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Cloud point extraction of lanthanide(III) ions via use of Triton X-100 without and with water-soluble calixarenes as added chelating agents

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Abstract

The use of water-soluble calixarenes: *p*-sulfonato thiacalixarene (ST), tetra-sulfonatomethylated calix[4]resorcinarene (SR), calix[4]resorcinarene phosphonic acid (PhR) as chelating agents in cloud point extraction (CPE) of La(III), Gd(III) and Yb(III) ions using Triton X-100 as non-ionic surfactant is introduced. The data obtained indicate that both complexation ability and structure of calixarenes govern the extraction efficiency of lanthanides. In particular ST and SR, forming 1:1 lanthanide complexes with similar stability in aqueous media, exhibit different extractability when used as chelating agents in CPE. First synthesized PhR was found to be the most efficient chelating agent exhibiting pH-dependent selectivity within La(III), Gd(III) and Yb(III) in CPE.

Keywords: Lanthanide(III) complexes; Calix[4]resorcinarene; Thiacalix[4]arene; Cloud point extraction; Triton X-100

1. Introduction

Calixarenes are well documented as efficient extractants of metal ions in liquid–liquid extraction, in particular of 4f- and 5f-ions [1]. Their application in liquid–liquid extraction requires both high complexation ability towards metal ions and high lipophilicity in order to provide sufficient solubility of the extractant and extracted complexes in organic phase. In turn the insertion of polar substituents (particularly, the ionized groups) into calixarene matrix may result in an enhanced solubility in aqueous phase, which restricts the applicability of calixarenes as extractants. For example calixarenes, bearing sulfonate [2] or phosphonate groups [3,4] on their rims and thus exhibiting high complexability towards metal ions, are water soluble and can not serve as extractants in traditional liquid–liquid extraction.

An interesting alternative to traditional liquid–liquid extraction is the micelle-mediated extraction, firstly developed by Watanabe and Tanaka [5]. Micelles of such well-known non-ionic surfactants as Triton X-100 or -114, have a non-polar core and extended polar layer, where both extractants and extracted complexes can be solubilized [6–9]. The separation of aqueous and micelle-enriched phases can be achieved by heating the solution. This simple procedure called cloud point extraction (CPE) [6–10] enables to avoid hazardous organic solvents and allows to achieve a much higher concentration of recovered metal ions than in the case of liquid–liquid extraction, because the micellar phase volume is about 10–100-fold less than the volume of an aqueous phase [7]. Accordingly, any metal ions that either directly interact with micelles or after prerequisite binding with hydrophobic chelating ligand, can be extracted from the parent solution by CPE procedure. The first example of the lanthanides(III) separation through CPE technique with 8-hydroxyquinoline as chelating ligand and Triton X-114 as non-ionic surfactant was published recently

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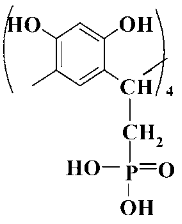
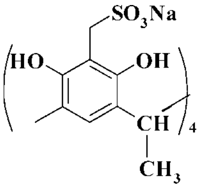
[11]. The extraction of Er(III) through CPE procedure with 2-(3,5-dichloro-2-pyridylazo)-5-dimethylaminophenol as chelating agent and PONPE-7.5 as non-ionic surfactant was exemplified in 1997 by Silva et al. [12]. Later a similar procedure was used for the preconcentration of Dy(III) as a step of the spectrophotometric determination of Dy(III) in urine [13].

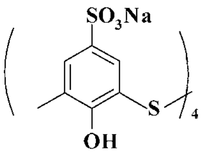
Taking into account the attractiveness of both the CPE technique and the enhanced selectivity of calixarenes, bearing ionized groups, for the lanthanide group [14,15], the main goal of the present work is to investigate the micelle-mediated extraction of lanthanide (La^{3+}, Gd^{3+} and Yb^{3+}) complexes with water-soluble calixarenes using CPE technique with Triton X-100 (TX100) as non-ionic surfactant. Three water-soluble calixarenes: *p*-sulfonato thiacalixarene (ST), tetra-sulfonatomethylated calix[4]resorcinarene (SR), calix[4]resorcinarene phosphonic acid (PhR), able to bind lanthanide ions, were chosen as ligands. So far as there is a lack of information about cloud point extraction of lanthanide ions by Triton X-100 without chelating agents, the above-mentioned extraction was also examined.



PhR



SR



ST

2. Experimental

2.1. Reagents

The non-ionic surfactant TX100 from ICN Biomedicals was used as received. Stock solution of TX100 was prepared in calibrated flask dissolving the appropriate amount in doubly distilled water. Stock solutions of $LnCl_3$ (Ln = La, Gd and Yb) were prepared by dissolving the appropriate amounts of their salts $LnCl_3 \cdot nH_2O$ of analytical grade in doubly distilled water with further standardization with EDTA at pH 6, using xylenol orange as indicator [16]. Compounds ST, SR were synthesized by literature methods [17,18].

2.1.1. Synthesis of PhR (4,6,10,12,16,18,22,24-octahydroxy-2,8,14,20-tetra-[dihydroxymethylphosphino-1-yl]-pentacyclo[19.3.1.$1^{3,7}$.$1^{9,13}$.$1^{15,19}$]-octa-cosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen

Solution of 1.2 g (0.007 mol) of dichloranhydride of 2-ethoxyvinylphosphonic acid in 2 ml of ethanol was added dropwise under stirring to the mixture of 0.76 g (0.007 mol) of resorcinol, 7 ml of water, 5 ml of ethanol and 1 ml of concentrated HCl within a half of an hour. The reaction mixture was then heated under stirring for a half of an hour at 50–60 °C. After 7 days staying at the room temperature all solvents were evaporated from the reaction mixture, dry residue was dissolved in ethanol and reprecipitated in ether and then dried in a vacuum of water-jet and oil pumps. Yellow powder 1.09 g, yield 92.37% with mp >350 °C was obtained. ^{31}P NMR (100 MHz, CD_3OD) δ 28.28. ^1H NMR (400 MHz, D_2O) δ 1.07 (m, $-PCH_2-$); 3.79 (m, –CH–); 6.28 (s, *o*-CH, aromatic); 7.04 (s, *m*-CH, aromatic). Anal. calcd. for $C_{32}H_{36}O_{20}P_4$ %, C 44.44, H 4.17, P 14.35. Found, %, C 44.35, H 4.71, P 13.48. MALDI-TOF ($m/z + K$) 901.

Stock solutions of ST, SR and PhR were also prepared by dissolving their appropriate amounts in doubly distilled water.

2.2. Apparatus

UV–vis spectra were recorded on a Perkin-Elmer Lambda 35 UV–vis spectrophotometer using a 10 mm cell. pH-metric measurements were performed in a thermostatically controlled cell at 25 ± 0.1 °C by use of “ThermoOrion 420A+” meter with combined electrode (the instrumental error less than 0.05 pH-units). The pH-meter was calibrated by standard buffer solutions (Mettler Toledo). The mass spectra were recorded on “MALDI 2 V5.2.0” with the 1,8,9-TGA matrix.

2.3. Determination of observed dissociation constants of PhR

The pH-metric titration of PhR was recorded both in aqueous and micellar solutions with 1.5% (w/v) of TX100 in the range of pH 2.0–11.0 with the 2.7×10^{-3} mol l^{-1} PhR concentration. Free of carbonates KOH (3×10^{-2} mol l^{-1}) solution was used as the titrant in titrations run in aqueous medium. Analogous KOH solution additionally containing 1.5% (w/v) of TX100 was used in experiments in micellar medium. The lack of surfactant effect on a glass electrode potential was proved by the identity of titration curves of HCl (1.0×10^{-2} mol l^{-1}) in aqueous and micellar solutions with 1.5% (w/v) of TX100. Thus concentration of H^+ can be determined by the equation $[H^+] = 10^{-pH}$ both in aqueous and micellar solutions. No extra salts were added in pH-measurements to maintain definite value of ionic strength in order to avoid precipitation due to salting-out effect. That is why the value of ionic strength results from the ions used themselves in titration. All pH-metric measurements have been performed twice. The data obtained were used in calculating of PhR dissociation constants $K_{(i)}$-values ($K_{(i)}$ is the constant of *i*th step dissociation). The mathematical treatment of the pH-metric data (30–40 experimental points) was carried out using CPESSP computer program [19]. The mathematical treatment by CPESSP is based on a search for the best fit between the experimentally observed Bjerrum function ($\tilde{n}_{exp.}$), (equilibrium (1)) and their theoretical analogues calculated from the law of mass action ($\tilde{n}_{calc.}$) by finding the minimum of F function, (equilibrium (2)), by iteration:

$$\tilde{n} = 2 - \left[\frac{(V_{\mathrm{HCl}}C_{\mathrm{HCl}})/(V_0 + V_{\mathrm{HCl}}) - 10^{-\mathrm{pH}}}{(C_0^M V_0)/(V_0 + V_{\mathrm{HCl}})}\right] \quad (1)$$

$$F = \sum[(\tilde{n}_{\mathrm{exp.}} - \tilde{n}_{\mathrm{calc.}})w_m]^2 \quad (2)$$

where m varies from 1 to N (N: number of experimental points) and w_m is a mean-square error. The validity of the chosen model was evaluated using transformed Fisher's criteria F_{min}:

$$F_{\mathrm{min}} \leq F\sigma^2(N - k) \quad (3)$$

where σ^2 is the dispersion and k is the number of complex species.

2.4. Typical cloud point extraction procedure

Solutions, containing La(III), Gd(III) and Yb(III) ions (C = 1.7×10^{-4} mol l^{-1}), TX100 (1.5% (w/v)) in the presence, as well as in the absence of calixarenes were prepared from the stock solutions of lanthanide salts (6.6×10^{-3} mol l^{-1}), TX100 (15% (w/v)) and calixarenes in calibrated flask. The pH-values of solutions for CPE were adjusted by the addition of appropriate amounts of HCl and NaOH, while ionic strength (I) was adjusted to 2.6×10^{-2} mol l^{-1} by the addition of appropriate amounts of NaCl. Concentrations of ST and SR were $C = 5.0 \times 10^{-4}$ to 4.0×10^{-3} mol l^{-1}, PhR-$C = 1.0 \times 10^{-4}$ to 4.0×10^{-4} mol l^{-1} in solutions under extraction. The solution thus prepared was heated up to definite temperature, where separation into the surfactant-rich and aqueous phases occurred, and kept at this temperature for 15 min. The temperature of cloud point phenomenon is 65–66 °C for TX100 solutions without chelating agents and in the presence of PhR, 73–75 °C for TX100 solutions with SR and ST as chelating agents. After cooling to 20 °C no mixing of phases was observed. The upper aqueous phase was then removed, and the concentration of lanthanides in this phase was determined spectrophotometrically at 570 nm, using Xylenol Orange as an indicator at pH 6.0 in acetic acid–sodium acetate buffer [20]. E-value of CPE were calculated through the Eq. (4) [11] with the error less than 4%:

$$E = \left[\frac{(C_{\mathrm{i}} - C_{\mathrm{f}})}{C_{\mathrm{i}}}\right] \times 100 \quad (4)$$

where C_{i} is the initial concentration of metal ion in micellar solution and C_{f} is the concentration of metal ion in aqueous phase after CPE. All the values reported are the averages of triplicate measurements.

Table 1
Extraction efficiency (E, %) of lanthanide ions ($C = 1.7 \times 10^{-4}$ mol l^{-1}) in CPE at pH 2 without and with SR (2.0×10^{-3} mol l^{-1}) or PhR (1.0×10^{-4} mol l^{-1}) as chelating agents, C_{TX100} = 1.5%(w/v), pH 2

Lanthanide ion	Chelating agent	E (%)
La(III)	Without chelating agent	0
	SR	22
	PhR	4.8
Gd(III)	Without chelating agent	2.2
	SR	17
	PhR	53.2
Yb(III)	Without chelating agent	18.4
	SR	18
	PhR	[a]

[a] Precipitation restricts the evaluation of E.

3. Results and discussion

3.1. Extractability of TX100 using CPE technique towards La^{3+}, Gd^{3+} and Yb^{3+} ions with water-soluble calixarenes at pH 2

The complexability of polyoxyethylated chains of non-ionic surfactants towards metal ions is known to be the underlay of the practically full CPE without chelating agents of lead(II) [21] and gold(III) [22]. Rather poor (less than 10%) ligand-free CPE of Gd^{3+} and La^{3+} ions was detected in the literature [11]. The CPE experiments were performed at pH 2 in order to avoid the effect of hydroxy complexes. In the case of ST and SR the extraction efficiency was correlated with the stability of their lanthanide complexes existing in aqueous solutions at pH 2 [23,24]. At definite concentration conditions (1.5%(w/v), pH 2) TX100 exhibits no extractability towards La^{3+} and Gd^{3+}, while detectable towards Yb^{3+} (Table 1).

According to their stability constants ($\log \beta_{\mathrm{ST}} = 3.30$ [23] and $\log \beta_{\mathrm{SR}} = 3.10$ [24]) the 10-fold excess of both ligands is enough to bind all lanthanide ions into 1:1 complexes at pH 2 in aqueous solutions. No extraction occurs at pH 2 when using ST as chelating agent, while SR at the same conditions ($C_{\mathrm{SR}} = 2.0 \times 10^{-3}$ mol l^{-1}) exhibits detectable extractability towards La, which slightly decreases on going to Gd and Yb. Taking into account that ST and SR bind Gd(III) in aqueous solution at pH 2 with nearly same stability constants [23,24] the above-mentioned result indicates that lanthanide complexes with SR exhibit higher affinity to micellar pseudophase than the complexes with ST. According to Abraham equation [25] hydrophobicity and proton-donor capacity are the key factors affecting the solubilization of molecules into non-ionic micelles [26,27]. Thus, the structural differences of both calixarenes, in particular the presence of four methyl groups on the "lower rim" and of eight hydroxy-groups on the "upper rim" are the reasons of the enhanced hydrophobicity and proton-donor capacity of SR and its lanthanide complexes. The attempt was made to correlate E-value with Gd–SR complex formation degree (α). The latter is defined as

Table 2
Values of E and α for Gd(III) at various concentrations of SR at pH 2

C_{SR} (mol × l^{-1})	E (%)	α (%)
5×10^{-4}	10	35.6
1×10^{-3}	17	53.4
2×10^{-3}	17	70.3
3×10^{-3}	10	78.3
4×10^{-3}	5	82.9

Table 3
Values of stepwise dissociation of PhR in aqueous and micellar (1.5%(w/v) of TX-100) media

Medium	p$K^{(7)}$[a]	p$K^{(8)}$[a]	p$K_{1,2}$[b]	pK_3	pK_4	pK_5	pK_6
Aqueous	4.45	11.67	4.99	5.81	8.61	9.79	10.4
Micellar	4.63	12.69	5.45	6.1	9.04	10.28	10.97

[a] $K^{(7)}$ and $K^{(8)}$ are the constants of equilibriums (7) and (8).
[b] $K_{1,2}$ is the constant of equilibrium (5).

$\alpha = [\mathrm{Gd(SR)}]/C_{\mathrm{Gd}}$, were [Gd(SR)] is the equilibrium concentration of 1:1 Gd(III)–SR complex, C_{Gd} is the initial concentration of Gd(III). The α-values are calculated according to the law of acting masses using stability constant, determined in aqueous solution [24]. E and α are presented in Table 2 for C_{SR} concentration range 5.0×10^{-4} to 2.0×10^{-3} mol l^{-1} and $C_{\mathrm{Gd}} = 1.7 \times 10^{-4}$ mol l^{-1}.

Up to α ~50% such correlation is evident. But when the α-value increases with further rise of SR concentration to 4.0×10^{-3} mol l^{-1}, the E-value decreases. The decrease of E under the excess amounts of SR can be explained by competitive extraction of SR along with its Gd(III) complex.

The complexation ability of PhR towards lanthanide ions have not been studied yet, but according to its structure it should possess comparable or even more pronounced complexability towards lanthanides than phosphonic acid derivatives, such as (*o*-hydroxyphenyl)bis-methylenephosphonic acid [28]. The mixing of PhR with lanthanide salts in aqueous solutions results in precipitation of the complex even at high dilution ($C_{\mathrm{PhR}} < 1 \times 10^{-4}$ mol l^{-1}). Though the solubility of complexes formed increases on going from aqueous to micellar media, high dilution ($C_{\mathrm{PhR}} = 1 \times 10^{-4}$ mol l^{-1}) is required even in 1.5% (w/v) TX100 solution to avoid precipitation under mixing with lanthanide salts at pH 2. According to the data obtained (Table 1) the extraction of Gd(III) is much more efficient than that of La(III), while mixing with Yb(III) ions at the same conditions results in precipitation.

3.2. Effect of pH on CPE of La^{3+}, Gd^{3+} and Yb^{3+} ions with TX100 as surfactant and PhR as chelating agent

Taking into account the acidity of $\mathrm{PO(OH)_2}$ groups it is naturally to propose that the complexability of PhR is pH-dependent and thus can be studied by pH-metric titration method. Indeed according to pH-metric data PhR in both aqueous and micellar solutions (1.5% (w/v) of TX-100) undergoes stepwise deprotonation with pK_i-values (i = 1–6) presented in Table 3. The computer treatment of the data obtained reveals that the first deprotonation step results in the deprotonation of two protons (equilibrium (5)). Further deprotonation occurs stepwise according to equilibrium (6):

$$\mathrm{PhR} \leftrightarrows \mathrm{PhR}^{-2} + 2\mathrm{H}^{+} \tag{5}$$

$$\mathrm{PhR} \leftrightarrows \mathrm{PhR}^{-(n-1)} + \mathrm{H}^{+} \tag{6}$$

Equilibriums (5) and (6) with n = 2–5 does not provide sufficient fitting between $\tilde{n}_{\mathrm{exp.}}$ and $\tilde{n}_{\mathrm{calc.}}$, which is evident from $F_{\min}$ being much more ($F_{\min}/(N-k) > 1$), than it should be in the case of sufficient fitting ($F_{\min}/(N-k) \ll 1$). According to Eq. (2) $F_{\min}$-value quantitatively evaluate the deviation of experimentally observed curve n versus pH from the calculated $\tilde{n}$ versus pH. Thus, if the set of stepwise deprotonation equilibriums (5, 6) does not provide sufficient fitting between experimental and calculated curves at definite pH range, it is very likely that some additional equilibriums occur, which contribute to $\tilde{n}$-values. So far as PhR possesses sufficient quantity of proton-donor and -acceptor groups, fixed on cyclophanic matrix, both PhR and its deprotonated forms should be assumed to form intra and inter-molecular hydrogen bonds. Such hydrogen bonding along with cooperative non-covalent Van der Waals interactions, typical for cyclophanic molecules and ions [29], can result in the binding of both PhR and its deprotonated forms into dimers. As it is evident from equilibrium (7) the dimerization of PhR and its deprotonated forms may result in the elimination of even or odd number of protons, which seems as the elimination of integer-valued or fractional number of protons per one molecule of PhR. The comparison of $F_{\min}$-values for various sets of deprotonation equilibriums of PhR, reveals that two additional deprotonation equilibriums with the elimination of 3/2 and 5/2 protons per one PhR molecule are required to achieve sufficient fitting between $\tilde{n}_{\mathrm{exp.}}$ and $\tilde{n}_{\mathrm{calc.}}$. Such deprotonation can result from the dimerization according to equilibrium (7) with m = 2 and k = 1 and further loss of proton from dimeric form $[\mathrm{PhR}^{-2}][\mathrm{PhR}^{-1}]$ according to equilibrium (8):

$$2\mathrm{PhR} \leftrightarrows [\mathrm{PhR}^{-m}][\mathrm{PhR}^{-k}] + (m+k)\mathrm{H}^{+} \tag{7}$$

$$[\mathrm{PhR}^{-2}][\mathrm{PhR}^{-1}] \leftrightarrows [\mathrm{PhR}^{-3}][\mathrm{PhR}^{-2}] + 2\mathrm{H}^{+} \tag{8}$$

The data presented in Table 3 reveals that the deprotonation of PhR in micellar solutions undergoes with pK-values, greater than those in aqueous solutions.

Unfortunately, the precipitation of Ln-complexes hinders the performance of pH-metric titration of PhR in the presence of lanthanide ions both in micellar and aqueous solutions.

Nevertheless the pH-metric measurements shows that the precipitate formed dissolves with increase of pH, and the pH-value of the precipitate dissolving decreases on going from 1:1 to 2:1 PhR:Gd concentration ratio (Fig. 1).

According to the data shown on Fig. 2 the extraction extent rises on increasing of PhR:Gd concentration ratio up to 3:1.

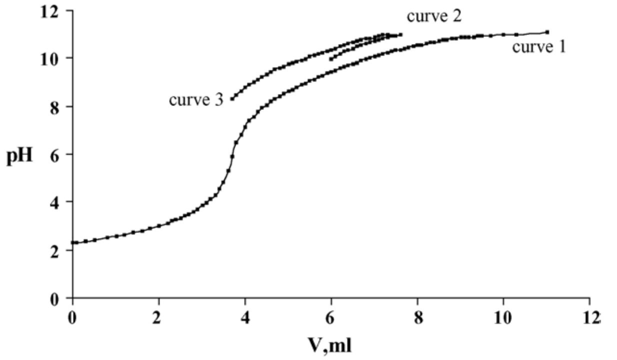


Fig. 1. Titration curves of PhR (curve 1), PhR and Gd(III) in 1:1 (curve 2) and 2:1 (curve 3) concentration ratio (PhR:Gd) with free of carbonates KOH (3×10^{-2} mol l^{-1}) aqueous micellar solution (1.5% (w/v) of TX100) as the titrant.

Further increase of PhR:Gd ratio does not affect on the extraction efficiency.

As far as PhR is efficient pH-dependent chelating agent, the CPE of lanthanide complexes with PhR should be examined in a wide range of pH. Taking into account that the increase of pH can result in hydrolysis of lanthanide ions along with their complexation, it seems necessary to study the effect of hydroxy complexes formation on the CPE of lanthanide ions. That is why the CPE of lanthanide ions without chelating agents was also examined in pH range 2–10 (Fig. 3). The sharp *E*-increase for La(III) and Gd(III) at pH >6 indicates that hydroxy complexes $(\mathrm{Ln(H_2O)}_n\mathrm{(OH)}_m{}^{3-m})$ are extracted into micellar pseudo-phase much more efficiently than ionic associates $(\mathrm{Ln}^{3+})(\mathrm{Cl}^-)_3$. In accordance with its least radius Yb(III) possesses more pronounced affinity to both chloride and hydroxy anions and thus is efficiently extracted in more acidic media (pH 3–6). For all three lanthanide ions *E* mounts to 90–100% at pH >6.5.

The pH-dependence of E with PhR as chelating agent was obtained under 2:1 (PhR:Gd) concentration ratio. According to the data obtained the complex or complexes, dominating in the pH range 2.5–5.0 for Gd(III) and 3.5–5.0 for La(III) exhibit enough hydrophobicity and proton-donor capacity [21] for efficient extraction into micellar pseudo-phase. Analogous Yb(III) complexes become enough soluble in micellar solutions at pH >3.8 and are efficiently ($E > 90\%$) extracted by CPE procedure up to pH 5.5 (Fig. 4).

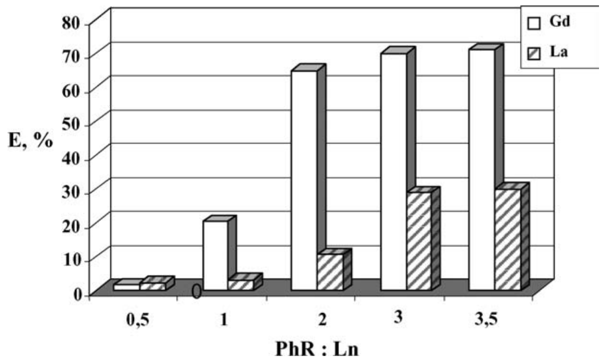


Fig. 2. The extraction efficiency of Gd(III) and La(III) vs. concentration ratio PhR:Ln under the use of PhR as chelating agent at pH 2.7.

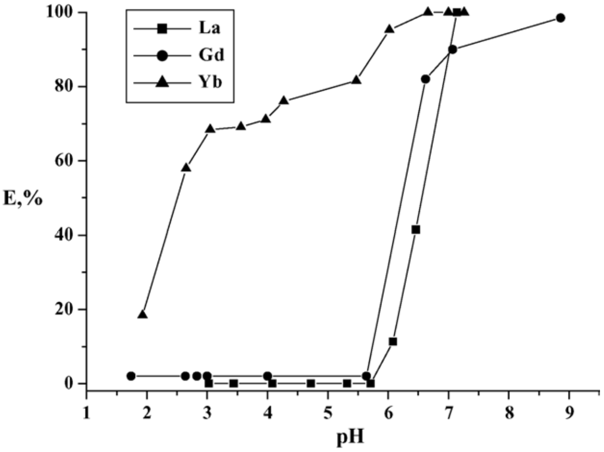


Fig. 3. The extraction efficiency (*E*, %) of La(III), Gd(III) and Yb(III) ($C = 1.7 \times 10^{-4}$ mol l^{-1}) vs. pH without chelating agents.

The decrease of *E* with pH increase over 5.0 for all lanthanides studied is quite different from the pH-dependence of *E* without chelating agent (Figs. 3 and 4). This indicates that further deprotonation of corresponding complexes diminishes their affinity to micellar pseudo-phase due to the decreased hydrophobicity and proton-donor capacity [25]. Thus, micellar solutions of PhR exhibit pH-dependent selectivity towards La(III), Gd(III) and Yb(III), which is high in acidic and neutral media, but negligible in alkaline solutions. The analysis of CPE efficiency in wide range of pH reveals that using PhR as chelating agent provides some advantages for La(III) and Gd(III) at 2.5< pH <5.5, while in alkaline media the CPE of hydroxy complexes is more efficient. The $\mathrm{Gd}^{3+}/\mathrm{La}^{3+}$ selectivity at 2.5< pH <5.5 exceeds that for CPE without chelating agents.

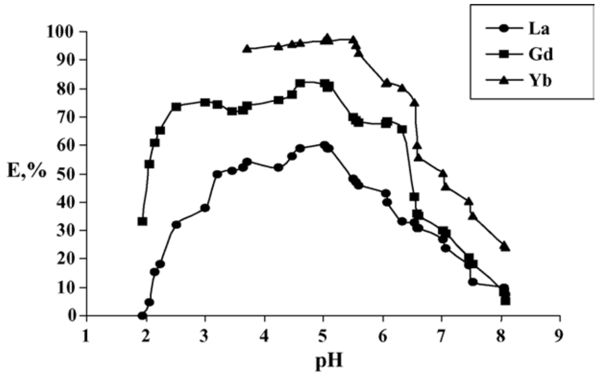


Fig. 4. The extraction efficiency (*E*, %) of La(III), Gd(III) and Yb(III) ($C = 1.7 \times 10^{-4}$ mol l^{-1}) vs. pH under the use of PhR ($C = 4 \times 10^{-4}$ mol l^{-1}) as chelating agent.

4. Conclusion

From the results obtained can be concluded that cloud point extraction of lanthanide ions is moderately efficient on using water-soluble calixarenes as chelating agents. The extraction efficiency of lanthanides via CPE procedure was found to be much more enhanced under the use of SR than that of ST, though both ligands exhibit nearly the same complexability towards lanthanide ions in aqueous media. First synthesized ligand PhR was found to be efficient chelating agent, exhibiting pH-dependent selectivity within lanthanide series in cloud point extraction from diluted solutions. The evaluation of the regularities of cloud point extraction of lanthanide complexes with water-soluble calixarenes requires further investigations, which are in progress now.

Acknowledgements

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