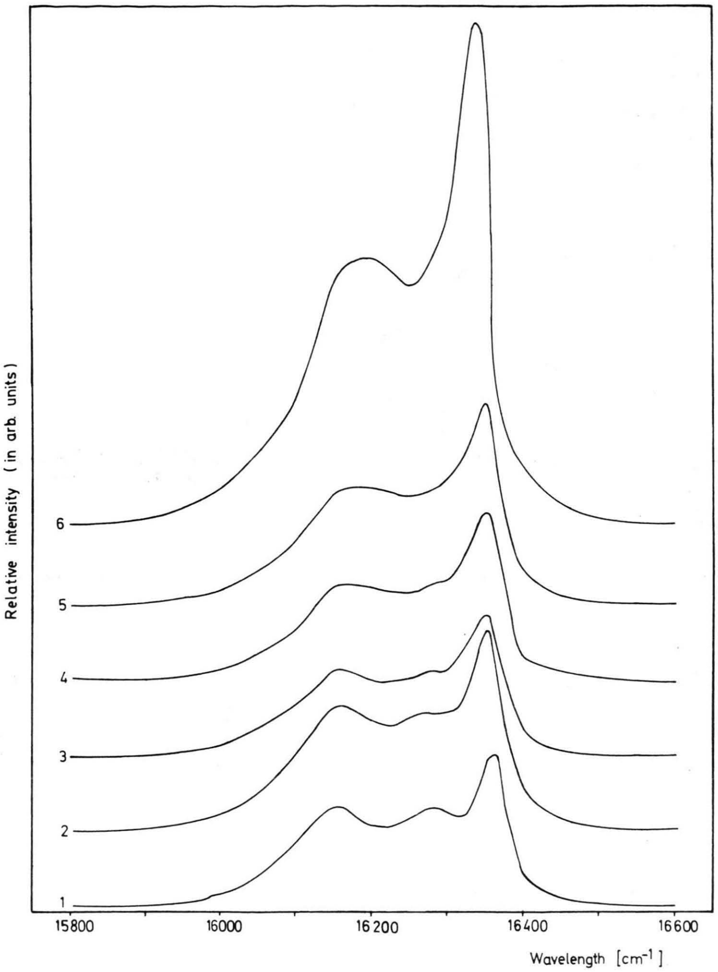

Fig. 6. The variation of hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition for $EuCl_3$ in DMF. 1: (0.0998 M), 2: (0.200 M), 3: (0.267 M), 4: (0.356 M), 5: (0.475 M), 6: (0.950 M).

The conductivity measurements show no peculiarities. For the solutions in question the results indicate that $Eu(ClO_4)_3.H_2O$ in mono- and disubstituted amide is of the 1:3 type of electrolyte, while $Eu(NO_3)_3{\cdot}H_2O$ is the 1:2 electrolyte type in DMF but 1:3 in MFA.

The ultrasonic absorption measurements provide more helpful information. It has been observed (see Fig. 4) tha $Eu(NO_3)_3$ and $EuCl_3$ show ultrasonic absorption in DMF in the region 10 ÷ 50 MHz at room temperature due to exchange of a solvent molecule with NO_3^- and Cl^- in the first coordination sphere of Eu^{+3}. No absorption has been found for

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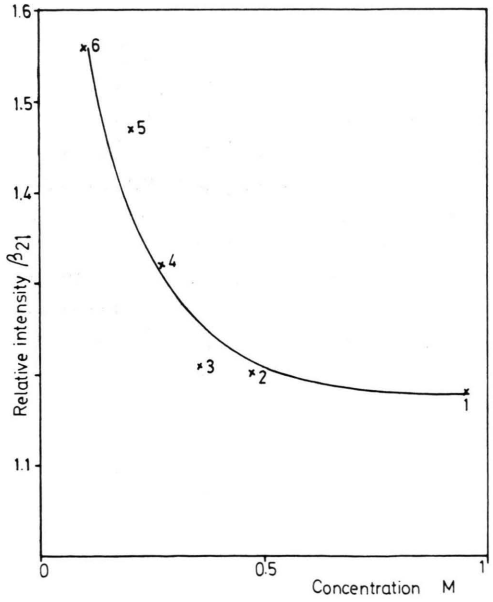

Fig. 7. The dependence of β on the concentration of $EuCl_3$ in DMF. 1: (0.950 M), 2: (0.475 M), 3: (0.356 M), 4: 0.267 M), 5: (0.200 M), 6: (0.0998 M).

$Eu(ClO_4)_3$ in DMF and MFA solutions. These data are identical with those previously reported by us for other lanthanides [4, 5].

The fluorescence spectra are known to be very sensitive to perturbations of the first coordination sphere. An analysis of the fluorescence transitions may be a source of additional information about the relation between the structure of europium compounds and relaxation mechanisms of f-f transitions. From among the three bands of Eu^{+3} ion in solution, the two associated with the hypersensitive transitions $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_0$ are very much affected by the closest environment of the ion.

Figure 5 shows the variation of the hypersensitive band $^5D_0 \rightarrow {}^7F_2$ of europium compounds in different solvents at the low concentration limit. The band shape differs significantly only for $Eu(NO_3)_3$ and $EuCl_3$ in DMF. In the latter there are three characteristic peaks. The picture of the band changes with concentration (see Figure 6). At high concentrations of $EuCl_3$ in DMF the band consists of two peaks. This variation is followed by the relative intensity of the $^5D_0 \rightarrow {}^7F_2$ transition, represented by the ratio of intensities $\beta = I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_4)$. The $^5D_0 \rightarrow {}^7F_4$ transition, which is weakly affected by solvent, was taken as a reference. With increase in concentration the relative intensity of the hypersensitive band declines gradually, reaching a plateau at high concentrations (see Figure 7).

These results provide evidence for the assumption that at low concentration of $EuCl_3$ in DMF $[EuCl(DMF)_{y-1}]^{+2}$ is predominant, whereas at high concentration the species of higher symmetry $[EuCl_2(DMF)_{y-2}]^{+1}$ is predominant. This conclusion is followed by the intensity decrease of the hypersensitive $^7F_0 \rightarrow {}^5D_2$ transition. Therefore for $EuCl_3$ at low concentration in DMF $P_{\text{exp}} \times 10^8 = 21.24$, whereas at high concentration $P_{\text{exp}} \times 10^8 = 15.92$.

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