ISSN 1063-455X, Journal of Water Chemistry and Technology, 2015, Vol. 37, No. 2, pp. 90–95. © Allerton Press, Inc., 2015.
Original Russian Text © O.V. Perlova, V.V. Chernetskaya, 2015, published in Khimiya i Tekhnologiya Vody, 2015, Vol. 37, No. 2, pp. 167–178.

WATER TREATMENT AND DEMINERALIZATION TECHNOLOGY

Flotation Recovery of Rare-Earth Metal Compounds from Dilute Aqueous Solutions

O. V. Perlova* **and V. V. Chernetskaya**

Odesa Mechnikov National University, Odessa, Ukraine

**e-mail: olga_perlova@onu.edu.ua*

Received December 12, 2013

Abstract—The possibility of flotation extraction of lanthanum and cerium (III) compounds from diluted sulfate solutions was shown by using finely dispersed solid solutions of different radical phosphine oxide in paraffin. Optimal conditions for conducting the flotation have been determined. The effect of electrolyte additions on the process efficiency was studied. In addition, the mechanism of interaction of rare earth metal compounds with flotation collector was proposed.

DOI: 10.3103/S1063455X15020083

Keywords: rare earth metals, different radical phosphine oxide, flotation.

INTRODUCTION

Rare-earth elements (REE) and REE-based compounds possess unique properties making them irreplaceable in many branches of technology, such as metallurgy and oil refining, production and processing of optical materials, quantum electronics and radioelectronics, nuclear engineering, optics, production of new construction materials, etc. [1]. The rapid development of these branches facilitates the growing need of industry in REE that results in increasing quantities of waste waters containing REE compounds which are toxic substances [2] that negatively affect the living organisms. Therefore, the search for new effective methods of aqueous solution treatment from REE compounds is a vital problem.

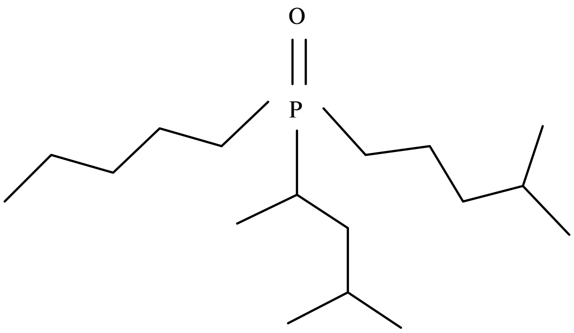
The flotation process can be expediently applied for extraction of small quantities of dissolved compounds from large volumes of aqueous solutions [3]. For the extraction of ions of rare earth elements (including cerium and lanthanum) it is proposed to use for flotation collectors the potash soaps of fatty acids and potassium abietate [4], diphenylguanidine [5], polyphos [6], dialkyl phosphoric acids [7], sodium dodecylsulfate [8–10], and others [11]. However the consumption of these collectors is fairly high (3 moles of SAS is usually required per 1 mole of REE), and their regeneration is a difficult task. Finely dispersed solid solutions of SAS in paraffin [12] are proposed for the extraction of ions of heavy metals by the sorptive flotation method or flotation with carrier [3]. Such reagents (carriers) are characterized by simple regeneration and the possibility of repeated use, significantly reduced consumption, and the elimination of secondary contamination of treated solutions with SAS.

The purpose of this paper is to study the possibility of using the finely dispersed solid solution of different radical phosphine oxide (DRFO) in paraffin as a carrier during the flotation extraction of rare-earth metal compounds from diluted aqueous solutions (using a case study of lanthanum and cerium (III)).

EXPERIMENTAL

The targets of research in this study included sulfate solutions of lanthanum and cerium (III) with concentrations 5–50 mg/dm^3. The concentration of sulfate ions amounted to 0.02 mol/dm^3. The initial values of solution pH were 2. Additions of salts (sodium, calcium and aluminum nitrates, sodium and magnesium sulfates, and calcium chloride) were introduced into the specified solutions in the form of 1% aqueous solutions before the addition of carrier.

Finely dispersed 0.5-M DRFO solid solution in paraffin was used as a carrier. It was prepared using homogenized paraffin with melting point 53 ± 2°C. DRFO has the following structure:



The DRFO choice was determined by its high stability to acidic media, good complexation properties, biological safety, availability (this reagent is produced at the pilot-scale production facility in the Institute of organic chemistry, NAS of Ukraine). Solid solutions of DRFO in paraffin were prepared by dissolving the required amount of DRFO in liquid paraffin heated to 60–70°C with subsequent cooling of the solution.

The dispersion of DRFO solid solutions in paraffin was performed by using an UZG13–01/22 ultrasonic disperser with a strictor frequency of 22 kHz during 300 s. Prior to dispersion the water and dispersible substance (for melting) were heated to 60–70°C. During the dispersion of DRFO solid solution in paraffin the SAS molecules were oriented on the surface of paraffin particles in such way that their polar groups were directed into water (polar liquid). The resultant emulsion was cooled to the indoor temperature.

The carrier was introduced into REE sulfate solutions in a form of 0.5% aqueous suspension in a amount of 1.25 mol of DRFO per 1 mol of REE in two–three minutes before the beginning of flotation (except the tests directed on studying the effect of the time of suspension agitation (maturing) on the efficiency of the flotation process). The flotation treatment of suspensions was performed on a setup for flotation by way of passing the air dispersed by the porous material through the solution. This setup represented a glass column having height 0.11 and diameter 0.03 m. The glass porous plate served simultaneously as the column bottom and the air disperser. The volume of solution poured into the column amounted to 5×10^{-2} dm^3; flotation duration was 15 min (except the tests directed on the study of the flotation process kinetics). The air was fed into column from bottom through the porous plate at the rate of 5×10^{-7} m^3/s. The tests were conducted at room temperature. Sublates (the products of interaction of REE compounds with the carrier) formed at the surface of solutions during flotation were removed mechanically.

Suspensions (solutions) after flotation were periodically analyzed for the content of lanthanum or cerium (III). The analysis was performed using the standard technique [13]. The efficiency of flotation process was assessed in terms of the extraction degree of lanthanum and cerium from solution (α).

Infrared spectra of the carrier and sublates separated from solutions with pH 8.5 and pelletized with KBr were recorded on an infrared spectrometer with Fourier transformer Perkin Elmer 2011 in the wavelength interval of 400–4000 cm^{-1}. The interpretation of findings was performed in accordance with the known correlations [14–15].

The attraction energy of sublate particles toward air bubbles (U_m) determined by the action of Van der Waals-London forces was calculated by equation describing the interaction of two spheres [16]:

$$U_m = -\frac{\mathrm{A}^* \bar{R}_\mathrm{p} \bar{R}_\mathrm{b}}{6H(\bar{R}_\mathrm{p} + \bar{R}_\mathrm{b})}, \tag{1}$$

where A^* is the complex constant of Hamaker's molecular attraction forces assumed to be equal to 4.04×10^{-14} erg [16]; $\bar{R}_\mathrm{p}$ is the averaged radius of sublate particles (0.5×10^{-6} m) [17], $\bar{R}_\mathrm{b}$ is the averaged radius of air bubbles equal to ~ 7.5×10^{-5} m [18]; H is the thickness of the solution layer separating the air bubble and sublate particle.

The energy of ion-electrostatic interaction of air bubbles and sublate particles (U_i) determined by the overlapping of their double electric layers was determined by the following equation [16]:

$$U_i = \frac{\varepsilon \bar{R}_\mathrm{p} \bar{R}_\mathrm{b}(\bar{\psi}_\mathrm{p}^2 + \bar{\psi}_\mathrm{b}^2)}{4(\bar{R}_\mathrm{p} + \bar{R}_\mathrm{b})} \left[\frac{2\bar{\psi}_\mathrm{p}\bar{\psi}_\mathrm{b}}{\bar{\psi}_\mathrm{p}^2 + \bar{\psi}_\mathrm{b}^2} \ln\frac{1 + e^{-\chi H}}{1 - e^{-\chi H}} + \ln(1 - e^{-e^{-2\chi H}}) \right], \tag{2}$$

where $\chi = (8\pi e^2 \sum n_i z_i^2/\varepsilon kT)^{1/2}$ is the Debye parameter (quantity inverse to the effective thickness of double electric layer) depending on the charge (z_i) and concentration (n_i) of counter-ions; k is the Boltzmann constant; *e* is the charge of electron; T is the absolute temperature.

The averaged Stern potentials of sublate particles ($\overline{\psi}_p$) and air bubbles ($\overline{\psi}_b$) were assumed to be equal to their electrokinetic ξ-potentials due to the impossibility of their direct measurement. ξ-potentials of sublate particles and paraffin balls simulating air bubbles were determined by the microelectrophoresis method [19]. The possibility of simulating the air bubbles with paraffin balls is based on the fact that the latter, similar to air bubbles, are hydrophobic; the surface of paraffin balls and air bubbles is immobile (they can be viewed as rigid spheres at the bubble size of 7.5×10^{-5} m); the formation of double electric layer on paraffin balls and air bubbles occurs in accordance with the same mechanism [20, 21].

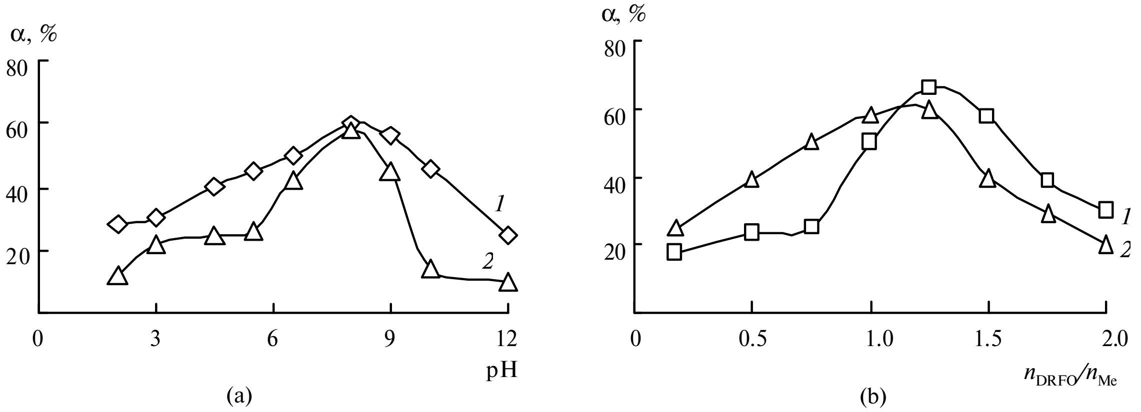
The total amount of interaction energy of air bubbles and sublate particles or the energy barrier of repulsion *U* was calculated by the following equation [17]:

$$U = U_m + U_i. \tag{3}$$

Values of solution pH were changed by using 1M KOH solution and measured by a multipurpose EV-74 ionometer with a glass electrode.

RESULTS AND DISCUSSION

The investigations showed that the finely dispersed solid solution of DRFO in paraffin could be used as a carrier during the flotation extraction of compounds of rare-earth metals (lanthanum and cerium (III)) that were present in diluted sulfate solutions (Figs. 1, 2). The process efficiency depends on the solution composition (its concentration and pH, content of electrolytes), the amount of introduced carrier and conditions of process implementation (duration of flotation and agitation).



(a) (b)

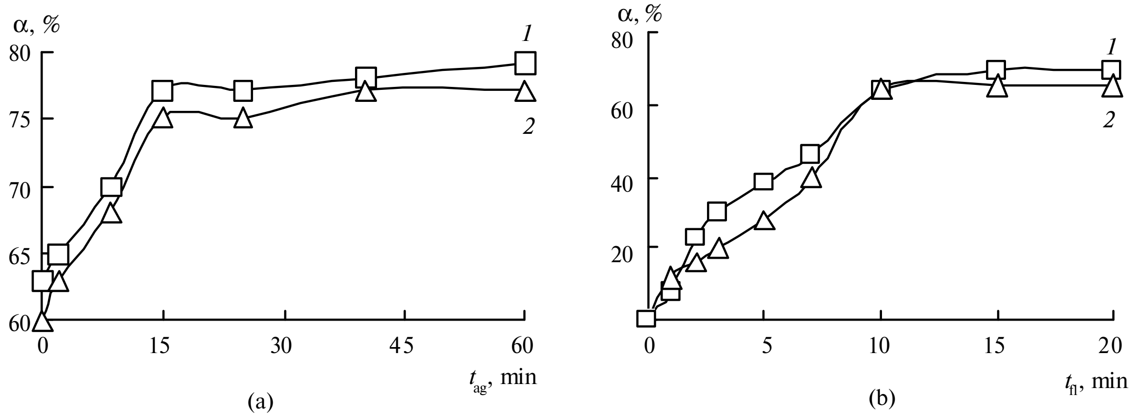
Fig. 1. Relationship of the extraction degree of lanthanum (*1*) and cerium (*2*) from sulfate solutions using the finely dispersed solid solution of DRFO in paraffin as a function of the solution pH (a) and the carrier consumption (n_{DRFO} / n_{Me}) (b) (solution pH 8.5). The initial concentration of solutions of rare-earth elements is 50 mg/dm^3; electrolytes are not added.

Medium pH essentially affects the flotation recovery degree of lanthanum and cerium (III) (see Fig. 1a). The maximum flotation recovery degree of REE is observed at pH 8.5. As a result of hydrolysis of sulfate complexes of these metals, the cation hydroxocomplexes of lanthanum and cerium (III) are formed as well as their hydroxides [9] having the molecular degree of dispersity that can interact with polar groups of DRFO and can be extracted by flotation.

The study of the mechanism of interaction of extractable compounds with carrier involves the need of performing the infrared spectroscopic investigations of the carrier, lanthanum- and cerium-containing sublates recovered by flotation from the solutions of metal salts at optimal pH values.

The comparison of infrared (IR) spectra of the carrier and sublates shows (Table 1) that they contain absorption band corresponding to the stretching and deformation vibrations of hydrocarbon radicals and polar groups of SAS. The difference lies in the fact that IR spectra of sublates include weak absorption bands with maximums at 890 and 850 cm^{-1} that can be referred [16] to deformation vibrations of the Me–OH group and also the absorption bands with maximums at 618 cm^{-1} that can be referred to stretching vibrations of Me–O bond. The aggregate of obtained data makes it possible to suggest that the composition of sublates along with

DRFO includes hydroxides and hydroxocomplexes of recoverable metals. The band shift of stretching vibrations of P–O group of carrier (1157cm^{-1}) in the direction of lower frequencies occurring in IR spectra of samples of lanthanum- and cerium-containing sublates (1124 and 1123 cm^{-1}, respectively) indicates the interaction of the phosphoryl group with compounds of recoverable metals owing to the formation of coordination and hydrogen bonds.



(a) (b)

Fig. 2. Relationship of the flotation extraction degree (α) of lanthanum (*1*) and cerium (*2*) using the finely dispersed solid solution of DRFO in paraffin as a function of the agitation duration (a) and flotation (b). The initial concentration of REE solutions is 50 mg/dm^3, solution pH 8.5. Electrolytes are not added.

Table 1. Infrared spectra of the carrier, lanthanum-containing (A) and cerium-containing (B) sublates

Reference of bands	Samples under study		
	Collector	A	B
	$\tilde{\nu}$, cm^{-1}		
ν (OH)	3436	3436	3436
ν (CH$_3$)	2957	2957	2957
ν (CH$_2$)	2874	2918	2918
	2849	2849	2849
δ (O–H)	1632	1630	1631
δ_{as} (C–CH$_3$)	1473	1473	1473
δ (–CH$_2$–)	1463	1463	1463
δ_s (C–CH$_3$)	1379	1378	1379
ν (P = O)			
ν (P = O) in terms of hydrogen bond	1157	1124	1123
δ (Me–OH)	–	889	891
		851	838
ρ (–CH$_2$–)$_n$	730	730	730
	720	720	720
ν (Me–O)	–	618	617

The maximum recovery of lanthanum and cerium (III) from solutions at optimum pH involves the need of adding 1.25 mol of DRFO per 1 mol of metal present in solution (see Fig. 1b). At a smaller consumption of the carrier not all extracted REE compounds get bound in sublate, while the introduction of large surplus of the carrier results in the reduced degree of REE extraction owing to the competition of sublate and carrier particles for the place on the surface of air bubbles.

The use of finely dispersed solid solutions of DRFO in paraffin makes it possible to achieve an effective recovery of REE compounds from solutions with initial concentration (C_0) of 30–50 mg/dm^3 (lanthanum) and 40–50 mg/dm^3 (cerium):

C_0, mg/dm^3	5	10	20	30	40	50
α(La), %	50	55	60	71	64	63
α(Ce), %	26	27	39	41	56	60

One of the ways for enhancing the metal recovery efficiency is the agitation (maturing) of sublate suspensions prior to flotation. This operation is performed for the sake of improving the interaction of the collector with extractable compounds, and also for upsizing the sublate particles due to the dehydration of their surface and the loss of aggregate stability. It has been found out that the agitation of suspensions of lanthanum- and cerium-containing sublates during 15–60 min leads to the maximum (under the specified test conditions) degree of REE extraction from solutions at pH 8.5 (see Fig. 2a).

The time required for achieving the maximum possible degree of flotation extraction of lanthanum and cerium using the finely dispersed solid solution of DRFO in paraffin amounts to 10–15 min (see Fig. 2b). The kinetics of process is described by the first-order equation. The values of speed constants found by experiment amount to (s^{-1}): 1.58×10^{-3} (lanthanum) and 1.03×10^{-3} (cerium). The first order of the process indicates that the limiting stage is diffusion of sublate particles to the surface of air bubbles. This process is not hampered by laminar coagulation of sublate particles at the liquid–gas interface.

However, even under optimal conditions for running the process, the extraction degree of lanthanum and cerium (III) compounds did not exceed 77% and 74%, respectively; therefore, for enhancing the efficiency of this process we studied the effect of additions of inorganic salts on the flotation extraction degree of lanthanum and cerium compounds using the proposed reagent.

Optimal concentrations of salts (Table 2) were determined that ensured the rise of lanthanum and cerium extraction degrees by 5–13 and 10–16%, respectively. Positive effect of cations and anions increases with the increasing positive hydration of ions [22], i.e., with the strengthening effect of water orderliness in the close neighborhood of ions. It results in hydrophobization of sublate particles and enhances the sublate flotation recovery.

Table 2. Flotation extraction degree (α) of REE compounds and their residual concentration (C_{res}) in solution at optimal concentrations (C_{el}) of added electrolytes (the initial concentration of REE solutions is 50 mg/dm^3, solution pH 8.5, agitation duration is 20 min)

Indicator	Na_2SO_4	$MgSO_4$	$NaNO_3$	$Ca(NO_3)_2$	$Al(NO_3)_3$	$CaCl_2$
Flotation extraction of lanthanum compounds						
C_{el}, g/dm^3	1.4	2.2	1.8	2.2	0.04	0.8
α, %	90	85	70	89	82	89
C_{res}, mg/dm^3	3.0	4.5	9.0	3.6	5.4	3.3
Flotation extraction of cerium compounds						
C_{el}, g/dm^3	1.0	1.6	1.8	2.6	0.04	1.4
α, %	90	90	80	89	85	87
C_{res}, mg/dm^3	3.0	3.0	6.0	3.6	4.5	3.9

The efficiency of flotation process depends on the cation charge of the metal entering into composition of added salt. Hence, for example, additions of sodium nitrate insignificantly affect the extraction degree of lanthanum and cerium, while at the same time additions of calcium nitrate and aluminum nitrate enhance the REE extraction degree by 12–15% and 5–11%, respectively. These findings can be explained by the fact that particles of the dispersive phase of sublates are charged negatively (Table 3); therefore the metal cations representing counter ions compress double electric layer (DEL) of sublate particles thereby reducing their ζ-potential and the energy barrier of repulsion between sublate particles and air bubbles that contributes to fixation of sublate particles on air bubbles.

The results of calculations based on the DLVO theory (see Table 3) show that the value of the energy repulsion barrier is reduced from 29 kT (in the absence of electrolyte) to 6 kT (with addition of 7.4×10^{-5} mol/dm^3 of aluminum nitrate). The size of the secondary minimum increases in the case of transition from the sublate obtained in the absence of electrolytes to the sublate obtained in the presence of aluminum nitrate additions.

Small values of energy repulsion barriers between the sublate particles and air bubbles explain reasonably high extraction degrees of REE.

Table 3. Chemical-and-colloidal characteristics of particles of cerium-containing sublates and air bubbles (initial data for calculations) and calculation results of the energy of their interaction using the DLVO theory

System	C_{el}, mol/dm^3	α, %	ζ_p	ζ_b	χ, cm^{-1}	U_{max}	U_{min}
			mV			kT	
Ce(III) + DRFO	–	74	–15.6	–7.8	1.6×10^6	29	–
Ce(III) + $NaNO_3$ + DRFO	2.15×10^{-2}	80	–11.6	–21.2	6.95×10^6	13	–1.5
Ce(III) + $Ca(NO_3)_2$ + DRFO	5.9×10^{-3}	88	–8.4	–21.6	3.63×10^6	11	–2.5
Ce(III) + $Al(NO_3)_2$ + DRFO	7.4×10^{-5}	85	–5.5	–4.8	1.86×10^6	6	–6

CONCLUSIONS

Thus, the possibility in principle of using the finely dispersed solid solution of DRFO in paraffin as a carrier during the flotation extraction of rare-earth metals (lanthanum and cerium) has been experimentally shown. Under the optimal condition of flotation process the recovery degree of lanthanum and cerium amounts to 90%.

The authors express their gratitude to V. I. Kal'chenko and S. I. Miroshnichenko (The Institute of Organic Chemistry, NAS of Ukraine) for provision of the different radical phosphine oxide used in our investigations.

REFERENCES

1. Azhazha, V.M., Borts, B.V., Vanzha, A.F., et al., *Voprosy atom. nauki i tekhniki,* 2008, vol. 17, no. 1, pp. 195–201.
2. Rybal'skii, N.G., *Ekologicheskie aspekty ekspertizy izobretenii: spravochnik eksperta i izobretatelya* (Ecological Aspects of Examination of Inventions: Expert and Inventor Handbook), Moscow: VNIIPI, Part 1, 1989.
3. Gol'man, A.M., *Ionnaya Flotatsiya* (Ionic Flotation), Moscow: Nedra, 1982.
4. Sazonova, V.F., *Cand. Sci. (Chem.) Dissertation* [in Russian], Odessa, 1980.
5. Rudenko, E.I. and Barkovskii, V.F., Uralskii politechn. in-t, Sverdlovsk, 1978, *Dep. v ONNIGEKhIM* (Deposit in ONNIGEKhIM), Cherkassy, no. 2009/78, August 21, 1978.
6. Vershkova, Yu.A., *Cand. Sci. (Eng.) Dissertation* [in Russian], Apatity, 2000.
7. Vershkov, A.V., *Extended Abstract of Doctoral Sci. (Chem.) Dissertation* [in Russian], Apatity, 2000.
8. Mezhov, E.A., Samatov, A.V., and Troyanovskii, L.V., *Radiokhimiya,* 1989, vol. 31, no. 5, pp. 45–49.
9. Dzhevaga, N.V., *Extended Abstract of Cand. Sci. (Chem.) Dissertation* [in Russian], St. Petersburg, 2011.
10. Chirkst, D.E. and Sulimov, M.A., *Zhurn. prikl. khimii,* 2009, vol. 82, issue 8, pp. 1273–1276.
11. Skrylev, L.D., Nilova, O.V., and Menchuk, V.V., *Izv. Vuzov. Gornyi zhurn.,* 1993, no. 1, pp. 120–124.
12. Kostik, V.V. *Cand. Sci. (Chem.) Dissertation* [in Russian], Odessa, 1988.
13. Prshibil, R., *Kompleksony v khimicheskom analize* (Complexons in Chemical Analysis), Moscow: Izd-vo inostr. lit-ry, 1960.
14. Bellami, L., *Infrakrasnye spektry slozhnykh molekul* (Infrared Spectra of Complex Molecules), Moscow: Izd-vo inostr. lit-ry, 1963.
15. Nakamoto, K., *IK-spektry i spektry KR neorganicheskikh i koordinatsionnykh soedinenii* (IR Spectra and Raman Scattering Spectra of Inorganic and Coordination Compounds), Moscow: Mir, 1991.
16. Zontag, G. and Shtrenge, K., *Koagulyatsiya i ustoichivost dispersnykh sistem* (Coagulation and Stability of Dispersive Systems), Leningrad: Khimiya, 1973.
17. Chernetska, V.V. and Korniichuk, I.M., *Tez. dop. Vseukr. Mizhnar. konf. molodykh vchenykh* (Synopsis of All-Ukrainian Intern. Conf. of Young Scientists) (Kyiv, 15–16 May 2012), Kiev, 2012.
18. Skrylev, L.D., Perlova, O.V., and Sazonova, V.F., *Zhurn. Prikl. Khimii,* 1993, vol. 66, no. 5, pp. 1170–1175.
19. Frolov, Yu.G. and Grodskii, A.S., eds., *Laboratornye raboty i zadachi po kolloidnoi khimii* (Laboratory Studies and Problems in Colloid Chemistry), Moscow: Khimiya, 1986.
20. Collins, G.L., Motarjemi, M., and Jameson, G.J., *J. Colloid and Interface Sci.*, 1978, vol. 63, no. 1, pp. 69–75.
21. Sazonova, V.F. and Kozhemyak, M.A., *J. Water Chem. and Technol.,* 2009, vol. 31, no. 1, pp. 30–41.
22. Krestov, G.A., *Termodinamika ionnykh protsessov v rastvorakh* (Thermodynamics of Ionic Processes in Solutions), Leningrad: Khimiya, 1984.

Translated by A. Zheldak