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Article

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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 equilibriums 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 $\sigma_{min} = 29$ mN·m^{-1}, surface activity $G = 0.031$ N·m^{2}·mol^{-1}, critical concentration of micelle formation $1 \cdot 10^{-3}$ mol·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 pH ≥ 7.5, lanthanum hydroxide can co-precipitate. The formation of compounds in a solution with molar ratios [La]:[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.

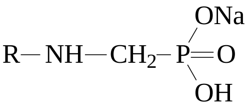
Introduction

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 $La(NO_3)_3$ prepared by dissolving a weighed portion of La_2O_3 in 6 M HNO_3 followed by evaporation of excess acid and dilution with distilled water. The FM-1 reagent (H_2L) as a 30 % aqueous solution served as an object to be assayed (formula 1).



$$R-NH-CH_2-\underset{OH}{\overset{ONa}{P}}=O \qquad (1)$$

Herein, R is a normal (linear) hydrocarbon radical C_{10}-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:

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

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).

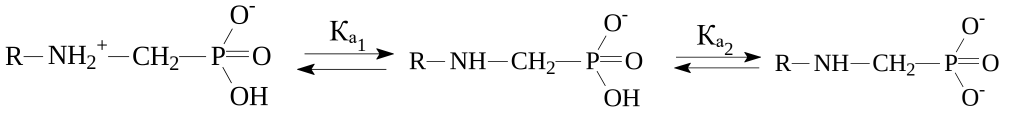
To determine adsorption of FM-1 on the water-air boundary interphase, the drop count method and a stalagmometer ST-1 (Russia) were employed [13, 14]. The first measurement was taken with a background solution (distilled water), all the successive ones — with the reagent solutes under study, at progressively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

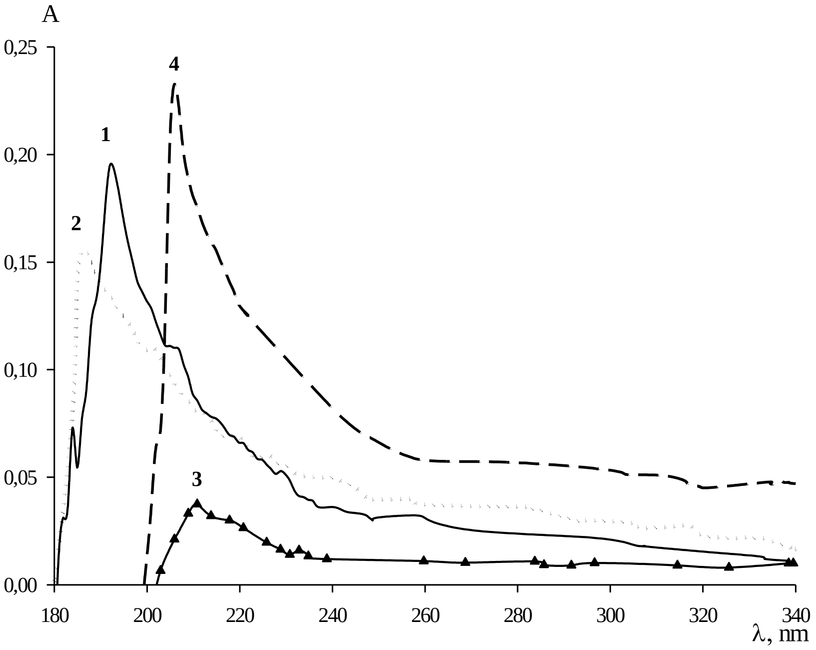


$$R{-}NH_2^+{-}CH_2{-}P(=O)(O^-)(OH) \xrightleftharpoons{K_{a_1}} R{-}NH{-}CH_2{-}P(=O)(O^-)(OH) \xrightleftharpoons{K_{a_2}} R{-}NH{-}CH_2{-}P(=O)(O^-)(O^-) \tag{3}$$

H_2L HL^- L^{2-}

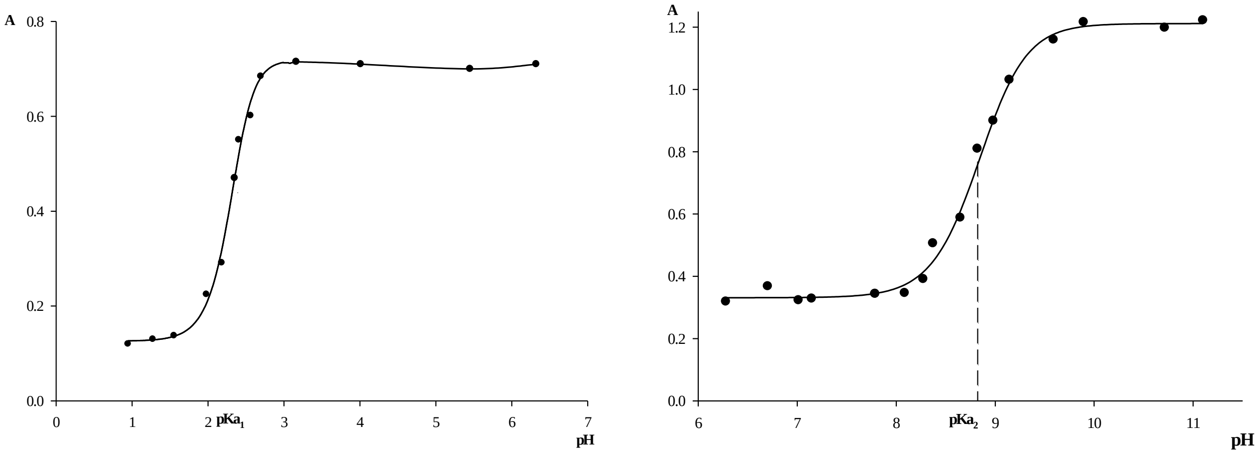
The electronic absorption spectra of solutions differ with varying pH values, thereby corroborating availability of different forms of the reagent (Figure 1).

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. $C_{FM\text{-}1} = 1 \cdot 10^{-4}$ mol·L^{-1}



l = 1.0 cm; λ, nm = 184.9 (*a*) и 196.9 (*b*)

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

The ionization constants' values calculated as per formulas (2) equaled: $pK_{a1} = 2.31 \pm 0.26$ and $pK_{a2} = 8.82 \pm 0.34$.

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 (σ_{min} of FM-1soluties equals 29 mN·m^{-1}; σ_{H_2O} = 72.75 mN·m^{-1} at 20 °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 N·m^{2}·mol^{-1}; the critical concentration of micelle formation equaled $1 \cdot 10^{-3}$ mol·L^{-1}.

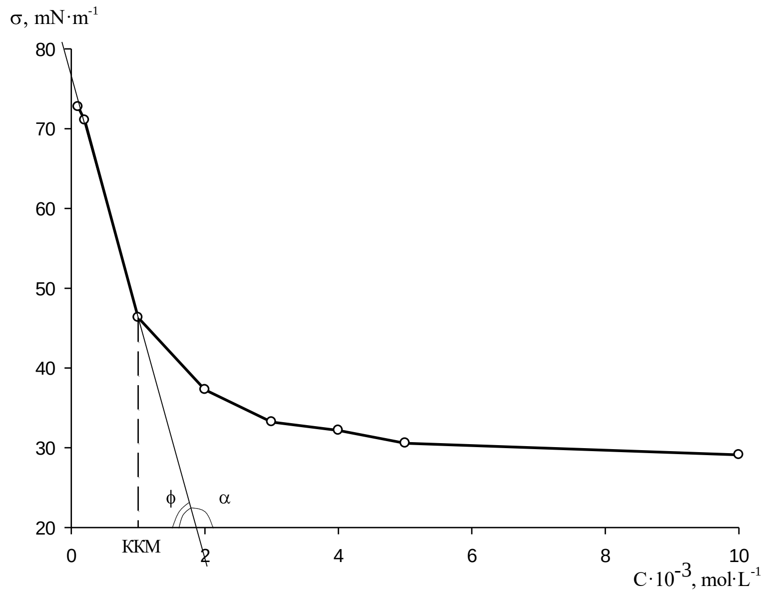


Figure 3. The surface tension isotherm of FM-1 solutions on liquid-gas boundary

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

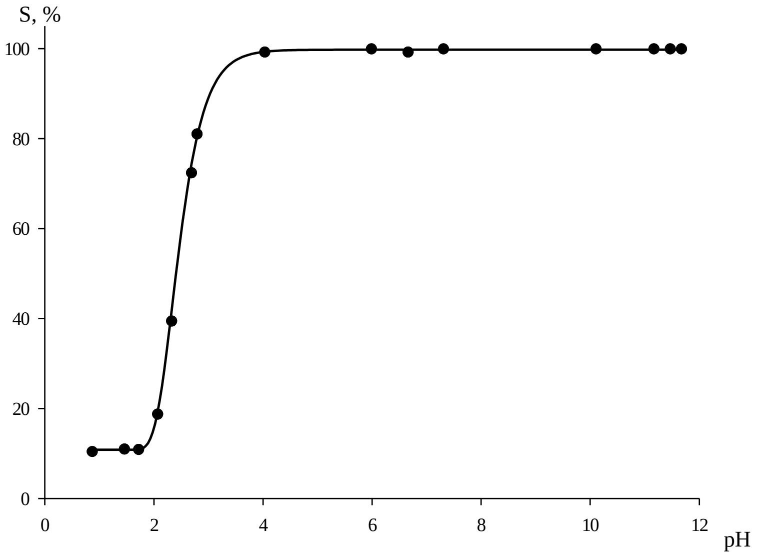
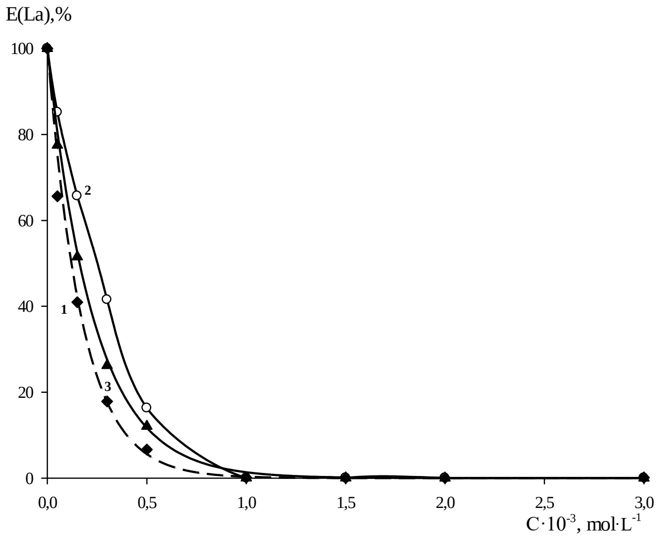


Figure 4. The degree of precipitation (S, %) of La (III) ions with FM-1 vs pH values of solution

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 pH ≥ 7.5, lanthanum hydroxide can co-precipitate in solution [18]. Therefore, all the precipitation regularities were studied at pH = 4.77; 5.70; 6.85 (acetate-ammonium buffer solutions were used).

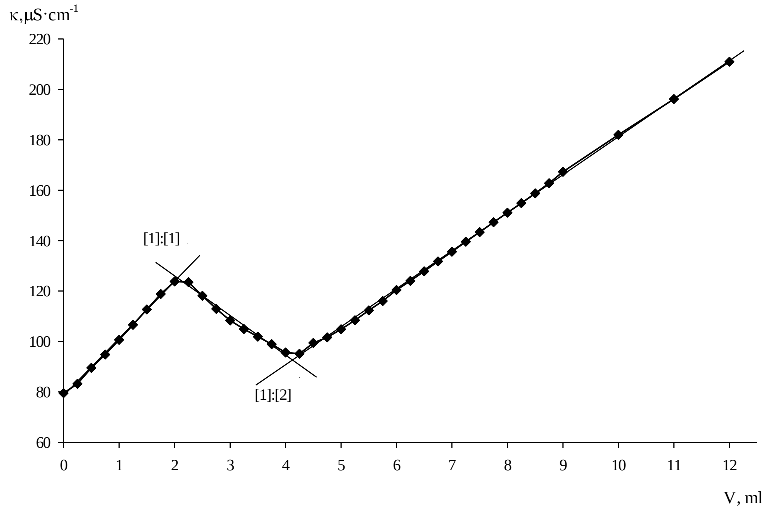
By using the saturation method (Figure 5), the qualitative binding of La^{3+} ions was ascertained to occur already at ratio [La]:[FM-1] = 1:1. Within the interval mentioned above, the pH values of the medium do not markedly affect the degree of precipitation.



$C_{La(III)} = 1 \cdot 10^{-3}$ mol·L^{-1}; $V_{(buffer)} = 5.0$ ml; $V_{total} = 25$ 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).



$C_{starting}$(FM-1) = $C_{starting}$(La(III)) = $1 \cdot 10^{-2}$ mol·L^{-1}; $V_{La(III)} = 2.5$ ml; $V_{total} = 60$ ml; [EtOH]:[H_2O] = 1:1

Figure 6. Electrical conductivity of $La(NO_3)_3$ 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 = $C_{12}H_{25}^{-}$).

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 cm^{-1} are absent. The wide band appears in the La – FM-1 compounds in the region of 3500–3300 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].

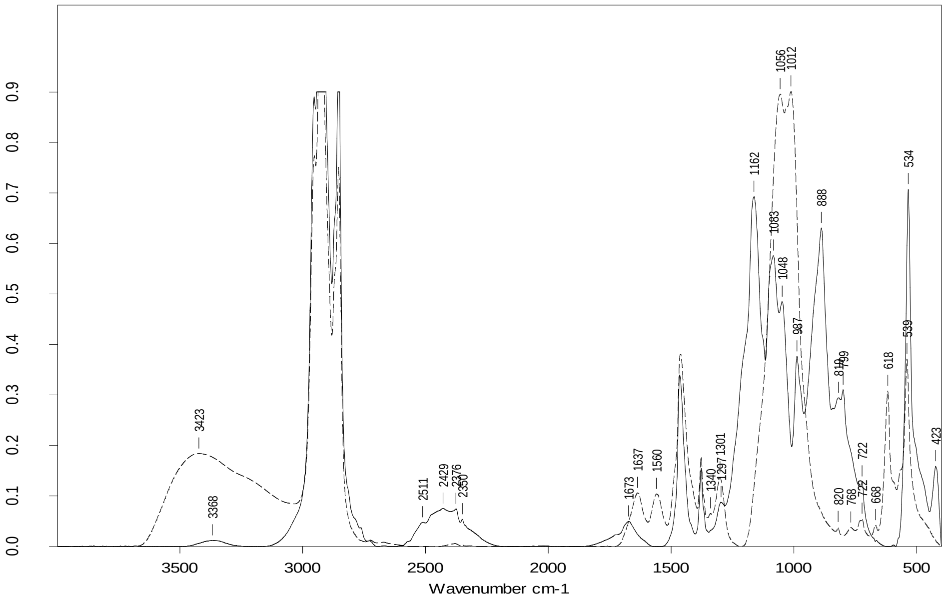
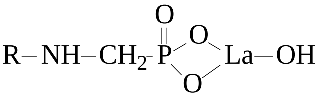


Figure 7. FTIR spectra of the reagent (firm line) and of its compound with lanthanum (III) at ratio 1:1 (dotted line)

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



(4)

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;
$C_{La(III)} = 1\cdot10^{-3}$ mol·L^{-1}; $C_R = 1\cdot10^{-3}$ mol·L^{-1}; flotation duration 5 minutes

№	pH	$C_{remaining\ La}$ mg·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 (pKa_1 = 2,31±0,26; pKa_2 = 8,82±0,34) and was classified as a strong surface-active substance (with the reagent at concentrations from $5.0\cdot10^{-5}$ to $1.0\cdot10^{-2}$ 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 [La]:[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 % ($C_{remaining}$ = 15.29 mg/l at pH 5.61, [La]:[R] = 1:1).

Acknowledgments

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References

1 Чиркст Д.Э. Ионная флотация редкоземельных металлов с додецилсульфатом натрия / Д.Э. Чиркст, О.Л. Лобачева, Н.В. Джевага // Журн. прикл. хим. — 2011. — Т. 84, № 9. — С. 1424–1430.

2 Lobacheva, O.L., Dzhevaga, N.V., & Danilov A.S. (2016). The method of removal yttrium (III) and ytterbium (III) from dilute aqueous solutions. Journal of Ecological Engineering, 17(2), 38-42.

3 Shetty, S., Ponnurangam, S., & Chernyshova I.V. (2020). Foam flotation of rare earth elements by conventional and green surfactants. Minerals Engineering, 158, 106585.

4 Abaka-Wood, G.B., Zanin, M., Addai-Mensah, J., & Skinner, W. (2019). Recovery of rare earth elements minerals from iron oxide–silicate rich tailings — Part 2: Froth flotation separation. Minerals Engineering, 142, 105888.

5 Радушев А.В. Реагенты для ионной флотации цветных металлов / А.В. Радушев, Л.Г. Чеканова, Г.В. Чернова // Цветные металлы. — 2005. — № 7. — С. 34–39.

6 Marion, C., Li, R.H., & Waters K.E. (2020). A review of reagents applied to rare-earth mineral flotation. Advances in Colloid and Interface Science, 279, 102142.

7 Мартыненко Л.И. Особенности комплексообразования редкоземельных элементов (III) / Л.И. Мартыненко // Успехи химии. — 1991. — Т. 60, № 9. — С. 1969–1998.

8 Belova, V.V., Tsareva, Y.V., Zakhodyaeva, Y.A., Ivanov, V.K., & Voshkin A.A. (2021). Solvent extraction of lanthanides (III) in the presence of the acetate ion acting as a complexing agent using mixtures of cyanex 272 and caprylic acid in hexane. Processes, 9(12), 2222.

9 Radushev A. V. α-Branched tertiary carboxylic acid hydrazides as extractants of rare-earth metal ions from sulfate media / A.V. Radushev, V.A. Nikitina, T.D. Batueva // Russian Journal of Applied Chemistry, 2021. — Vol. 94, No. 5. — P. 595–600.

10 Healy, M.R., Ivanov, A.S., Karslyan, Y., Bryantsev, V.S., Moyer, B.A., & Jansone-Popova S. (2019). Efficient separation of light lanthanides(III) by using bis-lactam phenanthroline ligands. Chemistry A European Journal, 25(25), 6326-6331.

11 Евразийский патент № 014001. Способ воздействия на нефтяной пласт / А.Г. Тэслер, С.Н. Кайдалов, И.А. Перминов, И.В. Бармин, С.Е. Ильясов, Л.В. Закшевская и др. // Опубл. 2010.

12 Бернштейн И.Я. Спектрофотометрический анализ в органической химии / И.Я. Бернштейн, Ю.Л. Каминский. — Л.: Химия, 1975. — 232 с.

13 Фролов В.И. Методы определения поверхностного натяжения / В.И. Фролов, Д.Ю. Митюк, Р.Е. Твердый. — М.: РГУ нефти и газа им. И.М. Губкина, 2013. — 48 с.

14 Ланге К.Р. Поверхностно-активные вещества: синтез, свойства, анализ, применение; пер. с англ. / К.Р. Ланге. — СПб.: Профессия, 2004. — 240 с.

15 Chekanova, L.G., Manylova, K.O., Pavlov, P.T., Baigacheva, E.V. & Tiunova T.G. (2015). Complexation of ethyl 2-aryl(alkyl)sulfonylamino-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxylates with nonferrous metal ions. Russian Journal of Inorganic Chemistry, 60(4), 531–535.

16 Шварценбах Г. Комплексонометрическое титрование / Г. Шварценбах, Г. Флашка. — М.: Химия, 1970. — 360 с.

17 Чеканова Л.Г. N′, N′-Диалкилгидразиды как потенциальные реагенты для ионной флотации меди (II) / Л.Г. Чеканова, Е.В. Байгачева, А.В. Радушев, Т.Д. Батуева // Химическая технология. — 2008. — Т. 9, № .9. — С. 476–480.

18 Химия и технология редких и рассеянных элементов. Ч. 2 / под ред. К.А. Большакова. — М.: Высш. шк., 1976. — 360 с.

19 Тарасевич Б.Н. ИК спектры основных классов органических соединений / Б.Н. Тарасевич. — М.: МГУ, 2012. — 55 с.

А.А. Юминова, Е.А. Гиниятуллина, Л.М. Кариева, Л.Г. Чеканова

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

«ФМ-1» өнеркәсіптік реагентінің иондық флотация әдісімен сирекжер металл иондарын концентрлеу процестерінде 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: $pKa_1 = 2,31±0,26$ және $pKa_2 = 8,82±0,34$. Ерітінді-ауа шекарасындағы реагент ерітінділерінің беттік керілуі анықталған. «ФМ-1» күшті беттік белсенді заттар класына жататыны дәлелденген. Ерітінділердің беттік керілуінің минималды мәні ($\sigma_{мин.}$) 29,0 мН/м құрады; беттік белсенділігі (G) — 0,031 $Н·м^2$/моль, мицеллалардың шекті концентрациясы (МШК) — $1·10^{-3}$ моль/л шамасына тең болды. «ФМ-1» реагентінің лантан (ІІІ) иондарымен әрекеттесу заңдылықтары зерттелді. «ФМ-1» лантан (ІІІ) 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 (pH ≥ 7,5 кезінде лантан гидроксидінің тұндырылуы мүмкін). Кондуктометриялық титрлеу (pH 4,8–6,8) әдісі молярлық қатынасы бар ерітіндіде қосылыстардың түзілуін анықтады [La(III)]:[R] = 1:1 және 1:2. Химиялық талдау, ИҚ-спектроскопия және бөлінген шөгінділерді элементтік талдау деректері негізінде олардың құрылымдық формуласы ұсынылды. «ФМ-1» реагентін лантанның (ІІІ) иондық флотациясы үшін жинақтаушы ретінде пайдалану мүмкіндігі көрсетілген.

Кілт сөздер: иондық флотация, сирекжер элементтері, аминдіметиленфосфон қышқылдары, жинақтаушы, физика-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: $pK_{a1} = 2,31±0,26$ и $pK_{a2} = 8,82±0,34$. Изучено поверхностное натяжение растворов реагента на границе раствор-воздух. Установлено, что «ФМ-1» относится к классу сильных ПАВ. Минимальное значение поверхностного натяжения ($\sigma_{мин.}$) растворов составило 29,0 мН/м; поверхностная активность (G) — 0,031 $Н·м^2$/моль, критическая концентрация мицеллообразования (ККМ) — $1·10^{-3}$ 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 pH — от 4,0 до 12,0 (при pH ≥ 7,5 возможно соосаждение гидроксида лантана). Методом кондуктометрического титрования (pH 4,8–6,8) установлено образование соединений в растворе с молярными соотношениями [La(III)]:[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.

References

1 Chirkst, D.E., Lobacheva, O.L, & Dzhevaga, N.V. (2011). Ionnaia flotatsiia redkozemelnykh metallov s dodetsilsulfatom natriia [Ion flotation of rare-earth metals with sodium dodecyl sulfate]. *Zhurnal prikladnoi khimii — Russian Journal of Applied Chemistry, 84, 9,* 1424–1430 [in Russian].

2 Lobacheva, O.L., Dzhevaga, N.V., & Danilov, A.S. (2016). The method of removal yttrium (III) and ytterbium (III) from dilute aqueous solutions. *Russian Journal of Ecological Engineering, 17*(2), 38–42.

3 Shetty, S., Ponnurangam, S., & Chernyshova I.V. (2020). Foam flotation of rare earth elements by conventional and green surfactants. *Minerals Engineering, 158*. 106585.

4 Abaka-Wood, G.B., Zanin, M., Addai-Mensah, J., & Skinner, W. (2019). Recovery of rare earth elements minerals from iron oxide–silicate rich tailings — Part 2: Froth flotation separation. *Minerals Engineering, 142,* 105888.

5 Radushev, A.V., Chekanova, L.G., & Chernova, G.V. (2005). Reagenty dlia ionnoi flotatsii tsvetnykh metallov [Reagents for ion flotation of non-ferrous metals]. *Tsvetnye metally — Russian Journal “Non-Ferrous Metals”, 7,* 34–39 [in Russian].

6 Marion, C., Li, R.H., & Waters K.E. (2020). A review of reagents applied to rare-earth mineral flotation. *Advances in Colloid and Interface Science, 279,* 102142.

7 Martynenko, L.I. (1991). Osobennosti kompleksoobrazovaniia redkozemelnykh elementov (III) [Peculiarities of rare-earth metals (III) complexation]. *Uspekhi khimii — Russian Chemical Reviews,* 60(9), 1969–1998 [in Russian].

8 Belova, V.V., Tsareva, Y.V., Zakhodyaeva, Y.A., Ivanov, V.K., & Voshkin A.A. (2021). Solvent extraction of lanthanides (III) in the presence of the acetate ion acting as a complexing agent using mixtures of cyanex 272 and caprylic acid in hexane. *Processes, 9*(12), 2222.

9 Radushev, A.V. (2021) α-Branched tertiary carboxylic acid hydrazides as extractants of rare-earth metal ions from sulfate media. *Russian Journal of Applied Chemistry, 94*(5), 595–600.

10 Healy, M.R., Ivanov, A.S., Karslyan, Y., Bryantsev, V.S., Moyer, B.A., & Jansone-Popova, S. (2019). Efficient separation of light lanthanides(III) by using bis-lactam phenanthroline ligands. *Chemistry A European Journal, 25*(25), 6326–6331.

11 Tesler, A.G., Kajdalov, S.N., Perminov, I.A., Barmin, I.V., Ilyasov, S.E., Zakshevskaya, L.V. et al. (2010). Sposob vozdeistviia na neftianoi plast [A method of acting on an oil reservoir]. *Yevraziiskii patent – Eurasian patent No. 014001* [in Russian].

12 Bernstein, I.Ya., & Kaminsky, Yu.L. (1986). *Spektrofotometricheskii analiz v organicheskoi khimii [Spectrophotometric analysis in organic chemistry].* Leningrad: Khimiia [in Russian].

13 Frolov, V.I., Mityuk, D.Yu., & Tverdyi, R.E. (2013). *Metody opredeleniia poverkhnostnogo natiazheniia [Methods for determining surface tension].* Moscow: RGU nefti i gaza imeni I.M. Gubkina [in Russian].

14 Lange, K.R. (2004). *Poverkhnostno-aktivnye veshchestva: sintez, svoistva, analiz, primenenie [Surface-active substances: synthesis, properties, analysis, application].* Saint Petersburg: Professiia [in Russian].

15 Chekanova, L.G., Manylova, K.O., Pavlov, P.T., Baigacheva, E.V., & Tiunova T.G. (2015). Complexation of ethyl 2-aryl(alkyl)sulfonylamino-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxylates with nonferrous metal ions. *Russian Journal of Inorganic Chemistry, 60*(4), 531–535.

16 Shvarcenbah, G., & Flashka, G. (1970). *Kompleksonometricheskoe titrovanie [Complexometric titration].* Moscow: Khimiia [in Russian].

17 Chekanova, L.G., Bajgacheva, E.V., Radushev, A.V., & Batueva, T.D. (2008). N’,N’-Dialkilgidrazidy kak potentsialnye reagenty dlia ionnoi flotatsii medi (II) [N’,N’-Dialkylhydrazides as potential reagents for ionic flotation of copper (II)]. *Khimicheskaia tekhnologiia — Russian Journal of Chemical Technology, 9, 9,* 476–480 [in Russian].

18 Bolshakov, K.A. (1976). *Khimiia i tekhnologiia redkikh i rasseiannykh elementov [Chemistry and technology of rare and dispersed elements].* Moscow: Vysshaia shkola [in Russian].

19 Tarasevich, B.N. (2012). *IK spektry osnovnykh klassov organicheskikh soedinenii [IR-spectra of basic classes of organic compounds].* Moscow: MGU [in Russian].

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