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## Physical-chemical properties of FM-1 reagent as a potential collector for ion flotation of lanthanoids

The physical-chemical properties of the industrial reagent “FM-1” have been investigated. These properties are necessary for evaluating its use as a collector in the processes of concentration of rare earth metal ions by ion flotation. “FM-1”, which is based on sodium salts of aminomethylenephosphonic acids, is used as a flocculant for oil production and purification of process waters from suspended particles and petroleum products. Protolytic equilibria in aqueous solutions of the reagents were studied. The values of dissociation constants equaling  $pK_{a1} = 2.31 \pm 0.26$  and  $pK_{a2} = 8.82 \pm 0.34$  were determined spectrophotometrically. Surface tension of the reagent solutions at the solution-air interface was studied. The “FM-1” reagent was classified as a strong surface-active substance with the following parameters: Minimal surface tension  $\sigma_{\min} = 29 \text{ mN}\cdot\text{m}^{-1}$ , surface activity  $G = 0.031 \text{ N}\cdot\text{m}^{-2}\cdot\text{mol}^{-1}$ , critical concentration of micelle formation  $1 \cdot 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ . The regularities of the reagent's interaction with lanthanum (III) ions were studied. A high degree of lanthanum ions' precipitation (over 99.7 %) was observed over a rather wide interval of pH values (4.00–12.00); at this point, at  $\text{pH} \geq 7.5$ , lanthanum hydroxide can co-precipitate. The formation of compounds in a solution with molar ratios  $[\text{La}]:[\text{FM-1}] = 1:1$  and  $1:2$  was established by conductometric titration method. The findings of chemical analysis, FTIR spectroscopy and elemental analysis of the isolated precipitates suggested their structural formula. A possibility for the “FM-1” reagent to be used as a collector for the ion flotation of lanthanum (III) ions was shown.

**Keywords:** ion flotation, rare-earth elements, aminomethylenephosphonic acid salts, collector, physical-chemical properties, surface-active substance, lanthanum, FM-1.

### Introduction

Ion flotation has been one of promising techniques for extracting small amounts of rare-earth elements, first of all for producing collective concentrates from technological solutions [1–4]. In interaction with metal ions, collectors form highly stable structures and are of the most current importance [5]. Reagents having in their compositions heteroatoms capable of forming complex compounds are of most interest [6]. Three-valence lanthanoids form many complexes with organic ligands, more often with oxygen- and/or nitrogen-containing ones [7–10]. A commercial reagent termed FM-1 containing aminomethylenephosphonic acid salts is known as a flocculant for collecting suspended particles and oil products in the oil industry and purification of waste/technological waters [11]. The functional group “FM-1” contains nitrogen and oxygen atoms capable of interacting with rare earth element ions and long alkyl radicals that give the compound surfactant properties. Therefore, this reagent can be considered a potential collector for ion flotation processes.

The purpose of the research is to study the physical-chemical properties of the reagent “FM-1” to establish the possibility of using it in the processes of lanthanoids (III).

### Experimental

We used solutions of  $\text{La}(\text{NO}_3)_3$  prepared by dissolving a weighed portion of  $\text{La}_2\text{O}_3$  in 6 M  $\text{HNO}_3$  followed by evaporation of excess acid and dilution with distilled water. The FM-1 reagent ( $\text{H}_2\text{L}$ ) as a 30 % aqueous solution served as an object to be assayed (formula 1).



Herein, R is a normal (linear) hydrocarbon radical  $\text{C}_{10}\text{-C}_{14}$  (Technical Conditions 2483-001-79102376-2005, Russia). The main substance's content was calculated in terms of phosphorus content determined by

atomic-emission spectroscopy with inductively coupled plasma model ICAP 6500 DUO (Thermo Fisher Scientific, USA).

Protolytic equilibriums in the reagent solutes were studied spectrophotometrically [12]. The values  $pK_{a1}$  and  $pK_{a2}$  were calculated using the formulas below:

$$pK_{a_1} = pH + \lg \frac{A_{HL^-} - A_i}{A_i - A_{H_2L}}; \quad pK_{a_2} = pH + \lg \frac{A_{L^{2-}} - A_i}{A_i - A_{HL^-}}, \quad (2)$$

Here,  $pK_{a1}$  and  $pK_{a2}$  are negative logarithms of acidic dissociation constants for neutral and ionized forms of the reagent, respectively;  $A_{H_2L}$  is optical density of solution containing neutral form of the reagent;  $A_{HL^-}$  is optical density of solution containing ionized form of the reagent;  $A_{L^{2-}}$  is optical density of solution containing doubly ionized form of the reagent;  $A_i$  is optical density of solution at a certain pH value.

UV spectra were acquired on a SF-2000 spectrophotometer (OKB-Spectr, Russia), pH values were measured on a MultiTest IPL-01c ionometer with use of a combined electrode ESK-10603/7 (Russia).

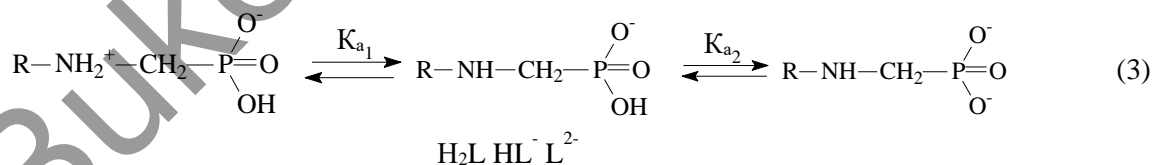
To determine adsorption of FM-1 on the water-air boundary interphase, the drop count method and a stalagmometer ST-1 (Russia) were employed [13, 14]. The first measurement was taken with a background solution (distilled water), all the successive ones — with the reagent solutes under study, at progressively increasing concentration.

The interaction processes between FM-1 and La (III) ions were explored by the precipitation technique [15]. HCl or NaOH solutions were used for creating necessary pH values of working solutions. The content of micro-amounts of La (III) in solution after precipitation was determined by atomic-emission spectroscopy (Thermo ICAP 6500 DUO, USA), that of macro-amounts of La (III) — by direct complexometric titration (Mettler Toledo T70, Switzerland) with xylenol orange [16]. The composition of La — FM-1 compounds being formed in solution was determined by the molar-ratio method [12]. The preparative isolation of precipitates and their analysis were performed in accord with a known method [15]. A Vario EL cube CHNS analyzer (Elementar, Germany) was used to determine the content of elements in precipitates; a Vertex 80V spectrometer (Bruker, Germany) was used to register the FTIR spectra of samples (a suspension in vaseline oil). Molar ratios [La]: [FM-1] in solutions were ascertained by conductometric titration with use of a SEVEN MULTI S70-K conductometer (Mettler Toledo, Switzerland). The experimental procedure used to study ion flotation, along with a laboratory flotation cell, is described in [17].

We used the following reagents:  $La_2O_3$  (99,99 %, “TDM96”, Russia);  $HNO_3$  (chemically pure, 65 %, “RM Engineering”, Russia); HCl (chemically pure, “Component-Reaktiv”, Russia); NaOH (chemically pure, “Vekton”, Russia).

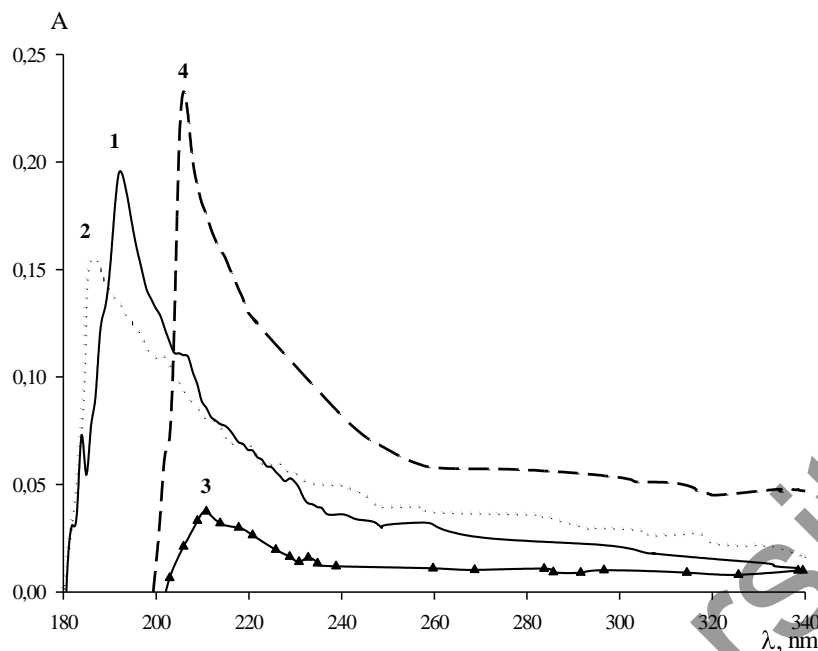
### Results and Discussion

Based on the structure, it can be assumed that “FM-1” is an amphoteric compound. The protolytic equilibria can be represented by the following scheme:



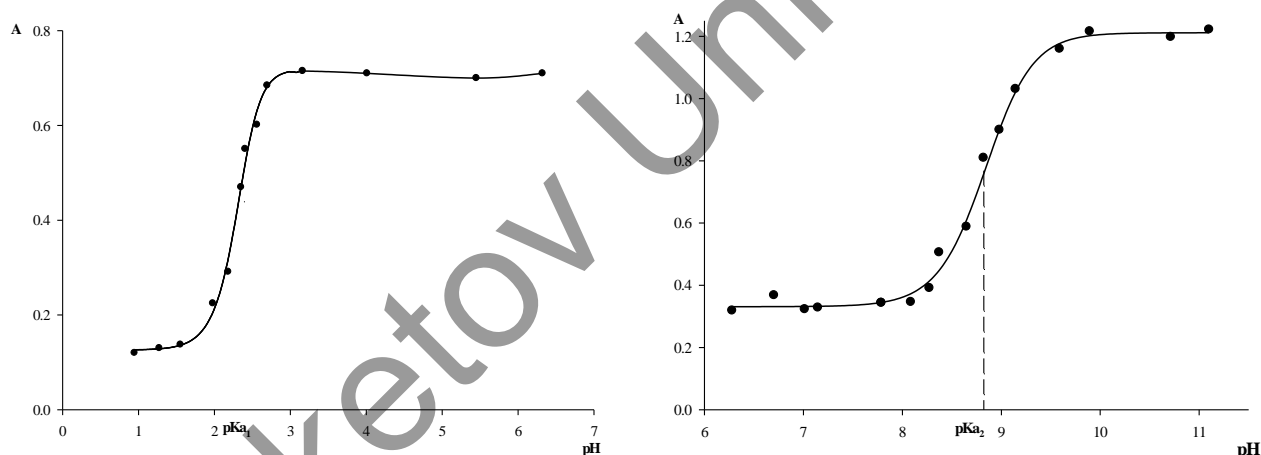
The electronic absorption spectra of solutions differ with varying pH values, thereby corroborating availability of different forms of the reagent (Figure 1).

The dependence of the optical density of FM-1 solutions on pH values was studied to calculate the values of ionization constants (Figure 2). The curves display two S-shaped inflections: the first one at pH 1.92-2.67, corresponding to dissociation of neutral form of FM-1 ( $H_2L$ ) (Figure 2a), the second one — at pH 8.4-9.3, corresponding to dissociation of  $HL^-$  form (Figure 2b).



1 — pH 2.64; 2 — pH 6.06; 3 — pH 8.08; 4 — pH 10.81 (with KOH and HCl solutions used)

Figure 1. Absorption spectra of FM-1 reagent in water vs pH values.  $C_{\text{FM-1}} = 1 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$



$l = 1.0 \text{ cm}$ ;  $\lambda$ , nm = 184.9 (a) и 196.9 (b)

Figure 2. Optical density (A) of FM-1 in aqueous solutions vs pH values.  $C_{\text{FM-1}} = 1 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ;

The ionization constants' values calculated as per formulas (2) equaled:  $\text{pK}_{\text{a}1} = 2.31 \pm 0.26$  and  $\text{pK}_{\text{a}2} = 8.82 \pm 0.34$ .

One of characteristics enabling a possibility for a compound to be employed as a flotation reagent is its ability to lessen surface tension on a liquid-gas boundary [13]. Figure 3 presents the surface tension isotherm of FM-1 solutes. With the reagent at concentrations from  $5.0 \cdot 10^{-5}$  to  $1.0 \cdot 10^{-2}$  added, surface tension lessens by a factor of 2-2.5 as compared with the background solution ( $\sigma_{\text{min}}$  of FM-1 solutes equals  $29 \text{ mN} \cdot \text{m}^{-1}$ ;  $\sigma_{\text{H}_2\text{O}} = 72.75 \text{ mN} \cdot \text{m}^{-1}$  at  $20^\circ \text{C}$ ). The results obtained enable the reagent to be classified as a strong surface-active substance.

The findings derived from Figure 3 gave rise to the following results: the surface activity (G) of the reagent calculated as the tangent value of the slope angle of the tangent line to the surface tension isotherm at  $C \rightarrow 0$  [14] equaled  $0.031 \text{ N} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ ; the critical concentration of micelle formation equaled  $1 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ .

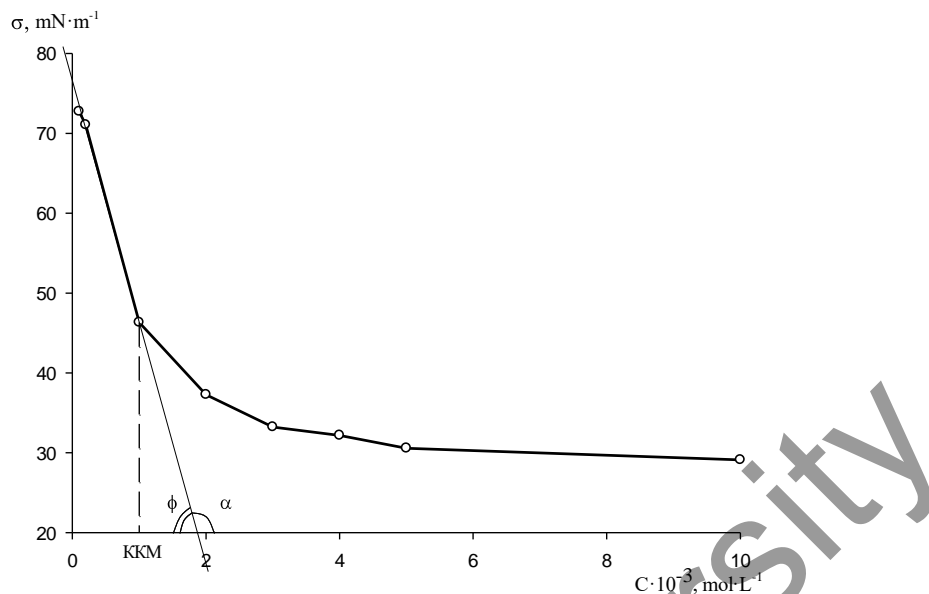


Figure 3. The surface tension isotherm of FM-1 solutions on liquid-gas boundary

Figure 4 shows the degree of precipitation ( $S$ , %) of La (III) ions with the reagent as dependent on the equilibrium pH value of solution.

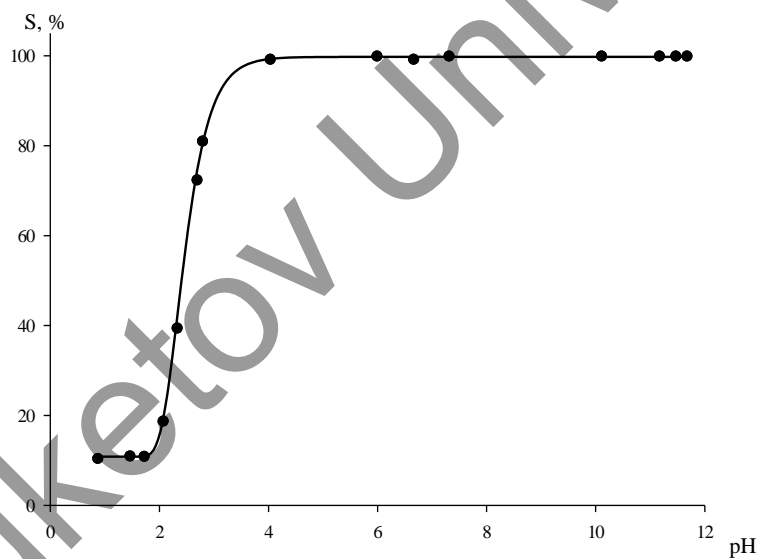
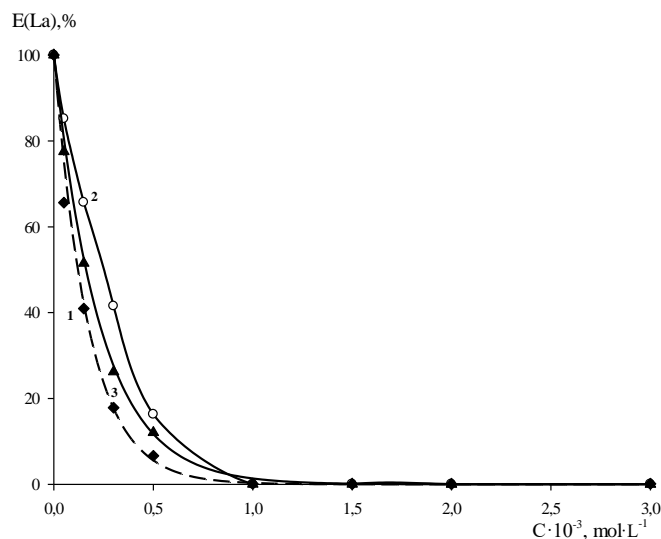


Figure 4. The degree of precipitation ( $S$ , %) of La (III) ions with FM-1 vs pH values of solution

A high degree of lanthanum ions' precipitation (over 99.7 %) was observed over a rather wide interval of pH values (4.00–12.00). It should be noted, however, that at  $\text{pH} \geq 7.5$ , lanthanum hydroxide can co-precipitate in solution [18]. Therefore, all the precipitation regularities were studied at  $\text{pH} = 4.77; 5.70; 6.85$  (acetate-ammonium buffer solutions were used).

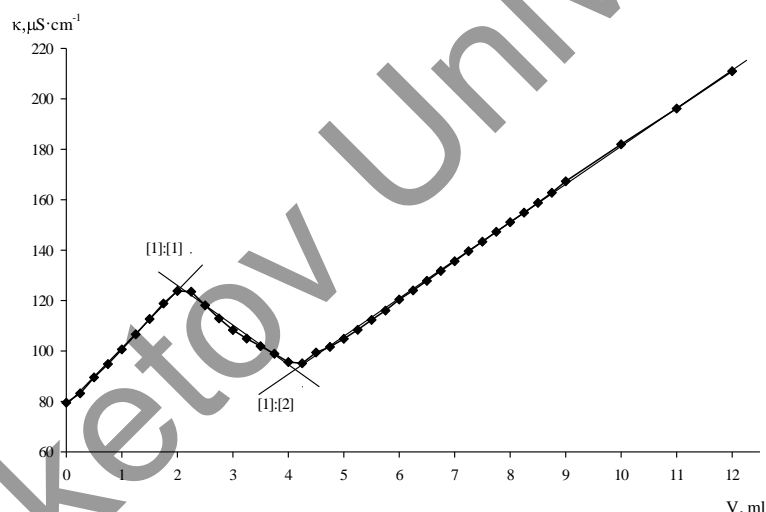
By using the saturation method (Figure 5), the qualitative binding of  $\text{La}^{3+}$  ions was ascertained to occur already at ratio  $[\text{La}]:[\text{FM-1}] = 1:1$ . Within the interval mentioned above, the pH values of the medium do not markedly affect the degree of precipitation.



$C_{\text{La(III)}} = 1 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ;  $V_{\text{(buffer)}} = 5.0 \text{ ml}$ ;  $V_{\text{total}} = 25 \text{ ml}$ ; 1 — pH 4.77; 2 — pH 5.70; 3 — pH 6.85

Figure 5. The degree of extraction of La (III) ions vs concentration of FM-1

The conductometric titration method enabled the formation of compounds in solutions with molar ratios [La]:[FM-1] = 1:1 and 1:2 to be established (Figure 6).



$C_{\text{starting}}(\text{FM-1}) = C_{\text{starting}}(\text{La(III)}) = 1 \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ ;  $V_{\text{La(III)}} = 2.5 \text{ ml}$ ;  $V_{\text{total}} = 60 \text{ ml}$ ;  $[\text{EtOH}]:[\text{H}_2\text{O}] = 1:1$

Figure 6. Electrical conductivity of  $\text{La}(\text{NO}_3)_3$  solution vs portions of the reagent added

The compounds with the ratios found were preparedly isolated. Elemental analysis of the compounds isolated at pH 5 is presented in Table 1. No sodium ions were detected in the samples after decomposition. The results of the analysis corroborated the ratio [metal]:[reagent] as equaling 1:1 for both compounds and were well in line with theoretical calculations.

Table 1

#### Chemical analysis of the compounds isolated

Compounds	Molecular mass	Found, %			Calculated*, %		
		N	P	La	N	P	La
[La]:[FM-1] = 1:1	416	3.30	8.51	35.47	3.38	7.45	33.41
[La]:[FM-1] = 1:2	693	3.36	8.34	36.41	4.04	8.95	20.06

Note: \*In terms of average molecular mass ( $R = \text{C}_{12}\text{H}_{25}^-$ ).

The analyzed FTIR spectra of the compounds isolated also corroborated them as being identical. In the FTIR spectra of La – FM-1 compounds, P–OH absorption bands typical of the reagent in the range 2700–2550  $\text{cm}^{-1}$  are absent. The wide band appears in the La – FM-1 compounds in the region of 3500–3300  $\text{cm}^{-1}$ . It can be considered as a result of the superposition of bands of N–H valence vibrations and the formed new O–H bond (Figure 7) [19].

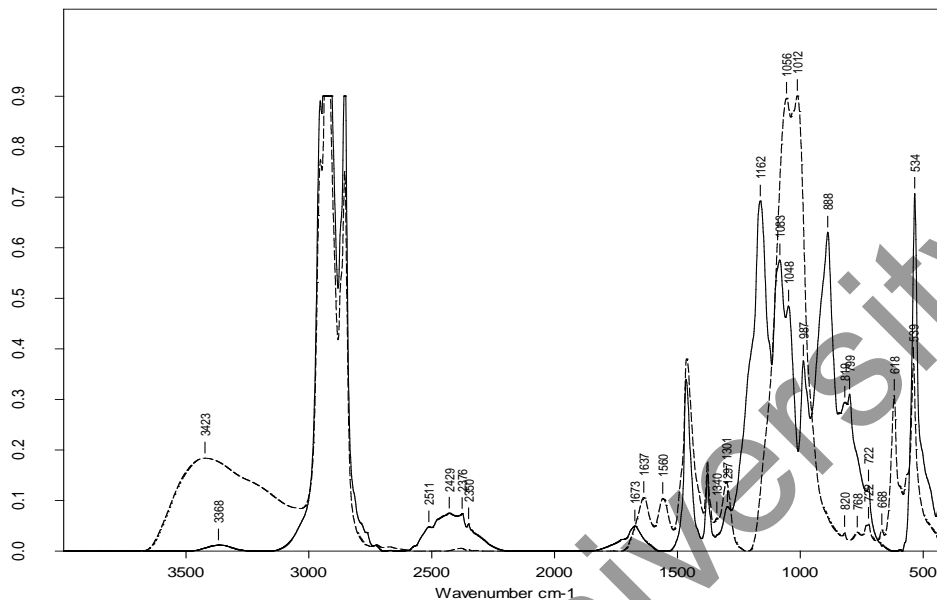


Figure 7. FTIR spectra of the reagent (firm line) and of its compound with lanthanum (III) at ratio 1:1 (dotted line)

With the findings of elemental analysis and FTIR spectroscopy as an underlying basis, the following structural formula of the reagent can presumably be presented:

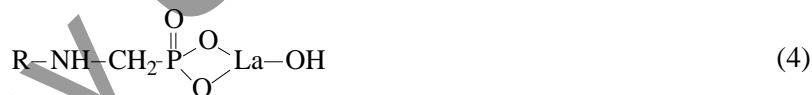


Table 2 lists the findings of FM-1 investigated as a collector for the ion extraction of lanthanum.

Table 2

**Ion flotation of La (III) with FM-1 reagent;**  
 $C_{\text{La(III)}} = 1 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ;  $C_{\text{R}} = 1 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ; flotation duration 5 minutes

№	pH	$C_{\text{remaining La}} \text{ mg} \cdot \text{L}^{-1}$	E, %
1	3.25	97.02	30.2
2	5.61	15.29	89.1
3	8.78	16.26	88.3

### Conclusions

Based on the research results of the reagent “FM-1” properties, it can be recommended as a collector in the processes of rare earth elements ion flotation. The FM-1 reagent was evinced to be an amphoteric compound ( $\text{pK}_{\text{a}1} = 2,31 \pm 0,26$ ;  $\text{pK}_{\text{a}2} = 8,82 \pm 0,34$ ) and was classified as a strong surface-active substance (with the reagent at concentrations from  $5.0 \cdot 10^{-5}$  to  $1.0 \cdot 10^{-2}$  added, surface tension lessens by a factor of 2–2.5 as compared with the background solution). Strong surface-active properties enable the “FM-1” compound to be employed in ion flotation procedures with no additional foaming agents added. In conjoint presence with lanthanum (III) ions in a solution, the reagent forms hardly-soluble compounds over a rather wide interval of pH values (4.00–12.00). The formation of compounds with molar ratios  $[\text{La}]:[\text{FM-1}] = 1:1$  and  $1:2$  was established in a solution (pH 4,8–6,8). The findings of chemical analysis, FTIR spectroscopy and elemental analysis of the isolated precipitates suggested their structure. A possibility for the “FM-1” reagent to be used

as a collector for the ion flotation of lanthanum (III) ions was shown, with a maximal degree of extraction equaling 89.1 % ( $C_{\text{remaining}} = 15.29 \text{ mg/l}$  at pH 5.61,  $[\text{La}]:[\text{R}] = 1:1$ ).

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### Лантаноидтардың иондық флотациясы үшін потенциалды жинақтаушы – «ФМ-1» реагентінің физика-химиялық қасиеттері

«ФМ-1» өнеркәсіптік реагентінің иондық флотация әдісімен сирекжер металл иондарын концентрлеу процесерінде жинақтаушы ретінде пайдалануды бағалау үшін қажетті физика-химиялық қасиеттері зерттелді. Негізі аминдіметиленфосфон қышқылдарының натрий тұздары болатын «ФМ-1» мұнай

өндіру және технологиялық суларды қалқыма бөлшектер мен мұнай өнімдерінен тазарту үшін флокулянт ретінде қолданылады. Реагенттің сулы ерітінділеріндегі протолиттік тепе-теңдігі зерттелді. Диссоциация тұрақтыларының мәндері спектрофотометриялық әдіспен анықталды:  $pK_{a1} = 2,31 \pm 0,26$  және  $pK_{a2} = 8,82 \pm 0,34$ . Ерітінді-ауа шекарасындағы реагент ерітінділерінің беттік керілуі анықталған. «ФМ-1» күшті беттік белсенді заттар класына жататыны дәлелденген. Ерітінділердің беттік керілуінің минималды мәні ( $\sigma_{\text{мин.}}$ ) 29,0 мН/м құрады; беттік белсенділігі (G) —  $0,031 \text{ Н} \cdot \text{м}^2/\text{моль}$ , мицеллалардың шекті концентрациясы (МШК) —  $1 \cdot 10^{-3}$  моль/л шамасына тең болды. «ФМ-1» реагентінің лантан (III) иондарымен әрекеттесу заңдылықтары зерттелді. «ФМ-1» лантан (III) иондарымен өзара әрекеттесу заңдылықтары зерттелді. La (III) иондарының реагентпен тұндырылуының жоғары деңгейі (99,7 % — дан астам) рН мәндерінің жеткілікті кең диапазонында байқалады (4,0-ден 12,0-ге дейін ( $\text{pH} \geq 7,5$  кезінде лантан гидроксидінің тұндырылуы мүмкін)). Кондуктометриялық титрлеу ( $\text{pH} 4,8\text{--}6,8$ ) әдісі молярлық қатынасы бар ерітіндіде қосылыстардың түзілуін анықтады  $[\text{La(III)}]:[\text{R}] = 1:1$  және  $1:2$ . Химиялық талдау, ИК-спектроскопия және бөлінген шөгінділерді элементтік талдау деректері негізінде олардың құрылымдық формуласы ұсынылды. «ФМ-1» реагентін лантанның (III) иондық флотациясы үшін жинақтаушы ретінде пайдалану мүмкіндігі көрсетілген.

*Кілт сөздер:* иондық флотация, сирекжер элементтері, аминдиметиленфосфон қышқылдары, жинақтаушы, физико-химиялық қасиеттері, беттік белсенді заттар, лантан, ФМ-1.

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### Физико-химические свойства реагента «ФМ-1» — потенциального собирателя для ионной флотации лантаноидов

Исследованы физико-химические свойства промышленного реагента «ФМ-1», необходимые для оценки его применения в качестве собирателя в процессах концентрирования ионов редкоземельных металлов методом ионной флотации. «ФМ-1», основу которого составляют натриевые соли аминометиленфосфоновых кислот, применяется в качестве флокулянта для нефтедобычи и очистки технологических вод от взвешенных частиц и нефтепродуктов. Изучены протолитические равновесия в водных растворах реагента. Спектрофотометрическим методом определены значения констант диссоциации:  $pK_{a1} = 2,31 \pm 0,26$  и  $pK_{a2} = 8,82 \pm 0,34$ . Изучено поверхностное натяжение растворов реагента на границе раствор-воздух. Установлено, что «ФМ-1» относится к классу сильных ПАВ. Минимальное значение поверхностного натяжения ( $\sigma_{\text{мин.}}$ ) растворов составило 29,0 мН/м; поверхностная активность (G) —  $0,031 \text{ Н} \cdot \text{м}^2/\text{моль}$ , критическая концентрация мицеллообразования (ККМ) —  $1 \cdot 10^{-3}$  моль/л. Исследованы закономерности взаимодействия «ФМ-1» с ионами лантана (III). Найдено, что высокая степень осаждения ионов La (III) реагентом (более 99,7 %) наблюдается в достаточно широком диапазоне значений рН — от 4,0 до 12,0 (при  $\text{pH} \geq 7,5$  возможно соосаждение гидроксида лантана). Методом кондуктометрического титрования ( $\text{pH} 4,8\text{--}6,8$ ) установлено образование соединений в растворе с молярными соотношениями  $[\text{La(III)}]:[\text{R}] = 1:1$  и  $1:2$ . На основании данных химического анализа, ИК-спектроскопии и элементного анализа выделенных осадков, предложена их структурная формула. Показана возможность применения реагента «ФМ-1» в качестве собирателя для ионной флотации лантана (III).

*Ключевые слова:* ионная флотация, редкоземельные элементы, аминометиленфосфоновые кислоты, собиратель, физико-химические свойства, поверхностно-активное вещество, лантан, ФМ-1.

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