Interaction Features of Sodium Oleate and Oxyethylated Phosphoric Acid Esters with the Apatite Surface

Vasiliy V. Sergeev, Olga V. Cheremisina, Alexander T. Fedorov,* Alexandra A. Gorbacheva, and Daniil A. Balandinsky

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ABSTRACT: Apatite ores are the most important phosphate materials used for the agricultural and livestock chemical production. With the global demand for phosphorous compounds, apatite and other phosphorus-bearing ores are being depleted. The main method of apatite ore enrichment at the moment is the flotation process, the efficiency of which depends on complex heterogeneous processes occurring at the boundary of three phases ("liquid–gas", "solid–liquid", and "solid–gas"). Significant influence on the process have the flotation modes and composition of the reagent mixture, which provide a synergistic effect. The purpose of this work was to investigate the reasons for the synergism of surfactants used in apatite ore flotation with fatty acid-based collectors. The object of the study is a monomineral fraction of apatite, separated from the apatite-nepheline ore of Khibiny deposits. In the course of the work, it was found that the mixture of sodium oleate and phospholane PE65 has a synergistic effect on the mineral surface of apatite during foam flotation. The ratio of reagents was determined at which the maximum synergistic effect was observed.
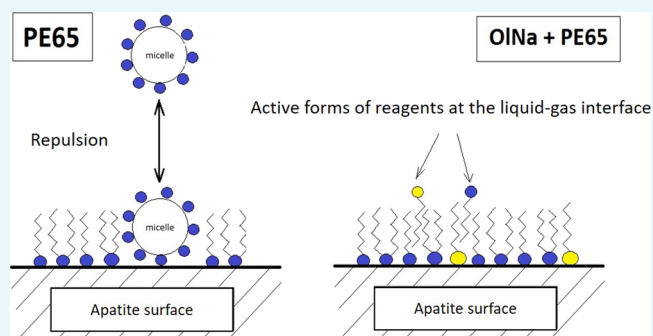
INTRODUCTION

Apatite ores are the most important phosphate raw materials used for the production of fertilizers, animal feed, and pesticides. Modern agricultural development is impossible without sustainable mining and processing of phosphate ores.[1,2]

The main method of apatite ore enrichment at the moment is flotation. With the global demand for apatite, which is a non-renewable mineral resource, phosphate ores are being depleted and their composition is changing. In addition, an increase in the alkalinity of recycled water causes a change in the composition of sorption mixtures used as reagents in the floatation enrichment method.[3–5]

The efficiency of a complex heterogeneous process occurring at the boundary of three phases ("liquid–gas", "solid–liquid", and "solid–gas") can be improved by a reasonable choice of flotation modes and the use of a reagent mixture that provide a synergistic effect.[6,7]

The purpose of this work is to investigate the reasons for the synergism of surfactants used in apatite ore flotation with fatty acid-based collectors.

Sources of fatty acids are usually various vegetable oils: Patau palm oil,[8] cottonseed oil,[9] jojoba oil,[10] and tall oil fatty acids.[11] Vegetable oils are mixtures of unsaturated fatty acids, the main ones of which are oleic, linoleic, and linolenic acids.

In[12] the optimal composition of these acids determined, the maximum hydrophobization of the mineral apatite surface was achieved reducing its wettability by water. The mixture contained 54 wt % oleic acid, 36 wt % linoleic acid, and 10 wt % linolenic acid. Despite the wide use of these acids, the formation of low-soluble compounds with hardness ions that do not exhibit surfactant properties, adsorption on waste rock minerals, which leads to a loss of selectivity, and high sensitivity to the environmental pH determine the use of surfactant mixtures that provide a synergistic effect.

The combination of fatty acids of different unsaturation degrees can slightly mitigate the above disadvantages, but cannot eliminate them completely. The disadvantages of using higher carboxylic acids include a high consumption of reagents and a significant dependence on the pulp temperature.

One promising direction to increase the efficiency of fatty acid collectors is the use of an additional component that provides a synergistic effect. Such a component is usually a
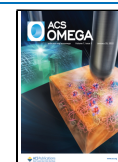
non-ionic surfactant. Substances from ethoxylated alkyl phenol groups[13−15] or ethoxylated fatty alcohols with different degrees of ethoxylation and a long aliphatic chain are widely used. These compounds do not adsorb directly on the mineral surface of apatite[16] and do not affect the adsorption value of the main collector.[17] Non-ionogenic components are attached to the mineral surface only after its treatment with the main collector. An important indicator of the non-ionic component's efficiency is the ratio between the polar and non-polar parts. For example, in the case of N-acylated aminoalcohols, the optimal number of oxyethylene groups should be equal to or less than 6. An increase in the number of such groups changes the surfactant properties of the alcohol and weakens its sorption capacity.[18] It was shown in ref 19 and 20 that fatty oxyethylated alcohols with similar ethoxylation degrees of 4 and 5 show a good synergistic effect. In ref 21, during flotation of apatite from South Africa, it was also confirmed that the use of alkyl phenols with a low ethoxylation degree, equal to 2, enhances the oleate flotation ability. At the same time, an increase of the ethoxylation degree up to 8−12 leads to a decrease of the concentrate quality as polar ethoxylate groups interact with water molecules, which prevents effective interaction of air bubbles with the mineral surface. The probable cause of synergism may be, first, a decrease in electrostatic repulsion between the negatively charged polar groups of the reagent−collector during the formation of a sorption layer on the mineral surface. The effect of electrostatic repulsion is particularly strong in an alkaline environment, when the oleate molecules form dimers $(RCOO-)_2$.[22] The existence of different forms of oleic acid on a mineral surface is graphically shown in Figure 1.
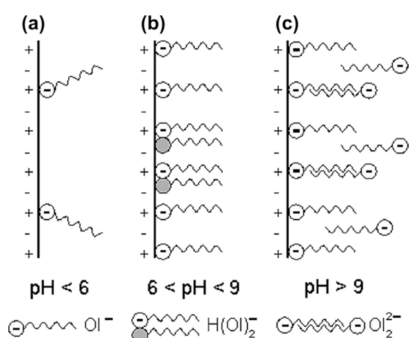

Figure 1. Interaction mechanism of the hydroxyapatite surface with sodium oleate in solution at different pH values: (a) pH < 6; (b) 6 < pH < 9; and (c) pH > 9 (sodium oleate concentration ≤1 × 10⁻⁴ mol/L).[a,22] Reprinted from Journal of Colloid and Interface Science, Volume 343, Dušica R. Vučinić, Dragan S. Radulović, Slaven Đ. Deušić, Electrokinetic properties of hydroxyapatite under flotation conditions, Page no. 7, 2010, with permission from Elsevier.

When using a component that provides a synergistic effect, a mixed sorption layer is formed, which somewhat reduces the electrostatic repulsion and, consequently, increases the hydrophobicity of the surface. This statement is well supported by the results of measurements of the peripheral wetting angle at different pH values of the surface of sodium oleate-treated scheelite CaWO4, as well as the surface treated with a mixture of sodium oleate with addition of iso-decanol polyoxyethylated ether with the degree of ethoxylation equal to 5 (reagent JFC-5).[19] According to the experimental data, the edge wetting angle of the scheelite surface increases with increasing solution pH, and to a greater extent in the case of using a surfactant mixture.

Second, the synergistic effect can be associated with an increase in the number of active reagent forms at the liquid−gas interface.[23−25] The high rate of the reagent film spreading at the time of flotation contact formation and at a high surface pressure increases the flotation process efficiency.

The use of surfactant compositions is a promising way to increase the sorption activity of the mixture. Ref 26 describes the synergistic effect of using two collectors: oleamide and sodium dodecylbenzosulfonate (SDBS). The maximum effect is achieved at a molar ratio of oleamide and SDBS of 2−1. It is noteworthy that despite the negative charge of the amide group (RCONH−), oleamide practically does not flotate apatite, unlike SDBS. However, the presence of oleamide increases the flotation activity of SDBS due to coadsorption on the mineral surface. A similar effect was described when a mixture of sodium oleate and oleamide was used.[27] The authors note the formation of a mixed adsorption layer with a denser packing of molecules.

The high efficiency of organophosphorus reagents phospholan PE65 and phospholan PE169 in apatite flotation is noted in a number of works. These reagents are a mixture of ethoxylated aliphatic esters of phosphoric acid with different ratios of mono- and diesters. In ref 28, during foamless flotation in the Hallimond tube of the Moroccan apatite ore with different collectors, it was shown that phospholan PE169 at a concentration of 10 μg/L provides a better extraction degree of calcium phosphate in comparison with ATRAC 50S, synthetic collector for mineral flotation by Nouryon (Netherland) and sodium oleate at a concentration of 60 mg/L. In ref 29, the high efficiency of the phospholan PE65 reagent in flotation of the apatite ore of Kovdorsky deposit is reported. At a collector consumption rate of 36 g/t, it was possible to obtain a concentrate with a P2O5 content of 28% and a recovery rate of 83.7%, while for saponified fatty acids, the P2O5 content and recovery rate did not exceed 27 and 55%, respectively. At present, phospholan PE65 is used in a mixture with a fatty acid collector in enrichment of the apatite ore of Khibiny deposits.[30,31] Nevertheless, there is no information in the
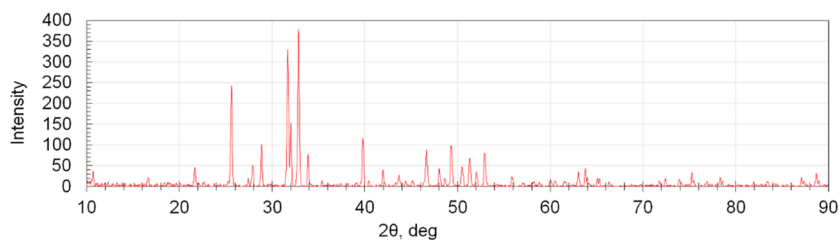
Figure 2. XRD pattern of the pure apatite sample.

literature about the mutual influence of these reagents in apatite flotation and about the mechanism of their interaction. A study of the interaction of phospholan PE65 with sodium oleate during flotation of the apatite ore is the purpose of this work. The results of the study will allow us to predict the use of organophosphorus reagents in conjunction with classical collectors—fatty carboxylic acids.

2. EXPERIMENTAL SECTION

2.1. Materials. The object of the study is a monomineral fraction of apatite, separated from the apatite-nepheline ore of Khibiny deposits and subjected to preliminary preparation. The surface of the samples under study was cleaned from organic inclusions (collector fragments) by calcination of the sample in a muffle furnace at 600 °C for 4 h. The phase composition was established by X-ray diffraction (XRD) on a XRD-6000 X-ray powder diffractometer manufactured by Shimadzu (Japan). The XRD spectrum of the ore surface is shown in Figure 2.

The only defined crystalline phase is calcium phosphate. The chemical composition of the sample was established by X-ray fluorescent analysis with an XRF-1800 device of Shimadzu company. The sample consists of 50.024% CaO; 42.30% P_2O_5; 3.00% SrO; and 2.0405% F, the remaining is impurities.

Oleic acid (technical degree of purity) with a main component concentration of at least 97.4% was chosen as a model fatty acid collector. Saponification of oleic acid with sodium hydroxide was carried out at 60 °C for 2 h per saponification number. Phospholan PE65 was provided by Akzo Nobel Chemistry AB (Stenungsund, Sweden) and was saponified under the same conditions before the flotation experiments. 0.10 mol/L HCl and 0.10 mol/L NaOH with analytical purity were used to adjust the pH of the flotation pulp. Preparation of solutions and flotation experiments were carried out using distilled water.

2.2. Methods. *2.2.1. Flotation Tests.* The experimental study was carried out using a laboratory flotation machine FMP-L1 manufactured by Vektis Minerals (Russia) under following conditions: a volume of flotation capacity of 0.5 L, a mass of the suspension of ore of 50 ± 0.01 g, 90% grain size less than 183 μm, the speed of the impeller of 1000 rpm with an air flow of 3.8 m^3/min, and stirring the suspension for 1 min. Flotation was carried out for 6 min.[32−34] The float and sink products were filtered, washed, dried, and weighed. Equation 1 was used to calculate the extraction degree

$$\varepsilon = \frac{m_1}{m_0} \times 100\% \qquad (1)$$

where m_0 is the mass of the initial sample of ore and m_1 is the mass of the washed and dried foam product.

2.2.2. FT-IR Analysis. The Fourier transform infrared spectroscopy (FT-IR) spectra of the samples were measured using a FT-IR Vertex-70 c (Germany Bruker, Karlsruhe, Germany) in the range of 400−4000 cm^{-1} with a resolution of 2 cm^{-1} at 32 scans. The conditions of each experiment are presented in Table 1. In each case, a mineral sample weighing 0.5 g was brought into contact with the surfactant solution within 24 h under static conditions. Each sample was then filtered and dried to a constant mass. After drying, some samples were washed with ethanol to remove the physically sorbed molecules and then were redried. A description of each of the samples is given in Table 1. In each case, contact with the collector was conducted at pH = 10.0 ± 0.1. Finally, 200

Table 1. Description of Samples for FT-IR Analysis

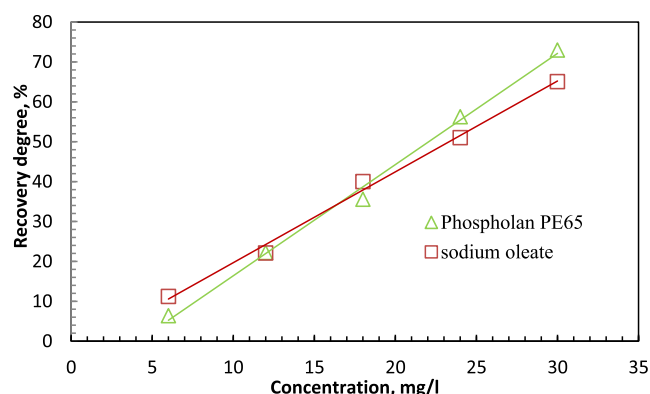| | concentration, g/L | | | |
no	phospholan PE65	sodium oleate	ethanol treatment	volume of the solution, mL
1		1.00		100
2	1.00			100
3	0.500	0.500		200
4		1.00	+	100
5	1.00		+	100
6	0.500	0.500	+	200

mg of the spectral pure KBr was mixed with 15 mg of the apatite samples and then pressed into a thin disk for FT-IR spectroscopy.

2.2.3. Interfacial Tension Measurement. An automatic tensiometer DCAT 21 (Germany) was used to determine surface tension. The measurements were performed using the Wilhelmy plate method. The measurements were performed in borate buffer medium at pH = 10.0.

3. RESULTS AND DISCUSSION

3.1. Review of Froth-Flotation Experiments. To verify the effectiveness of the fatty acid collector (sodium oleate) in a mixture with the reagent phospholan PE65, flotation of the monomineral fraction of apatite at different ratios of reagents in the collection mixture was carried out. The concentration of the added reagent in each case was 30 mg/L, temperature of flotation suspension T = 19 ± 1 °C, and pH of the reaction system according to ref 35 was set equal to pH = 8.7 ± 0.2 as these conditions are optimum for flotation of phosphate-bearing ores.

To prove the presence of a synergistic effect, we carried out flotation of apatite with individual reagents at different

Figure 3. Apatite recovery degree using sodium oleate and phospholan PE65 collectors.

concentrations (Figure 3) and calculated the theoretical degree of recovery using eq 2

$$\varepsilon_T = \varepsilon_{c1} + \varepsilon_{c2} \qquad (2)$$

where ε_T is the theoretical degree of recovery using a mixture of reagents and ε_{c1} and ε_{c2} are the degree of recovery of apatite at a given concentration of the first or second reagent in the mixture.

Graphs of the theoretical and experimental recovery degree are shown in Figure 4. As can be seen from Figure 4 when
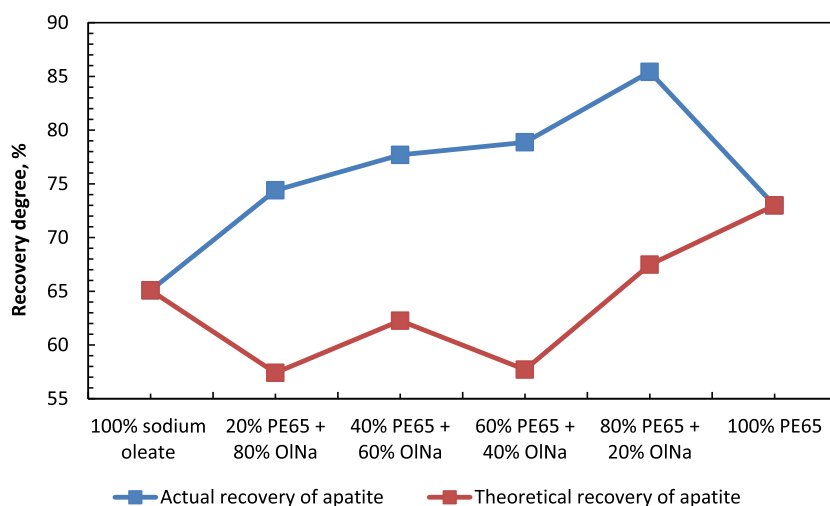
Figure 4. Theoretical and experimental recovery degrees of apatite using a mixture of collectors.
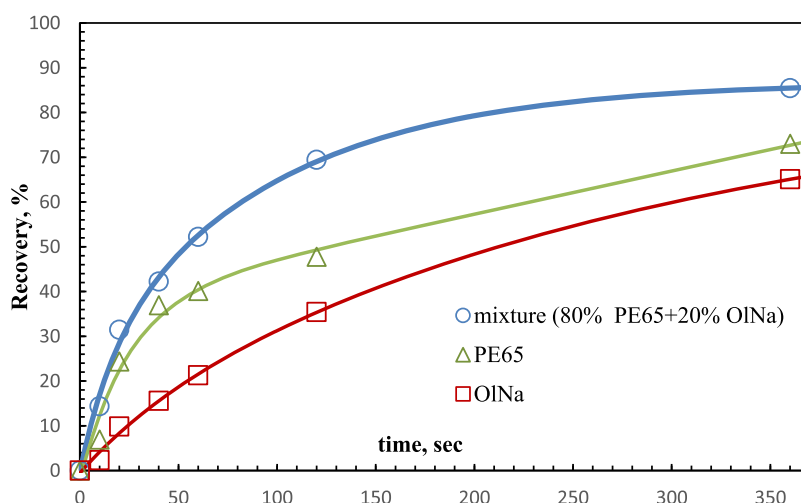

Figure 5. Dependence of apatite recovery on the flotation time.

using a mixture of reagents, there is an increased degree of extraction compared to the use of individual surfactants. The greatest degree of extraction is achieved by the use of a mixture consisting of 80% of phospholan PE65 and 20% of sodium oleate.

According to the experimental results, the synergetic effect due to the mutual influence of the mixture components during sorption on the apatite surface is observed. Moreover, this effect is not additive due to the difference between the experimental and theoretical results.

The kinetics of the flotation process, with both a mixture of reagents and individual surfactants, was studied, and the results of the experimental study are shown in Figure 5.

The obtained dependences were approximated by the equations of formal kinetics. Using the first-order reaction equation, the rate constant k was calculated

$$R = R_\infty(1 - e^{-kt}) \qquad (3)$$

where R is the degree of mineral recovery at time t; k is the flotation rate constant, sec^{-1}; and t is the flotation time, sec.

The effectiveness of the mixture was evaluated using the value of the index k_m, which combines the rate constant with the maximum degree of recovery

$$k_m = R_\infty \bullet k \qquad (4)$$

The results of the calculations are presented in Table 2.

Table 2. Values of Parameters of Flotation Speed and Efficiency of Using a Mixture of Surfactants

composition of collector	R_∞	k	k_m
mixture (80% PE65 + 20% OlNa)	85.42	0.0176 ± 0.0009	1.50
sodium oleate (OlNa)	65.08	0.0064 ± 0.0004	0.414
phospholan PE65 (PE65)	72.99	0.014 ± 0.0007	1.022

As can be seen from the dependence of the recovery degree on the flotation process time, in addition to the highest recovery rate, the mixture consisting of two components also shows a better rate of mineral extraction into the foam product.

The data obtained indicate the formation of a molecular structure at the interface, which can form an effective flotation contact faster, as well as provide stronger hydrophobization of the mineral surface.

3.2. Review of FT-IR Analysis. In order to explain the interaction mechanism of the reagent mixture with apatite, a spectral study of the mineral surface was conducted. The
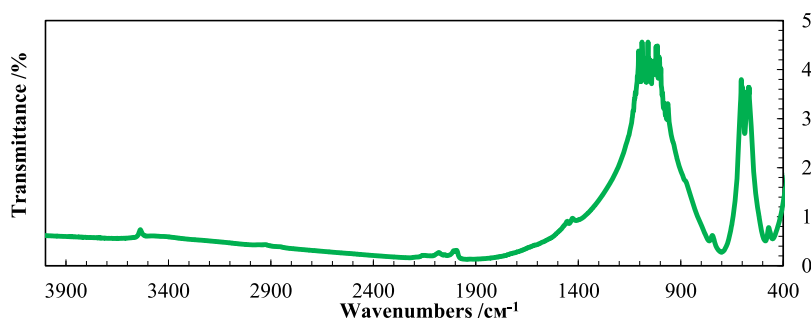
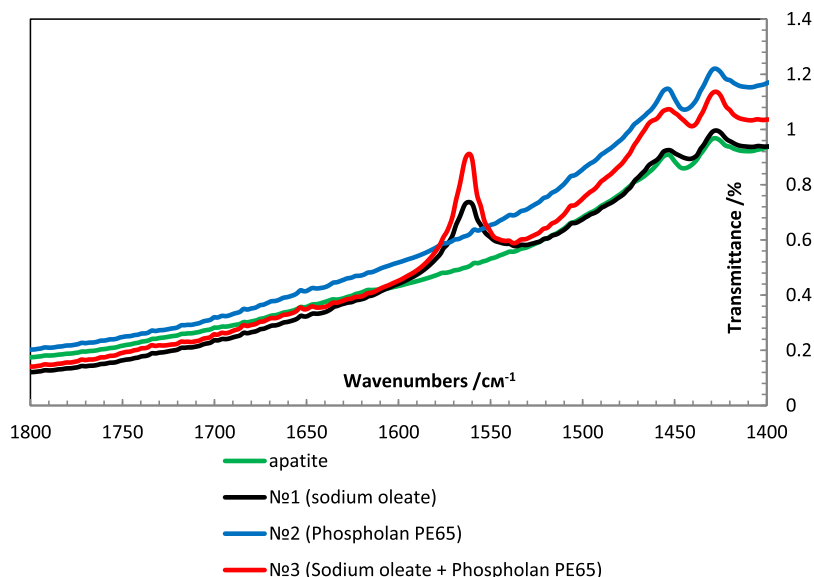**Figure 6.** Infrared spectrum of the apatite surface.

Figure 7. IR spectra of the mineral before and after surfactant treatment.

infrared spectrum of the initial apatite sample is shown in Figure 6.

The spectrum of the powdered apatite sample contains a characteristic intense doublet at the maximum frequencies of 605 and 570 cm^{-1}[36] corresponding to the strain vibrations of the P−O bond in the complex phosphate ion. Valence vibrations of the P−O bond correspond to characteristic frequencies of 964 and 1020−1100 cm^{-1}, while the frequencies of 1435 and 1458 cm^{-1} correspond to the valence vibrations of the carbonate ion CO_3^{2-}. The characteristic frequency of 748 cm^{-1} characterizes the presence of OH−F bonds in the mineral structure. Thus, the studied mineral sample consists of different types of apatites. Chemical analysis data also indicate the presence of various apatite structures. In fluorapatite, the Ca/F ratio is 5.0, while in the studied material samples this ratio is 17.51, indicating the presence of calcium in crystalline structures without fluorine.

Figure 7 shows the IR spectra of the mineral after treatment with sodium oleate, phospholan PE65, and their mixture compared with the spectrum of apatite in the range 1300−1900 cm^{-1}.

The appearance of the characteristic frequency peak at 1561 cm^{-1} is attributed to vibrations of the carboxyl group COO− on the surface of the mineral. This interaction is weak because the oscillations of the group disappear after washing the apatite samples with ethanol. Obviously, only the coordination interaction occurs between the apatite surface and the oleate

ion, which characterizes the presence of an ionic form of the surfactant on the mineral surface.[12,37]
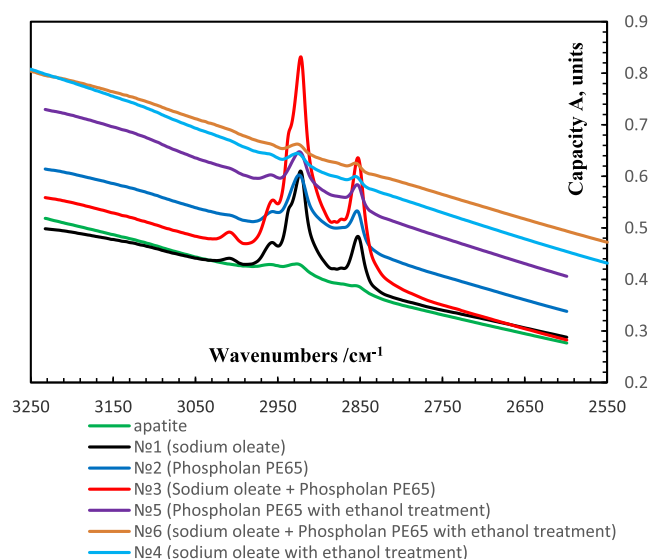
In the presence of phospholane, the intensity of the peak increases, which indicates an increase in the proportion of oleate molecules in the sorption layer of physically fixed molecules, and treatment with alcohol, practically, has no effect on the vibration intensity. Consequently, phospholane molecules, firmly holding oleate ions, are chemically sorbed by the apatite surface.

Spectral region in the range of 2550−3250 cm^{-1} is presented in Figure 8.

The peaks forming a doublet in this region are attributed to the asymmetric and symmetric vibrations of the −CH$_2$− group present in the molecules of both reagents.[38] The highest intensity of peak no 3 indicates a high density of the collector molecules in the sorption layer of the mineral. It should be noted that treatment of mineral samples with alcohol in the case of using phospholan PE65 slightly reduces the intensity of the peak, which characterizes the strong bond of the organophosphorus reagent with the apatite surface.

When a mixture of reagents is used, the intensity of the peak decreases sharply and becomes almost indistinguishable, which may indicate a more loosened structure, a different structure of molecular ensembles in the sorption layer.

3.3. Review of the Surface Tension Measurements. In order to identify the surface effects of the reagents, the

apatite
№1 (sodium oleate)
№2 (Phospholan PE65)
№3 (Sodium oleate + Phospholan PE65)
№5 (Phospholan PE65 with ethanol treatment)
№6 (sodium oleate + Phospholan PE65 with ethanol treatment)
№4 (sodium oleate with ethanol treatment)

Figure 8. Region of the IR spectrum in the wave number range of $2550-3250$ cm^{-1}.

dependences of surface tension on concentration at $t = 20$ °C were plotted, as shown in Figure 9.

According to the data obtained, the critical concentration of micelle formation (CMC) for sodium oleate was 0.33 g/L, that for phospholan PE65 is 0.033 g/L, and that for their mixture is 0.116 g/L.

Based on the data obtained, the surface pressure value was calculated (eq 5)

$$\pi_C = \sigma_0 - \sigma_c \qquad (5)$$

where π_C is the surface pressure of the surfactant at a given concentration, mN/m, σ_0 is the solvent surface tension, and σ_0 is the surface tension of the solution at given reagent concentration, mN/m.

At a low concentration (33 mg/L), phospholan PE65 reduces the surface tension more intensely, $\pi_{PE65(33\ mg/L)} = 14.74$ mN/m, compared to sodium oleate, $\pi_{OlNa(33\ mg/L)} = 8.44$ mN/m, which may be related to the diester present in its composition. However, the presence of diester causes high aggregation ability of the reagent, resulting in a low value of the CMC (phospholan PE65) = 33 mg/L.

At higher concentrations, , phospholan PE65 reduces the surface tension of the solution less than sodium oleate. Surface tension of phospholan PE65 solution at a concentration of 0.5 g/L is 52.5 mN/m ($\pi_{PE65(0.5\ mg/L)} = 19.82$ mN/m), while the surface tension of sodium oleate solution at the same concentration is 43.1 mN/m ($\pi_{OlNa(0.5\ mg/L)} = 29.23$ mN/m). The observed effect could be related, first, to the lower aggregation ability of oleate compared to phospholan PE65. Second, due to the low critical concentration of phospholan PE65 micelle formation as compared to sodium oleate, some amounts of non-ionic surfactant in the free form may be present in the content of the flotation agent used.[30] The appearance of an ether bond in the hydrophobic part of the collector contributes to the molecule reorientation at the gas–liquid interface, which reduces the value of specific sorption by almost two times.[23] A low surface concentration will contribute to a reduction in surface pressure and, therefore, collection capacity. The collector molecules without polar groups or substituents in the hydrocarbon radical are oriented along the normal to the gas–liquid interface, which explains the difference in the surface tension of sodium oleate and phospholan PE65.

Also, based on the data obtained, the interaction parameter β was calculated using the Ruben-Rosen method[39] (eqs 6 and 7)

$$\frac{(x_1)^2\ \ln(x_1)\left|\frac{\alpha_1 \cdot C_{12}}{x_1 \cdot c_1}\right|}{(1 - x_1)^2\ \ln\left|\frac{(1 - \alpha_1) \cdot C_{12}}{(1 - x_1) \cdot C_2}\right|} = 1 \qquad (6)$$

$$\beta = \frac{\ln\left[\frac{\alpha_1 \cdot C_{12}}{x_1 \cdot C_1}\right]}{[(1 - x_1)^2]} \qquad (7)$$

where β is the interaction parameter, α_1 and $(1 - \alpha_1)$ are fractions of components in the binary solution, in our case: α_1 is the fraction of phospholan PE65, $(1 - \alpha_1)$ is the fraction of sodium oleate; x_1 and $(1 - x_1)$ are shares of phospholan PE65 and sodium oleate in micelle; C_1, C_2 are CMC values of phospholan PE65 and sodium oleate; and C_{12} is the CMC of the binary solution.

The interaction parameter allows us to estimate the internal effects occurring between component molecules in mixed
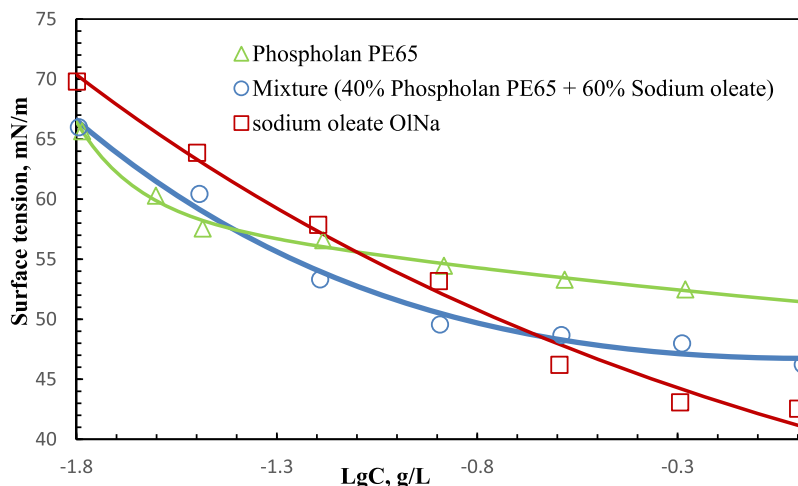
Figure 9. Surface tension dependence on the concentration of different reagents at a pH of 10.0.

micelles. When $\beta > 0$ and $|\beta| > |\ln(C_1/C_2)|$, there is antagonism in the system, indicating repulsion between the mixture components. When $\beta < 0$ and $|\beta| > |\ln(C_1/C_2)|$, there is synergy in the system, indicating mutual attraction of the components. In order to calculate the values corresponding to the ideal mixture composition, eqs 8 and 9 were used

$$\frac{1}{C_{12}} = \frac{\alpha_1}{C_1} + \frac{1 - \alpha_1}{C_2} \tag{8}$$

$$x_{\text{ideal}} = \frac{\alpha_1 C_2}{\alpha_1 C_2 + \alpha_2 C_1} \tag{9}$$

The calculated values are presented in Table 3.

Table 3. Parameters of Mixed Micelles Calculated using the Ruben−Rosen Method

	CMC, mg/L		x_1		
α	ideal	exp	ideal	exp	β
0.4	69.8	116	0.873	0.84	21.33

Thus, antagonism in the formation of mixed micelles is observed in the system. This may indicate the dispersion of molecular aggregates of the phospholan PE65 reagent by sodium oleate molecules.

3.4. Discussion. During flotation experiments, it was established that a mixture of reagents of unsaturated fatty acid groups and ethoxylated esters of phosphoric acid has a synergetic effect, which helps to increase the extraction degree of apatite in the foam product. A possible reason for the increase in sorption properties could be the formation of supramolecular structures of a mixed composition. In ref 40, on the example of Phosphenox H6B, a suggestion was made about the possible structure of the molecular ensemble of the ethoxylated organophosphorus ester (Figure 10).
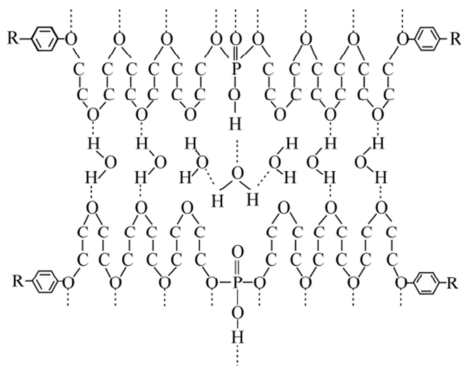
Figure 10. Structure of intermolecular interactions at the interface in the Phosphenox H6B molecule.[b,40] Reprinted by permission from Springer Nature Customer Service Centre GmbH: Springer Nature Journal of Mining Science Flotation as the Subject-Matter of Supramolecular Chemistry, Kurkov, A. V.; Pastukhova, I. V., 2010.

Phospholan PE65 probably forms similar structures in solution. The diester molecules contained in phospholan PE65 provide an increase in surface pressure at low concentrations of the reagent, but at the same time, increase the aggregation ability of the reagent. The presence of sodium oleate, on the other hand, allows neutralizing this disadvantage. Oleate ions disperse molecular aggregates of phospholan PE65

in the solution, which leads to increased reagent sorption on the mineral surface and also facilitates the formation of mixed molecular structures with weaker dispersion interactions. These structures are more active in relation to the "liquid−gas" surface, which contributes to their effective spreading on the mineral surface and removal of the liquid layer between the gas bubble and the solid phase of apatite. This assumption is also confirmed by kinetic experiments. The use of collectors with different structures of hydrocarbon radicals provides a uniform adsorption layer on the mineral surface due to their adsorption in areas with different surface energy.[18]

4. CONCLUSIONS

In this work, the effect of sodium oleate, phospholan PE65, and their mixture on flotation of a monomineral fraction of apatite was studied. It was found that the mixture of the above reagents has a synergetic effect in relation to the mineral surface of apatite during foam flotation. The maximum synergetic effect was observed at a ratio of reagents phospholan PE65 and sodium oleate of 4−1. Using infrared spectroscopy and surface tension measurements, an explanation for the observed synergism was proposed. Synergism occurs due to mutual amplification of reagent sorption as well as to the formation of molecular ensembles of a mixed composition at the liquid−gas interface. The high activity of the molecules at this interface provides effective removal of the liquid layer, which leads to an increase in the contact area of the gas bubble with the ore surface and, as a consequence, an increase in the extraction degree.

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Notes

The authors declare no competing financial interest.

ADDITIONAL NOTES

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