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Micellar extraction of the lanthanide ions from acidic media

Yu. G. Elistratova,* A. R. Mustafina, D. A. Tatarinov, V. F. Mironov, and A. I. Konovalov

A. E. Arbuzov Institute of Organic and Physical Chemistry,
Kazan Research Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation.
Fax: +7 (843) 273 2253. E-mail: yulenka@iopc.kcn.ru

A procedure of micellar extraction of the lanthanide ions (La, Gd, and Lu) from nitric acid media based on the use of novel phosphine oxide derivatives is developed. In the micellar extraction, complexes of the lanthanide ions with the extractant in the ratio of 1 : 2 (metal : extractant) form. The dependence of the selectivity of extraction on the length of hydrophobic radicals attached to the P=O group was shown. The conditions of the selective micellar extraction in the series La > Gd > Lu with the use of an extractant containing octyl substituents at the P=O group were found.

Key words: micelles, pseudophase separation, lanthanide ions, phosphine oxides, extraction.

The problem of radioactive wastes disposal, as well as the problem of waste water and waste soil monitoring at their burial places is still topical. The method of extractive concentration with the use of monodentate organophosphorus compounds (phosphates, phosphonates, and phosphine oxides) as the extractants has found the widest practical application in the radioactive waste processing.[1—7] Phosphine oxide derivatives,[4—7] including phosphomethylated calixarenes,[8] are the most efficient extractants of the series and can extract the cations of 4f- and 5f-elements from the strong acidic media.

The extraction is a mass transfer process from one phase to another immiscible with the former. There are various methods for the metal ion extraction and concentration. The method of liquid extraction has found the widest practical application due to the reversibility of the extraction process on the liquid—liquid interface and rapid equilibration.[1—3] However, the use of large volumes of organic solvents is necessary for efficient liquid extraction, which makes this process environmentally unsafe and leads to the necessity of additional metal concentration in the organic phase.

The method of micellar extraction is being currently rapidly developed, it is free from the above-mentioned drawbacks.[9—11] This method is based on pseudophase separation of aqueous and micellar phases. This separation can be achieved by increasing temperature,[11] varying the acidity[9] or ion strength[12] of micellar solutions. The variation of physical conditions, *e.g.*, heating of a micellar solution, reduces hydration of oxyethyl chains of surfactants. As a result, the spherical micelles reorganize into cylindrical ones, which results in its subsequent clusterization and emergence of a micellar or coacervate phase.[9—11] It should be noted that its volume is very small and consists of surfactant along with small amount of the solvent. Another pseudophase is the solvent where the surfactant content does not exceed critical micelle concentration (CMC).[13] The phenomenon of temperature-induced phase separation, called the separation at the cloud point (CP) and being the specific feature of solutions of nonionic and zwitterionic surfactants[14] has found the widest application in the separation processes.

The procedure of extraction at the CP is environmentally safe, as it requires no environmentally hazardous or explosive-suspect organic solvents. The second important advantage of this extraction method is the possibility of no less than 50-fold concentration of the metal ions.[9]

The use of aqueous solutions of nonionic surfactants for the extraction of the metal ions by temperature-induced phase separation is limited by their low affinity to the micellar phase. For enhancement of the extraction effectiveness; the so-called chelating agents are used, which form complexes with the metal ions thereby increasing their hydrophobicity and affinity to the micellar phase. In addition to binding ability to the metal ion, the chelating agent should be well soluble in the aqueous solutions of nonionic surfactants. Oxyquinoline and its derivatives found the widest application as chelating agents for micellar extraction of the lanthanide ions.[15,16] 2-(3,5-Dichloro-2-pyridylazo)-5-dimethylaminophenol was also used as a chelating agent.[17] The extraction procedure of U^{IV} at the CP in the form of its complex with Pyrocatechol Violet was developed[18] on the basis of mixed micellar solutions of Triton X100 (TX-100) and CTAB.

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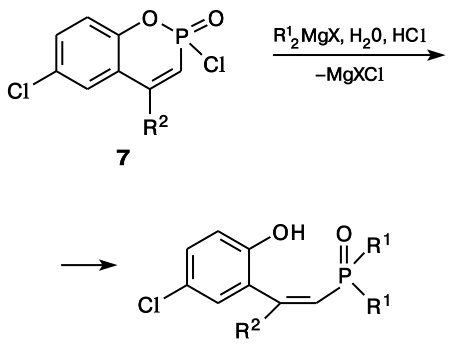
A method of extraction of lanthanides with micellar solutions of TX-100 and calix[4]resorcinarenephosphonic acid as a chelating agent is known.[19] However, the efficient extraction of lanthanides with above-mentioned chelating agents occurs only in neutral or weakly basic media; the extraction efficacy substantially decreases with an increase in acidity of aqueous solutions.[15—19] It is caused by protonation of both the extractants and oxyethyl chains of surfactants.

Therefore, the search for novel chelating agents for the extraction of lanthanides from acidic and stongly acidic media by environmentally safe extraction at the CP is a topical problem. Taking into account the above-mentioned extraction ability of phosphine oxide derivatives in liquid extraction, a comparison of the effectiveness of micellar and liquid extraction with novel phosphine oxide derivatives as the extractants is of interest.

Results and Discussion

Phosphine oxides **1—6** were synthesized by the reaction of chlorophosphorinine oxides **7** with the Grignard reagent (RMgX, X = Br, I) followed by quenching of the reaction mixture with water or aqueous hydrochloric acid (Scheme 1). Chlorophosphorinine oxides **7** are accessible compounds, which can easily be synthesized from phosphorus pentachloride, pyrocatechol, and phenyl- or butylacetylene (the methods of their synthesis have been described earlier).[20—22]

Scheme 1



Compound	R¹	R²	Compound	R¹	R²
1	Me	Ph	**4**	n-C_6H_{13}	Ph
2	Et	Ph	**5**	n-C_8H_{17}	Ph
3	Bu^n	Ph	**6**	Ph	Bu^n

The results of micellar extraction of the lanthanum, gadolinium, and lutetium ions at variable acidity of the aqueous phase and constant concentration (0.2 mmol L^{-1}) of phosphine oxides **1—6** in the micellar solutions are presented in Table 1. The results of liquid extraction for the same concentration of extractants **3—6** (the concentration of phosphine oxides in the liquid phase is 0.2 mmol L^{-1}), are given in Table 2.

The analysis of these data makes it possible to reveal the noticeable increase in the degree of extraction with the increase in acidity of the aqueous phase (liquid extraction) and micellar solution (micellar extraction). It should be noted that the degree of extraction from the

Table 1. The degree of micellar extraction (E (%)) of lanthanides in the systems TX-100—extractant (**1—6**)—Ln^{III} at various pH (pH = 1 corresponds to 0.1 M HNO_3)

Extractant	La			Gd			Lu		
	pH = 1	pH = 2	pH = 3	pH = 1	pH = 2	pH = 3	pH = 1	pH = 2	pH = 3
1	60	22	11	51	17	14	39	31	24
2	71	5	5	54	14	5	65	5	5
3	71	17	5	40	5	5	26	5	5
4	100	24	15	96	15	16	68	25	26
5	86	15	5	52	5	5	21	5	22
6	82	13	5	59	5	5	58	25	28

Table 2. The degree of liquid extraction (E (%)) of lanthanides in the systems extractant (**3—6**)—Ln^{III} at various pH (pH = 1 corresponds to 0.1 M HNO_3)

Extractant	La			Gd			Lu		
	pH = 1	pH = 2	pH = 3	pH = 1	pH = 2	pH = 3	pH = 1	pH = 2	pH = 3
3	71	17	5	57	5	5	36	5	5
4	100	24	15	91	20	5	54	10	23
5	86	15	5	42	5	5	34	5	5
6	82	13	5	60	5	5	38	16	15

aqueous phase are the same within the limits of the error for both procedures. The maximum degree of extraction is observed with phosphine oxide **4** used as the extractant. It is known that electron-donor character of the P=O group exerts big influence on the extraction ability of phosphine oxides.[7] The results obtained in the present study (see Tables 1 and 2) suggest the dependence of the degree of micellar and liquid extraction on the nature of the hydrocarbon radical R^1. However, the correlation of the degree of extraction with the length of the hydrocarbon radical R^1 is observed not for all of the lanthanide ions. Particularly, the noticeable decrease in the degree of micellar extraction of the gadolinium and lutetium ions is observed on going from extractant **2** to **3**. Taking into account the multifactor nature of the extraction process, the correct explanation of the observed regularity cannot be made on the basis of the results obtained. The nature of the radical R^2 does not have considerable influence on the efficiency and selectivity of the extraction in the series lanthanum—gadolinium—lutetium, because it does not affect directly the electron-donor character of the P=O group. Regardless of pH and the structure of the extractant used the lanthanum ion is extracted preferably. The most efficient extractant **4** is inferior to extractant **5** in selectivity, extraction of gadolinium and lanthanum being nearly the same and the degree of extraction of the lutetium ion being somewhat smaller. Extractant **5** is the most selective and at the same time it retains its efficiency toward the lanthanum ion. For example, the degree of micellar extraction of the La^{III} ion is ~1.6 and ~4.1 times higher than of Gd^{III} and Lu^{III}, respectively. The highest selectivity of extractant **5** in the series of extractants **1—6** can be explained on assumption that two octyl radicals produce much greater steric strain in the coordination sphere of the lutetium ion than in the coordination sphere of the gadolinium and lanthanum ions. It should be noted that the efficiency and the selectivity of the liquid and micellar extraction with extractants **3—6** are similar.

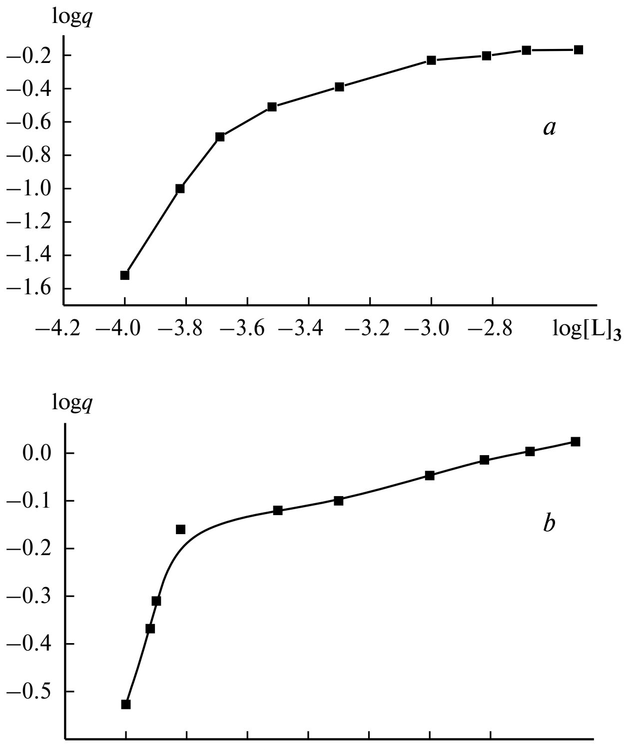


Fig. 1. The dependence of log*q* on $\log[L]_3$ in the system Gd^{III}—TX-100—**3** (*a*) and $\log[L]_5$ in the system Gd^{III}—TX-100—**5** (*b*); $[Gd^{III}] = 1.7 \cdot 10^{-4}$ mol L^{-1}, [TX-100] = $2 \cdot 10^{-2}$ mol L^{-1} ($\tan\alpha = 2$ on the linear region).

The results of quantitative analysis of the concentration dependence of the degree of micellar extraction of the Gd^{III} ions with extractants **3** and **5** at pH 1 are shown in Figure 1 in the coordinate system log*q*—log[L] (*q* is the extraction coefficient, $q = E/(100 - E)$). The increase in the degree of extraction is observed only in the region of 0—0.2 mmol L^{-1} and it is caused by the formation of a complex with the composition 1 : 2 (Gd : extractant). The subsequent increase in the extractant concentration almost does not influence on the degree of extraction. The observed regularity can be explained by aggregation of compounds **3** and **5** in the micellar pseudophase. Taking into account the structures of extractants **1—6**, it is natural to assume the possibility of their bidentate coordination with participation of the hydroxyl group in coordination. The stoichiometry of Gd^{III} complex with ligands **3** and **5** (1 : 2) confirms this assumption, since monodentate phosphine oxides form complexes with the lanthanide ions with the composition 1 : 3. The extraction constants calculated on the base of the results obtained are $\log K_{ex(3)} = 5.23\pm0.04$ and $\log K_{ex(5)} = 6.11\pm0.01$, respectively.

Thus, we developed for the first time a procedure of micellar extraction of the lanthanide ions from nitric acid media using novel phosphine oxide derivatives. The dependence of selectivity of extraction on the length of the hydrophobic radical at the P=O group was found. The conditions for selective micellar extraction in the series La > Gd > Lu at concentration of nitric acid 0.1 mol L^{-1} were established. It was shown that the stoichiometry of the complexes formed 1 : 2 (metal : extractant) is not typical of monodentate phosphine oxides due to bulkiness of hydrophobic radicals at the donor groups and suggests the possibility of bidentate coordination involving the hydroxyl group.

Experimental

NMR $^{31}P-\{^1H\}$ spectra were recorded on a Bruker CPX-100 instrument (36.48 MHz, ^{31}P) in DMSO-d_6 (35 °C) in the δ scale relative to H_3PO_4 (85%) as the external standard. IR spectra were obtained for Nujol mulls or KBr pellets on a

FTIR Vector-22 spectrometer (Bruker). Mass spectra were registered on a TRACE MS Finnigan MAT instrument with ionization energy of 70 eV and the temperature of the ion source 200 °C. Heating of the injection ampoule was performed in a temperature programmable regime from 35 to 150 °C with a 35 grad min^{-1} step. The mass spectra was processed with the use of an Xcalibur program.

Oxyethylated isooctylphenol (Triton X100) (ICN Biomedicals) was used, the mean number of the oxyethyl units is 10.

Lanthanum(III), gadolinium(III), and terbium(III) nitrates (99.9%, Alfa Aesar) were used. The concentration of Ln^{III} in the stock solution was determined by titration with Trilon B with Thymol Blue and Xylenol Orange as indicators.[23]

The phosphine oxide derivatives are water-insoluble, therefore they were dissolved in 0.1 *M* solution of TX-100. The stock solutions with the concentration in the range of 0.014—0.015 mol L^{-1} was prepared for all of the phosphine oxides studied.

The extraction was performed by the following procedure: the chloroform solution of an extractant (5 mL, 0.3 mmol L^{-1}) was added to the aqueous solution of Ln(NO$_3$)$_3$ (5 mL, $C = 0.17$ mmol L^{-1}) with variable acidity (achieved by addition of different amounts of nitric acid). The two-phase system was magnetically stirred for 1.5 h in a closed flask and kept for 24 h in darkness. After separation of the aqueous phase, it was analyzed for the lanthanide ion content by spectrophotometry with Xylenol Orange as the indicator.

2-(5-Chloro-2-hydroxyphenyl)-2-phenylethenyl(dimethyl)phosphine oxide (1). A solution of chlorophosphirinine oxide **7** (13.8 g, 44.4 mmol) in 25 mL of benzene was added dropwise to the Grignard reagent obtained from magnesium (2.2 g, 92.4 mmol) and methyl iodide (5.75 mL, 13.1 g, 92.4 mmol) in diethyl ether (100 mL). The reaction mixture was heated with vigorous stirring for 30 min (phase separation was observed), after cooling to ~20 °C it was quenched with 30 mL of water and 8 mL of hydrochloric acid with vigorous stirring; boiling of ether being observed. The organic layer was separated, acetone (2—4 mL) was added and the homogeneous organic layer obtained sedimented upon dilution with water. Compound **1** (13.0 g, 96%) in the form of a brownish powder with m.p. 172—175 °C was obtained. Found (%): C, 62.61; H, 5.29; Cl, 11.33; P, 10.11. $C_{16}H_{16}ClO_2P$. Calculated (%): C, 62.65; H, 5.26; Cl, 11.56; P, 10.10. MS, *m/z*: 306 $[M]^{+\bullet}$, 292 $[M - CH_2]$, 291 $[M - Me]$, 290 $[M - Me - H]$, 276 $[M - 2\,Me]$, 275 $[M - 2\,Me - H]$, 271 $[M - Cl]$, 255 $[M - Me - HCl]$, 230 $[C_{14}H_{11}ClO]$, 229 $[C_{14}H_{10}ClO]$, 228 $[C_{14}H_9ClO]$, 215, 202, 194, 166,165, 152, 139, 111, 105, 97, 83, 78, 57, 43. IR, ν/cm^{-1}: 422, 452, 534, 567, 637, 694, 759, 819, 879, 910, 940, 954, 1031, 1114, 1138, 1221, 1284, 1303, 1334, 1377, 1409, 1464, 1496, 1573, 1587, 1604, 2582, 2683, 2854, 2924, 3380. $^{31}P-\{^1H\}$ NMR (36.48 MHz, DMSO-d$_6$): δ_P 37.0.

2-(5-Chloro-2-hydroxyphenyl)-2-phenylethenyl(diethyl)phosphine oxide (2). A solution of chlorophosphirinine oxide **7** (2.5 g, 8.0 mmol) in 10 mL of benzene was added dropwise to the Grignard reagent obtained from magnesium (0.43 g, 17.9 mmol) and ethyl iodide (1.44 mL, 2.8 g, 17.9 mmol) in diethyl ether (20 mL) and heated under reflux for 0.5 h. The solution was cooled, quenched with 30 mL of water and 2.3 mL of hydrochloric acid. The organic and aqueous layers were filtred and separated. Then the solvent was evaporated, the solid greenish residue was washed with 10% hydrochloric acid (15 mL), separated by decantation, and dried *in vacuo*. Compound **2** (2.52 g, 94%) in the form of brownish powder with m.p. 75—77 °C was obtained. Found (%): C, 64.32; H, 6.12; Cl, 10.41; P, 9.41. $C_{18}H_{20}ClO_2P$. Calculated (%): C, 64.58; H, 6.02; Cl, 10.59; P, 9.25. MS, *m/z*: 334 $[M]^{+\bullet}$, 305 $[M - Et]$, 299 $[M - Cl]$, 289 $[M - Et - CH_4]$, 275 $[M - 2\,Et - H]$, 259 $[M - 2\,Et - OH]$, 241 $[M - 2\,Et - Cl]$, 230 $[C_{14}H_{11}ClO]$, 229 $[C_{14}H_{10}ClO]$, 228 $[C_{14}H_9ClO]$, 223, 215, 202, 194, 176,166, 165, 152, 139, 125, 111, 105 $[C_{14}H_{10}OP]$, 78, 63, 53, 49, 43, 29. IR, ν/cm^{-1}: 450, 505, 532, 583, 632, 653, 677, 693, 727, 743, 763, 823, 850, 887, 916, 941, 975, 991, 1036, 1119, 1187, 1218, 1235, 1284, 1332, 1377, 1414, 1460, 1495, 1569, 1586, 1601, 1812, 1876, 1959, 2588, 2687, 2856, 2930. $^{31}P-\{^1H\}$ NMR (36.48 MHz, CDCl$_3$): δ_P 47.5.

Dibutyl-2-(5-chloro-2-hydroxyphenyl)-2-phenylethenylphosphine oxide (3). 1-Bromobutane (4.05 mL, 5.14 g, 37.5 mmol) in ether (20 mL) was added with stirring in an argon atmosphere to magnesium chips (0.9 g, 37.5 mmol) preliminary activated with crystalline iodine and boiled under reflux for 35 min. A solution of chlorophosphorinine oxide **7** (5 g, 1.61 mmol) in benzene (5 mL) was added dropwise to the resulting solution. The reaction mixture was boiled for 30 min, cooled, quenched with water (10 mL) and a solution of hydrochloric acid (4 mL) in water (10 mL). The organic layer was separated, the solvents were evaporated. The residue was dried *in vacuo* (100 °C, 0.1 Torr). The product (6.0 g, 95%) in the form of brownish oil was obtained. Found (%): C, 69.86; H, 8.12; Cl, 7.93; P, 6.93. $C_{22}H_{28}ClO_2P$. Calculated (%): C, 67.60; H, 7.22; Cl, 9.07; P, 7.92. MS, *m/z*: 390 $[M]^{+\bullet}$, 376 $[M - OH^-]$, 355 $[M - Cl]$, 333 $[M - Bu]$, 276 $[M - 2\,Bu]$, 229 $[M - PO(Bu)_2]$, 161.6 $[C_8H_{18}OP]$, 57 [Bu], 43.1 [Pr], 29 [Bu]. $^{31}P-\{^1H\}$ NMR (162.0 MHz, DMSO-d$_6$): δ_P 42.38. IR, ν/cm^{-1}: 471, 634, 686, 763, 828, 899, 948, 1125, 1222, 1282, 1340, 1415, 1455, 1492, 1590, 2361, 2597, 2720, 2956, 3035.

(5-Chloro-2-hydroxyphenyl)-2-phenylethenyl(dihexyl)phosphine oxide (4). 1-Iodohexane (5.66 mL, 8.13 g, 38.3 mmol) in ether (30 mL) was added dropwise with stirring in an argon atmosphere to magnesium chips (0.92 g, 38.3 mmol) preliminary activated with crystalline iodine and boiled under reflux for 30 min. A solution of chlorophosphorinine oxide **7** (5 g, 1.61 mmol) in benzene (5 mL) was added dropwise to the resulting solution. The reaction mixture was boiled under reflux for 20 min, cooled, and quenched with water (10 mL) and a solution of hydrochloric acid (4 mL) in water (10 mL). The organic layer was separated, the solvents were evaporated. The residue was dried *in vacuo* (100 °C, 0.1 Torr). The product (6.9 g, 96%) in the form of brownish oil was obtained. Found (%): C, 69.56; H, 8.22; Cl, 8.05; P, 7.03. $C_{26}H_{36}ClO_2P$. Calculated (%): C, 69.86; H, 8.12; Cl, 7.93; P, 6.93. MS, *m/z*: 446 $[M]^{+\bullet}$, 411 $[M - Cl]$, 361 $[M - C_6H_{13} - H]$, 276 $[M - 2\,C_6H_{13}]$, 229 $[M - PO(C_6H_{13})_2]$, 43.1 $[Pr^\bullet]$. $^{31}P-\{^1H\}$ NMR (162.0 MHz, DMSO-d$_6$): δ_P 54.3. IR, ν/cm^{-1}: 699, 766, 824, 887, 975, 1116, 1214, 1278, 1342, 1411, 1458, 1490, 1595, 1884, 2596, 2731, 2861, 2927, 3065, 3737.

5-Chloro-2-hydroxyphenyl)-2-phenylethenyl(dioctyl)phosphine oxide (5). 1-Iodooctane (26.43 mL, 35.02 g, 145.8 mmol) in isooctane (60 mL) was added dropwise with stirring in an argon atmosphere to magnesium chips (3.5 g, 145.8 mmol) preliminary activated with crystalline iodine and boiled under reflux for 30 min. A solution of chlorophosphorinine oxide **7** (18 g, 57.9 mmol) in benzene (20 mL) was added dropwise to the resulting solution. The formation of a white emulsion was observed, which was boiled under reflux for 40 min, then cooled

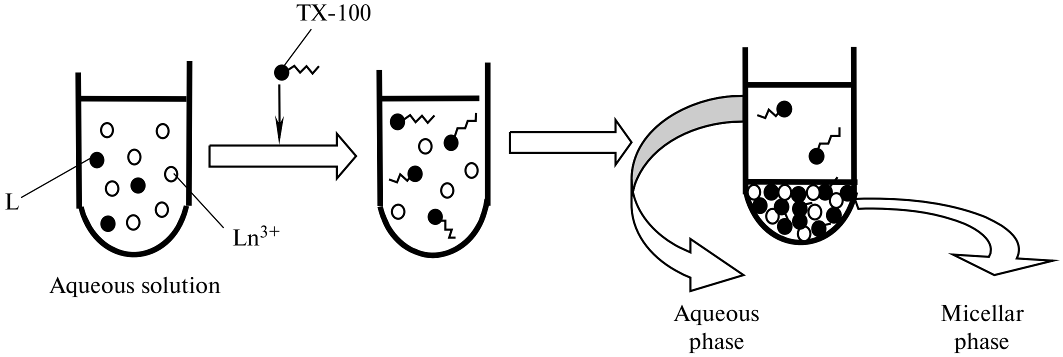


Fig. 2. The schematic presentation of micellar extraction.

and quenched with a solution of hydrochloric acid (10 mL) in water (30 mL). The organic layer was separated, the solvents were evaporated *in vacuo* (12 Torr). The residue was dried *in vacuo* (100 °C, 0.1 Torr). The product (27.9 g, 96%) in the form of greenish oil was obtained. Found (%): C, 71.22; H, 9.07; Cl, 7.15; P, 6.27. $C_{30}H_{44}ClO_2P$. Calculated (%): C, 71.64; H, 8.76; Cl, 7.05; P, 6.17. MS, *m/z*: 502 $[M]^{+\bullet}$, 467 [M – Cl], 389 [M – C_8H_{17}], 276 [M – 2 C_8H_{17}], 229 [M – $PO(C_8H_{17})_2$], 228 [M – $PO(C_8H_{17})_2$ – H]. $^{31}P-\{^1H\}$ NMR (162.0 MHz, DMSO-d_6): δ_P 40.8. IR, ν/cm^{-1}: 409, 472, 536, 567, 634, 671, 697, 724, 762, 822, 848, 885, 945, 1031, 1112, 1136, 1223, 1282, 1335, 1378, 1411, 1445, 1467, 1493, 1572, 1591, 1958, 2855, 2926, 2955, 3059.

2-Butyl-2-(5-chloro-2-hydroxyphenyl)ethenyl(diphenyl)phosphine oxide (6). A solution of chlorophosphirinine oxide **7** (10 g, 34.4 mmol) in 10 mL of benzene was added dropwise with stirring in a flow of argon to the Grignard reagent obtained from magnesium (1.8 g, 75.0 mmol) and bromobenzene (7.9 mL, 11.9 g, 75.0 mmol) in diethyl ether (100 mL). The reaction mixture was boiled under reflux for 0.5 h, cooled to ~20 °C, and quenched with water (20 mL). The solvents from the organic layer were evaporated, the glassy residue was dried *in vacuo* (100 °C, 12 Torr), the yield was 12 g (85%). Found (%): C, 70.24; H, 6.13; Cl, 8.75; P, 7.73. $C_{24}H_{24}ClO_2P$. Calculated (%): C, 70.16; H, 5.85; Cl, 8.63; P, 7.55. MS, *m/z*: 410 $[M]^{+\bullet}$, 290 [M – Ph – Pr], 277 [M – Ph – Bu], 202 [Ph_2PO], 153 [M – Ph_2PO – Bu], 152 [M – Ph_2PO – Bu – H], 77 [Ph]. $^{31}P-\{^1H\}$ NMR (162.0 MHz, DMSO-d_6): δ_P 19.7. IR, ν/cm^{-1}: 405, 436, 456, 512, 539, 605, 641, 695, 719, 738, 782, 822, 879, 906, 998, 1027, 1071, 1099, 1120, 1156, 1236, 1278, 1378, 1412, 1437, 1489, 1496, 1592, 1817, 1892, 1959, 2247, 2721, 2870, 2929, 2956, 3058.

The procedure of micellar extraction. Micellar extraction was conducted in 20 m*M* solution of nonionic surfactant TX-100 containing Ln^{III} (0.17 mmol L^{-1}). The chelating agents (phosphine oxide derivatives) were introduced in concentration of 0.2 mmol L^{-1}. The solution was heated to CP, which resulted in phase separation into the coacervate phase (the heavier one) and the phase depleted in surfactants (Fig. 2). The solution was kept at this temperature for 15 min. The cloud point of solutions of TX-100 in the presence of chelating agents was 65±1 °C, which is close to that of TX-100 solution. The pH values were varied by addition of different amounts of nitric acid.

The phase separation was registered by the appearance of a distinct interface. The ionic strength was maintained constant: I = 0.01 mol L^{-1}. Then the solution was cooled to 20 °C, no mixing of the solution occurred. The water phase was separated by decantation and analyzed for the content of lanthanide by spectrophotometry with Xylenol Orange as an indicator.[24] The degree of extraction (E) was calculated using equation

$$E = 100(A_0 - A_i)/A_0,$$

where A_0 is the optical density of the initial solution of lanthanide nitrate ($C = 1.7 \cdot 10^{-4}$ mol L^{-1}), A_i is the optical density of the solutions after extraction. The data obtained were used for the calculation of stoichiometry and the degree of extraction (equilibrium (1)) by the graphical solution of Eqs (2) and (3).

$$m\,Ln^{3+}{}_{(aq)} + n\,L_{(aq)} = Ln_mL_{n(aq)} \qquad (1)$$

According to equilibrium (1), the constant and the logarithm of extraction degree (K_{ex} and $\log K_{ex}$) can be calculated using the expressions

$$K_{ex} = [Ln_mL_n]/([L]^n[Ln^{3+}]^m), \qquad (2)$$

$$\log K_{ex} = \log([Ln_mL_n]/[Ln^{3+}]^m) - n\log[L], \qquad (3)$$

where $[Ln_mL_n]/[Ln^{3+}]^m = E/(1 - E)$ at $m = 1$; $[Ln_mL_n]$ is concentration of the complex; $[Ln^{3+}]$ is the equilibrium concentration of lanthanides in aqueous phase; [L] is equilibrium concentration of the extractant.

All data given in this work are the average results of at least two measurements.

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