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Preparation and Properties of Yttrium, Lanthanum and Lanthanide 3,4-Dinitrobenzoates

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Summary. The rare earth 3,4-dinitrobenzoates were prepared and their quantitative composition and solubilities in water at 298 K determined (they are of the order of 10^{-3} mol dm^{-3}). From the values of solubilities in water the solubility products were established (they are in the order of 10^{-11} mol^4 dm^{-12}). The IR and X-ray spectra for hydrated and dehydrated complexes were studied. All complexes are crystalline compounds. The condition of thermal decomposition of the complexes were also investigated. On heating above 573 K all 3,4-dinitrobenzoates decompose explosively undergoing a melting process. Thus, the thermal decomposition for complexes was carried out in the temperature range 273–573 K. The thermal stability data reveal them to dehydrate in one or two steps. From the obtained results it appears that during the dehydration process no isomerization of the nitro group to nitrito occurs.

Keywords. Yttrium; Lanthanum; Lanthanide; 3,4-Dinitrobenzoates; Complexes of rare earth elements.

Herstellung und Eigenschaften von Y-, La- und Lanthaniden-3,4-Dinitrobenzoaten

Zusammenfassung. Die Bedingungen zur Darstellung von Y-, La- und Lanthaniden-3,4-Dinitrobenzoaten wurden untersucht. Ihre quantitative Zusammensetzung und ihre Wasserlöslichkeit bei 298 K wurden bestimmt (die Löslichkeit ist in der Größenordnung 10^{-3} mol dm^{-3}). Die Infrarot- und Röntgenspektren der erhaltenen Komplexe sowie der 3,4-Dinitrobenzoate der seltenen Erden nach der Dehydratisierung wurden gemessen. Alle untersuchten Verbindungen waren kristallin. Das thermische Verhalten der erhaltenen Komplexe wurde untersucht: sie zerfallen über 573 K explosiv und schmelzen zugleich. Der thermische Zerfall der erhaltenen 3,4-Dinitrobenzoate der seltenen Erden wurde im Temperaturbereich von 273–523 K untersucht. Es wurde festgestellt, daß die Y-, La- und Lanthaniden-3,4-Dinitrobenzoate bei Temperaturzunahme oder im Dehydratisierungsprozeß keiner Umgruppierung in entsprechende Nitritoverbindungen unterliegen.

Introduction

3,4-Dinitrobenzoic acid being a cream, crystalline solid is sparingly soluble in water [1]. Its electrolytic dissociation constant is equal to $1.63 \cdot 10^{-3}$ ($t = 25$°C) [1]. A literature survey furnishes informations only on its salts with the cations Ca^{2+}, Ba^{2+} [1], and Na^+ [2]. Only 2,4- and 3,4-dinitrobenzoates with Y, La, and lanthanides were investigated [11, 12].

The object of the present investigation was to obtain in pure forms of solid state the unknown 3,4-dinitrobenzoates of Y, La, and lanthanides with a metal to ligand ratio of 1 : 3 and to examine some of their properties.

Experimental

3,4-Dinitrobenzoates of yttrium, lanthanum, and lanthanides were prepared by the addition of the equivalent quantities of 0.2 *M* ammonium 3,4-dinitrobenzoate ($pH \sim 5$) to a hot solution containing the rare earth element nitrates and crystallizing at 293 K. The solids formed were filtered off, washed with hot water to remove ammonium ions and dried at 303 K to constant mass. Carbon, hydrogen, and nitrogen microanalysis data for these complexes were determined by elemental analysis with V_2O_5 as oxidizing agent. The rare earth element contents were established by the oxalate method (Table 1).

The contents of crystallization water molecules were determined from the curve of TG and by isothermal heating the complexes at 573 K. IR spectra for the prepared complexes, the spectra for 3,4-dinitrobenzoic acid, sodium 3,4-dinitrobenzoate and dehydrated 3,4-dinitrobenzoates of yttrium, lanthanum, and lanthanides and for sodium nitrite were recorded as KBr discs on an UR-20 spectrophotometer (range 4 000–400 cm^{-1}). Some of the experimental data are presented in Table 2. The X-ray diffraction patterns of hydrated and dehydrated rare earth element 3,4-dinitrobenzoates and lanthanide oxides obtained from the ignition of the oxalates and 3,4-dinitrobenzoates of Y, La, and lanthanides were taken on a DRON-2 diffractometer using Ni filtered Fe Kα radiation. The measurements were made within the range $2\theta = 4$–$80°$ by means of the Debye-Scherrer method. The thermal stability of the complexes was studied by the use of TG, DTA and DTG techniques. The measurements were made with a θ-1500D derivatograph at a heating rate of 2.5 deg min^{-1}. Test samples of 200 mg were heated at a sensitivity TG – 50 mg, DTG – 500 µV, DTA – 500 µV (Table 3). The solubilities of 3,4-dinitrobenzoates of yttrium, lanthanum, and lathanides in water at 298 K were determined by measuring the concentration of Lu^{3+} ions in saturated solutions by the oxalate method (Table 3).

Table 1. Analytical data

Complex $L = C_7H_3N_2O_6$	%C		%N		%H		%*M*	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$YL_3 \cdot 2H_2O$	33.24	33.21	11.06	11.06	1.71	1.78	11.74	11.84
$LaL_3 \cdot 2H_2O$	31.19	31.22	10.39	10.40	1.60	1.62	17.19	17.29
$CeL_3 \cdot 2H_2O$	31.14	31.10	10.38	10.36	1.60	1.59	17.30	17.33
$PrL_3 \cdot 2H_2O$	31.11	31.12	10.37	10.35	1.60	1.58	17.39	17.30
$NdL_3 \cdot 2H_2O$	30.98	30.96	10.32	10.30	1.59	1.57	17.76	17.80
$SmL_3 \cdot 2H_2O$	30.75	30.72	10.25	10.22	1.58	1.54	18.34	18.40
$EuL_3 \cdot 2H_2O$	30.69	30.68	10.23	10.21	1.58	1.57	18.51	18.52
$GdL_3 \cdot 2H_2O$	30.50	30.48	10.16	10.14	1.57	1.55	19.03	19.04
$TbL_3 \cdot 2H_2O$	30.43	30.41	10.14	10.12	1.50	1.51	19.19	19.26
$DyL_3 \cdot 2H_2O$	30.30	30.31	10.10	10.12	1.56	1.60	19.54	19.51
$HoL_3 \cdot 2H_2O$	30.21	30.20	10.07	10.05	1.55	1.56	19.77	19.64
$ErL_3 \cdot 2H_2O$	30.13	30.10	10.04	10.02	1.55	1.53	20.00	19.95
$TmL_3 \cdot 2H_2O$	30.05	30.08	10.01	10.04	1.55	1.54	20.09	19.82
$YbL_3 \cdot 2H_2O$	29.92	29.94	9.97	9.91	1.54	1.52	20.55	20.58
$LuL_3 \cdot 2H_2O$	29.85	29.80	9.95	9.96	1.54	1.51	20.73	20.75

Table 2. Frequencies of absorption bands of the COO^- ion and the NO_2 group for Na, Y, La, and lanthanide 3,4-dinitrobenzoates and 3,4-dinitrobenzoic acid (cm^{-1})

Compound $L = C_7H_3N_2O_6$	ν_{as} OCO	ν_{sym} OCO	$\Delta\nu$	$\nu_{as}(NO_2)$	$\nu_{sym}(NO_2)$	$\Delta\nu(NO_2)$	$\nu_{M\text{-}O}$
$YL_3 \cdot 2H_2O$	1 615	1 435	180	1 560	1 370	190	505
$LaL_3 \cdot 2H_2O$	1 615	1 420	195	1 560	1 370	190	500
$CeL_3 \cdot 2H_2O$	1 610	1 420	190	1 560	1 365	195	500
$PrL_3 \cdot 2H_2O$	1 610	1 420	190	1 560	1 360	200	500
$NdL_3 \cdot 2H_2O$	1 605	1 420	185	1 560	1 365	195	500
$SmL_3 \cdot 2H_2O$	1 605	1 420	185	1 550	1 360	190	500
$EuL_3 \cdot 2H_2O$	1 610	1 425	185	1 560	1 370	190	500
$GdL_3 \cdot 2H_2O$	1 610	1 425	185	1 550	1 370	180	500
$TbL_3 \cdot 2H_2O$	1 610	1 425	185	1 555	1 370	185	505
$DyL_3 \cdot 2H_2O$	1 605	1 425	180	1 550	1 365	185	510
$HoL_3 \cdot 2H_2O$	1 610	1 430	180	1 560	1 370	190	510
$ErL_3 \cdot 2H_2O$	1 615	1 435	180	1 560	1 370	190	515
$TmL_3 \cdot 2H_2O$	1 615	1 435	180	1 560	1 370	190	520
$YbL_3 \cdot 2H_2O$	1 610	1 435	175	1 560	1 370	190	525
$LuL_3 \cdot 2H_2O$	1 610	1 435	175	1 555	1 370	185	525
$NaL \cdot 2H_2O$	1 660	1 405	255	1 540	1 365	170	–
HL	–	–	–	1 550	1 365	185	–

Results and Discussion

3,4-Dinitrobenzoates of yttrium, lanthanum, and lanthanides were obtained in crystalline form with the colour characteristic for Ln^{3+} ions and a metal to ligand ratio of 1 : 3 and a general formula: $Ln(C_7H_3O_6N_2)_3 \cdot 2H_2O$, where Ln = Y, La, Ce – Lu. The compounds were characterized by their elemental analyses (Table 1) and IR spectra which confirmed them to be nitro complexes of 3,4-dinitrobenzoic acid. All rare earth 3,4-dinitrobenzoates show similarity in their solid-state IR spectra. However, the characteristic frequencies according to the carbonyl group are changed markedly in going from acid to salts. The band of COOH at 1 710 cm^{-1}, present in acid spectrum, disappears in the spectra of complexes and two bands arising from asymmetric and symmetric vibrations of the COO^- group occur at 1 615–1 605 cm^{-1} and 1 435–1 420 cm^{-1}, respectively. The bands with the maxima at 3 600–3 430 cm^{-1} confirm the presence of crystallization water molecules and the bands at 1 560–1 550 cm^{-1} and 1 370–1 360 cm^{-1} represent the asymmetric and symmetric vibrations of NO_2 groups, respectively. The stretching vibrations of the benzene ring, $\nu(C-C)$, occur at 1 495–1 480 cm^{-1} whereas those of the C – H groups appear at 3 110–3 100 cm^{-1}. The out-of-plane deformation vibration bands of C – H group, $\gamma(C-H)$ are observed at 920 $^{-1}$ while those in plane, $\beta(C-H)$, at 1 060 cm^{-1}. The bands assigned to the metal-oxygen bond occur at 525–500 cm^{-1}. Their shift changes from La to Lu to higher frequencies are probably connected with the increase of stability of the M-O bond with increasing atomic number of element and its ionic potential (Table 2).

The magnitudes of separation, $\Delta\nu$, between the frequencies due to ν_{asym} OCO and ν_{sym} OCO in the complexes are lower than in the sodium salt, which probably suggests a smaller degree of ionic bond in the compounds compared to that of sodium one (Table 2). The close values of $\Delta\nu$ may denote the similar way of lanthanide ion coordinations with 3,4-dinitrobenzenecarboxylate ligands. They decrease slighly with decreasing ionic radii of element (which leads probably to the decrease of the OCO angle of the carboxylate group [3]) and show increasing bond covalency in the heavy lanthanides. The values of $\Delta\nu$ do not enable to define the degree of the covalent bond because of the changes of the OCO bond angle with ionic radii in the lanthanide ions [3, 4].

The directions of the shifts in the frequencies due to ν_{asym} OCO and ν_{sym} OCO are lower and higher, respectively, compared to those in the sodium 3,4-dinitrobenzoate. Accordingly, the carboxylate ion seems to be a bidentate, chelating ligand [5] but with incomplete equalization of its bond lengths.

For 3,4-dinitrobenzoates of heavy lanthanides the decrease of $\Delta\nu$ values is probably indicative of the small change in the carboxylate group structure (Table 2), which is connected with its greater symmetrization with an increase in the covalency bonds. The small shifts in the position of ν_{asym} (NO_2) and ν_{sym} (NO_2) bands for 3,4-dinitrobenzoates of rare earth elements (or their lack) relative to those in 3,4-dinitrobenzoic acid may indicate the only weak interaction of NO_2 groups with lanthanide ions (without their coordination to metal ions) (Table 2).

The small splittings of ν_{asym} (NO_2) bands presumably result from the interaction of the ligands and water molecules in the complexes and their polar properties. The spectra of the heavy lanthanide complexes characterized by relatively more intense aromatic bands relative to the light ones are closer to the spectrum of 3,4-dinitrobenzoic acid. This, being connected with an increase in covalency and the degree of delocalization of bond in the heavy lanthanides, causes presumably the increase of the delocalization of π electrons and the intensity of the aromatic bands of ν ($C \overset{\cdots}{-} C$) of the benzene ring. The spectra for hydrated and dehydrated complexes and for sodium nitrite reveal the 3,4-dinitrobenzoates of rare earth elements as solids forming nitro complexes. No isomerization of nitro group to nitrito takes place with rising temperature [6–9]. From X-ray spectra analysis it appears that dehydrated and hydrated 3,4-dinitrobenzoates of rare earth elements are crystalline compounds with low symmetry, large size of unit cells, various structures, and different degrees of crystallization. The anhydrous 3,4-dinitrobenzoates have a less degree of crystallinity than the hydrated ones. No changes of their structures compared to the hydrated salts are observed. Thus, it is possible to suppose that during heating in the temperature range 273–573 K all 3,4-dinitrobenzoates of rare earths do not yield the nitrito complexes and the loss of crystallization water molecules does not change their crystalline structures. The structures of all rare earth element oxides remain unchanged irrespective of the way of their formation (by roasting oxalates of 3,4-dinitrobenzoates of Y, La, and lanthanides).

Since 3,4-dinitrobenzoates of rare earth elements are stable up to 573 K (after which being explosively decomposed) their thermal stability was examined in the temperature range 273–573 K. Some of the obtained results are summarized in Table 3. 3,4-Dinitrobenzoates of rare earth elements dehydrate in one or two steps. The dehydration processes are accompanied by endothermic effects. The light lanthanide 3,4-dinitrobenzoates lose gradually each of the two water molecules in two stages proceeding in the temperature ranges: 324–409 K and 419–489 K, respectively, while those of the heavy lanthanides release them only in one step in

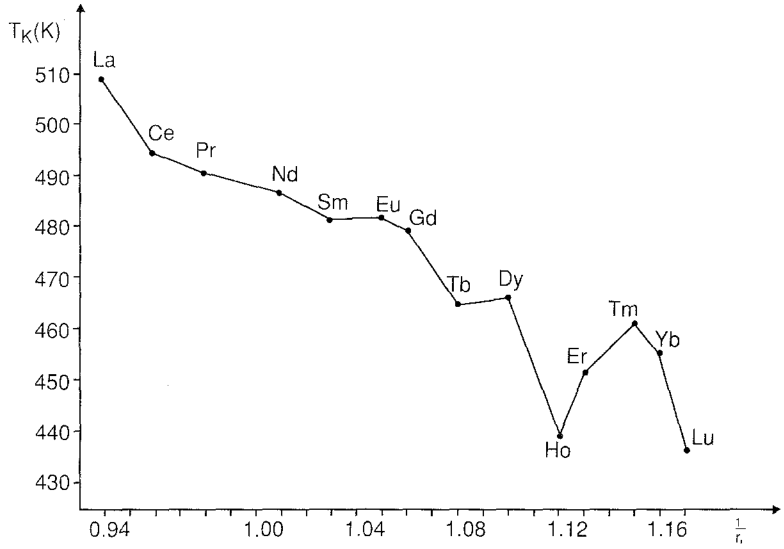

Fig. 1. Relationship between the temperature of anhydrous salt formation (T_k) and ionic potential of element (r_i Templeton's values)

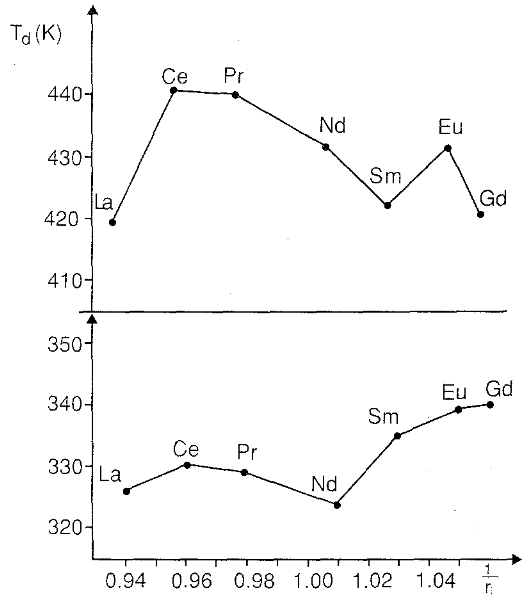

Fig. 2. Dependence between the initial temperature of dehydration process (T_d) for the loss of two water molecules being released in two steps for 3,4-dinitrobenzoates of light lanthanides and ionic potential of element (r_i Templeton's values)

the temperature range 341–442 K. In the temperature range 324–409 K the least thermally stable complex is the dihydrate of neodymium which starts to lose the crystallization water at 324 K whereas the thermally most stable one is gadolinum 3,4-dinitrobenzoate releasing it at 340 K. The 3,4-dinitrobenzoate of lanthanum, expelling the water molecule at 419 K, is the least thermally stable one in the temperature range from 419 K to 489 K, whereas cerium 3,4-dinitrobenzoate being

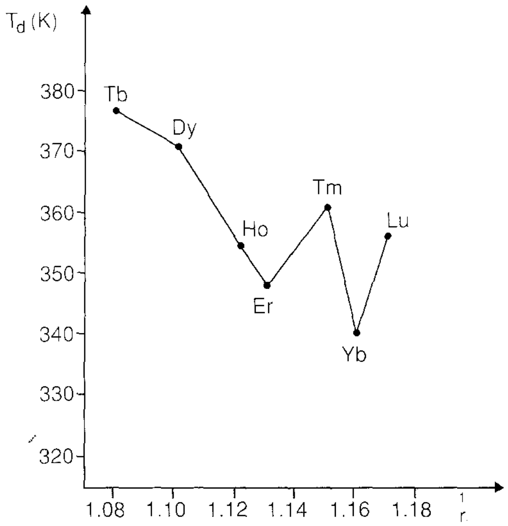

Fig. 3. Relationship between the initial temperature of dehydration process (T_d) for the loss of two water molecules expelled in one step for 3,4-dinitrobenzoates of heavy lanthanides and ionic potential of element (r_i Templeton's values)

the thermally most stable one starts to dehydrate at 442 K. For 3,4-dinitrobenzoates of yttrium and heavy lanthanides, the complex of terbium, as the most thermally stable one, starts to lose the crystallization water molecules at 377 K. Releasing the water molecules at 341 K, the ytterbium 3,4-dinitrobenzoate is the least thermally stable complex.

The anhydrous 3,4-dinitrobenzoates of Y, La, and lanthanides are formed in the temperature range from 436 K (for Lu) to 509 K (for La). The initial temperatures of dehydration processes and the temperatures of the anhydrous complex formation do not change regularly with the ionic potential of element (Figs. 1–3, r_i is Templeton's value).

Being lost at comparatively low temperatures in one or two steps the water molecules are supposed to represent outer-sphere water occupying the various positions in the same complex coordination sphere. From TG and DTA curves the activation energies of dehydration reaction for 3,4-dinitrobenzoates were calculated by means of the Fateev and Pletneev method [10] (Table 3). In the case of the loss of two water molecules in one step the activation energy of the dehydration reaction is the highest for 3,4-dinitrobenzoate of ytterbium, the smallest one for yttrium. For the light lanthanide and gadolinium 3,4-dinitrobenzoates, the complexes of europium and neodymium have the smallest values of activation energy for the dehydration reaction (calculated for the loss of each of the two water molecules) whereas gadolinum and cerium have the highest ones. The values of the activation energy of the dehydration reaction seem not to change smoothly with atomic number of element (Table 3). The solubilities of 3,4-dinitrobenzoates of Y, La, and lanthanides in water at 298 K were measured and their solubility products determined (Table 3). They are in the order of 10^{-3} mol·dm^{-3} and 10^{-11} mol^4·dm^{-12}, respectively. Ytterbium 3,4-dinitrobenzoate is the most soluble salt, while praseodymium the least soluble one. The values of solubility do not regularly change with ionic potential of element (Fig. 4). The solubilities of 3,4-

Table 3. Temperature ranges of the dehydration process, activation energies of dehydration reaction, solubility in water (293 K) and solubility products of 3,4-dinitrobenzoates of Y, La, and lanthanides

Complex $L=C_7H_3N_2O_6$	ΔT_1[a] (K)	Loss of weight (%)		n[d]	ΔT_2[a] (K)	Loss of weight (%)		n[d]	T_{max}[b] (K)	T_k[c] (K)	E (kJ mol^{-1})		Solubility as anhydrous salt $\cdot 10^{-3}$ mol dm^{-3}	Solubility products (I) $\cdot 10^{-11}$ mol^4 dm^{-12}	pI
		Calcd.	Found			Calcd.	Found				E_1	E_2			
$YL_3\cdot 2H_2O$	363–407	4.44	4.54	2	–	–	–		398	441	40		1.32	8.19	10.08
$LaL_3\cdot 2H_2O$	326–409	2.23	2.26	1	419–488	4.46	4.42	1	402 481	509	45	29	1.28	7.24	10.14
$CeL_3\cdot 2H_2O$	330–370	2.22	2.26	1	442–486	4.44	4.34	1	364 469	495	56	34	1.27	7.24	10.14
$PrL_3\cdot 2H_2O$	329–377	2.40	2.32	1	441–489	4.44	4.48	1	369 472	491	41	24	0.19	0.06	12.20
$NdL_3\cdot 2H_2O$	324–373	2.21	2.20	1	433–487	4.42	4.46	1	368 468	487	40	14	0.67	0.56	11.24
$SmL_3\cdot 2H_2O$	335–383	2.19	2.20	1	424–475	4.39	4.40	1	370 461	483	51	17	0.89	1.72	10.76
$EuL_3\cdot 2H_2O$	339–388	2.19	2.20	1	433–475	4.39	4.42	1	383 461	483	32	27	0.53	0.21	11.65
$GdL_3\cdot 2H_2O$	340–381	2.17	2.16	1	421–460	4.35	4.40	1	367 449	479	61	25	1.07	3.53	10.45
$TbL_3\cdot 2H_2O$	377–442	4.12	4.18	2	–	–	–	–	414	465	54		0.53	0.21	11.66
$DyL_3\cdot 2H_2O$	371–423	4.32	4.40	2	–	–	–	–	412	466	52		1.13	4.4	10.35
$HoL_3\cdot 2H_2O$	348–409	4.32	4.38	2	–	–	–	–	399	439	47		1.27	0.70	10.15
$ErL_3\cdot 2H_2O$	347–419	4.30	4.34	2	–	–	–	–	401	452	82		1.33	8.44	10.07
$TmL_3\cdot 2H_2O$	361–417	4.29	4.20	2	–	–	–	–	401	461	63		1.25	6.59	10.18
$YbL_3\cdot 2H_2O$	341–425	4.27	4.25	2	–	–	–	–	391	455	88		1.37	9.51	10.02
$LuL_3\cdot 2H_2O$	356–413	4.26	4.34	2	–	–	–	–	391	436	46		1.28	0.72	11.14

[a] ΔT_1, ΔT_2: temperature ranges corresponding to the endothermic loss of molecules of crystallization water

[b] T_{max}: temperature of the maximum of the endothermic effects in the DTA curve

[c] T_k: temperature of the anhydrous salt formation

[d] n: amounts of crystallization water molecules

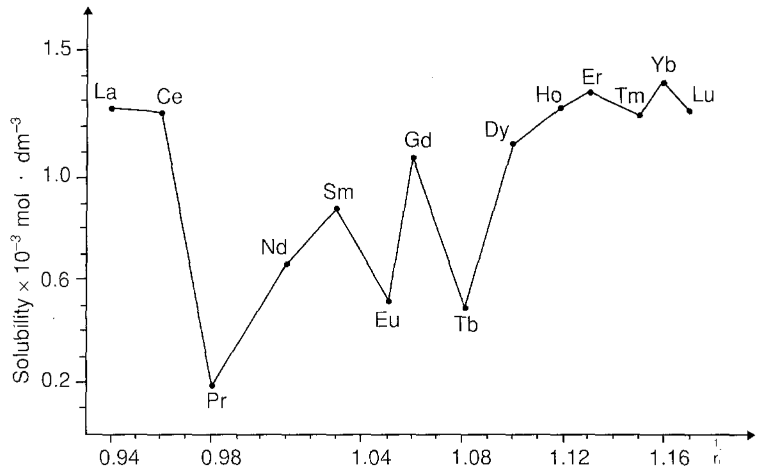

Fig. 4. Dependence between solubilities of 3,4-dinitrobenzoates of rare earths in water and ionic potential of element (r_i Templeton's values)

dinitrobenzoates of rare earths are smaller compared to those for 2,4- and higher relative to 3,5-dinitrobenzoates of corresponding elements which is probably connected with the different positions of NO_2 groups in the benzene ring [11, 12].

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