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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Influence of the Composition and Structure of α-Alkyldicarboxylic Acids on the Mineral Surface Hydrophobization under Flotation Conditions

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Abstract—The hydrophobization effect of α-alkyldicarboxylic acids in microflotation of pure apatite variety was examined in relation to the alkyl radical length, the total length of the hydrocarbon chain and the positional relationships of the carboxy groups in the molecule, and the presence of calcium cations in the liquid phase of suspension. These findings were compared with the analogous data for saturated monocarboxylic acids and unsaturated oleic acid.

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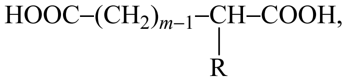
Our previous studies [1, 2] demonstrated that α-alkyldicarboxylic acids (DAs) with a total of 14–21 carbon atoms in the hydrocarbon chain are suitable as collecting reagents for flotation of apatite- and kyanite-containing ores. At the same time, it was shown that the collecting power of the DAs widely varies with the composition and structure of their molecules, pH, and ionic composition of the liquid phase of the flotation pulp, in particular, depending on the presence of calcium ions in it. These features of the flotation behavior of DAs are associated with variation in their physicochemical and surface properties, manifested both in the bulk of the liquid phase and at the water–air and water–mineral particle interfaces, and call for scientific substantiation.

We studied earlier the surface activity of Na and Ca salts of the examined DAs at the water–air interface and their micellization ability in alkaline aqueous solutions [3]. It was found that these properties are decided by the alkyl radical length, position of the second carboxy group in the hydrocarbon chain of the DA, and the associated ability for forming calcium compounds with various structures.

Here, we elucidated the trends in the hydrophobization effect exerted by DAs with various compositions on the mineral particle surface as manifested under flotation conditions. This will allow the substantiation of the choice of DAs with the structures best suited for the collector application and identifying their efficient application spheres.

EXPERIMENTAL

The surface activity of branched dicarboxylic acids at the solution–mineral particle interface was studied with the synthesized α-alkyldicarboxylic acids of the general formula



$$\mathrm{HOOC{-}(CH_2)_{\mathit{m}-1}{-}\underset{\displaystyle R}{\underset{|}{C}}H{-}COOH},$$

where R is the alkyl radical, from C_3H_7– to $C_{18}H_{37}$–, and m = 1–11 (see the table). For characteristics of these acids, see [3].

The surface activity of the acids was assessed from their hydrophobization effect on the monomineral fraction of apatite with the particle size from –0.16 to +0.1 mm, determined by the yield of the mineral in foamless flotation in the Hallimond tube.

Flotation conditions: apatite weighed portion 0.5 g; suspension volume 100 ml; air flow rate 5.3 ml $\mathrm{min^{-1}}$; pH adjuster H_2SO_4, NaOH; time of agitation with pH adjuster 1 min; time of agitation with collector 3 min; flotation time 3 min; flotation temperature 20 ±1°C.

α–Alkyldicarboxylic aliphatic acids

Acid	R	Symbolic designation C_{n-m}–DA[a]
α -Dodecylmalonic	$C_{12}H_{25}$	C_{13-1}–DA
α-Tridecylmalonic	$C_{13}H_{27}$	C_{14-1}–DA
α-Hexadecylmalonic	$C_{16}H_{33}$	C_{17-1}–DA
α-Octylsuccinic	C_8H_{17}	C_{10-2}–DA
α-Tetradecylsuccinic	$C_{14}H_{29}$	C_{16-2}–DA
α-Hexadecylsuccinic	$C_{16}H_{33}$	C_{18-2}–DA
α-Octadecylsuccinic	$C_{18}H_{37}$	C_{20-2}–DA
α-Decyladipic	$C_{14}H_{29}$	C_{17-3}–DA
α-Tetradecyladipic	$C_{10}H_{21}$	C_{14-4}–DA
α-Tetradecylglutaric	$C_{14}H_{29}$	C_{18-4}–DA
α-Tetradecylazelaic	$C_{14}H_{29}$	C_{21-7}–DA
α-Propylbrasilic	C_3H_7	C_{14-11}–DA
α-Octlybrasilic	C_8H_{17}	C_{19-11}–DA

[a] *n* is the total number of carbon atoms in the hydrocarbon chain of DA, and *m*, the number of carbon atoms separating the carboxylic groups.

The collecting power of the DAs was studied in alkaline (pH 10.0) and acid (pH 5.3–5.8) media and compared with that of monocarboxylic aliphatic acids, saturated (lauric, myristic, palmitic, and stearic) and unsaturated (oleic). In all the cases we used aqueous solutions of sodium salts of the carboxylic acids with pH ~10, prepared by saponification of the acids with sodium hydroxide (the term “carboxylic acid” is used here conditionally).

The hydrophobization effect of the examined acids as influenced by calcium ions was studied for two modes of supply of the latter. In mode *I*, the calculated amount of calcium chloride solution was added to the mineral suspension, the resulting mixture was agitated for 1 min, and the equivalent amount of the collector was added. The mixture was agitated for 2 min, after which flotation was carried out. In mode *II*, the preset equivalent amounts of solutions of calcium chloride and sodium salt of carboxylic acid were preliminary poured together and agitated for 1 min. The resulting mixture was fed into the apatite suspension with specific pH and mixed for 3 min, after which flotation was run.

Considering high rate of formation of calcium oleate in dilute solutions [4], we can suggest that mixing of more concentrated solutions containing Ca^{2+} and carboxylate ions of the examined acids yields virtually instantaneously their calcium salts which participate in flotation.

Mode *I* more adequately models the real conditions of apatite flotation from ore. Specifically, calcium ions can be partially adsorbed on the mineral surface, and the calcium salt can be formed both in the bulk of the liquid phase and at the water–mineral particle interface.

Figure 1 presents the concentration dependences of the flotability of apatite by Na salts of saturated mono- and dicarboxylic acids (with alkylsuccinic acids as an example). These plots suggest that, at comparable hydrocarbon chain lengths, they differ in the hydrophobization effect. In alkaline region (pH 9.8) where the salts are virtually completely dissociated, the hydrophobization effect of monocarboxylic acids tend to naturally increase with hydrocarbon radical size increasing from C_{11} to C_{15} and subsequently to decrease (for sodium stearate). Baldauf et al. [5] revealed a similar dependence and explained it as follows. The hydrocarbon chain lengthening causes enhanced association of the molecules in solution with formation of dimers and micelles characterized by lower flotation activity. Alkylsuccinic acids do not display such extremal run, and acids with ≥17 total carbon atoms in the hydrocarbon chain (C_{18-2}-DA, C_{20-2}-DA) exert a stronger hydrophobization effect. This is associated with higher solubility and weaker tendency for association for the Na salts of these acids [3]. Our data suggest that, for the homologous series of alkylsuccinic acids whose carboxylic groups are separated by two carbon atoms, the hydrophobization effect is decided by the hydrocarbon radical length. Similar results and conclusions were obtained for a series of alkylmalonic acids and can be extended to other homologous series of DAs.

The difference in the hydrophobization effect from mono- and dicarboxylic acids in flotation is most prominent for acid media where acids occur predominantly in the acid form (Fig. 1, pH 5.3–5.8). For saturated monocarboxylic acids, the flotability of apatite tends to sharply decrease with hydrocarbon radical lengthening, and in the case of stearic acid no flotation is observed. The DAs exhibit an opposite trend: $C_{17-1} > C_{14-1}$, $C_{16-2} \gg C_{12-2}$, and their flotation activity exceeds by more than order of magnitude that of monocarboxylic acids with the hydrocarbon chain

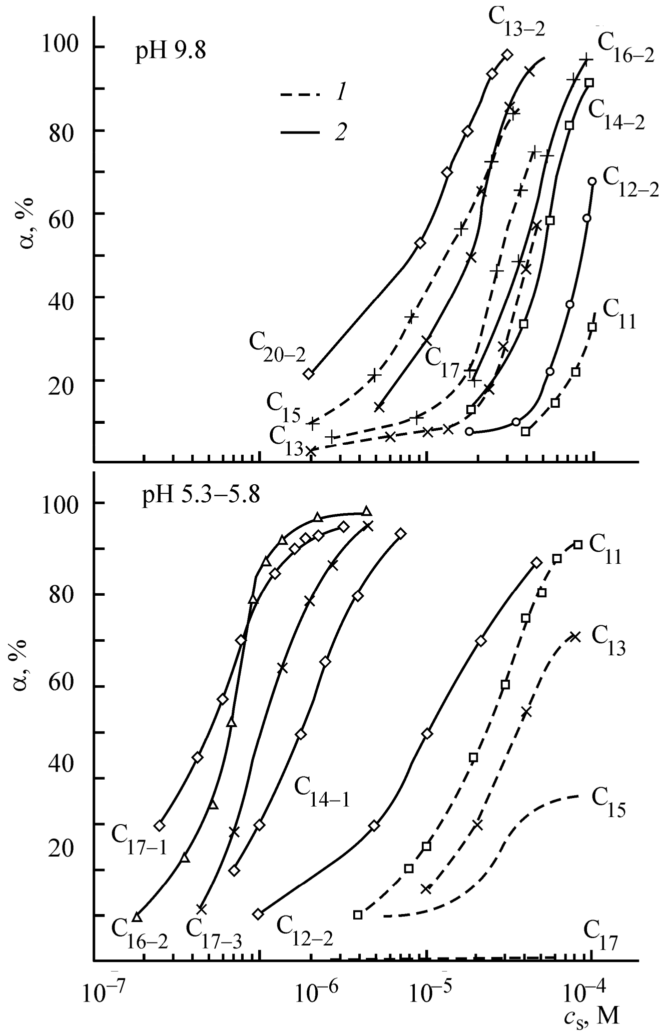


Fig. 1. Flotability of apatite by sodium salts of saturated (*1*) mono- and (*2*) dicarboxylic acids. Monocarboxylic acid: C_{11} lauric, C_{13} myristic, C_{15} palmitic, and C_{17} stearic. Dicarboxylic acid: C_{14-1}, C_{17-1}, C_{12-2}, C_{14-2}, C_{16-2}, C_{18-2}, C_{20-2}, and C_{17-3}. (α) Apatite yield and (c_s) salt concentration; the same for Figs. 2–5, 7.

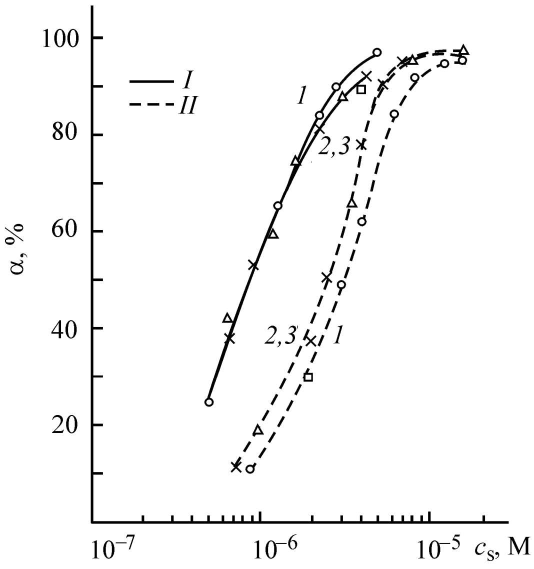


Fig. 2. Flotabilty of apatite with sodium oleate (*1*) without and (*2, 3*) with Ca^{2+} in the equivalent concentration for modes *I* and *II*, respectively; the same for Figs. 4, 5, 7. pH: (*I*) 5.8 and (*II*) 9.8.

of the same length. The revealed difference is associated with higher (by 1–2 orders of magnitude) solubility of DAs compared to monocarboxylic acids with identical hydrocarbon chain lengths [6].

Considering high hydrophobization effect of DAs, it is expedient to compare this effect with that of oleic acid, an efficient collector in flotation of nonsulfide minerals. The double bond in the oleic acid molecule (ΣC_{18}) at the C8 atom and its spatial isomerism are responsible for better, compared to saturated palmitic (ΣC_{16}) and stearic (ΣC_{18}) acids, solubility of salts, a weaker tendency to micellization, and a higher (by an order of magnitude) activity (Figs. 1, 2) both in alkaline and acid media. The hydrophobization effect of oleic acid at pH 5.8 is 3–4 times that in the alkaline medium.

The plots in Fig. 3 characterize the hydrophobization powers of Na salts of the DAs with a total of 17–21 carbon atoms in the hydrocarbon chain, which is comparable with that in oleic acid. It is seen that the flotation activity of the acids is affected by the position of the second carboxy group and the number (even or odd) of carbon atoms separating the COOH groups. This effect is most prominent in alkaline media (pH 10). Specifically, (1) for close in length hydrocarbon radicals R in α-position (C_{14}–C_{16}) the DAs with odd numbers of carbon atoms separating the carboxy groups (C_{17-3}, C_{21-7}) exhibit higher activities than do the DAs with even numbers (C_{18-2}, C_{18-4}); (2) the hydrophobization effect tends to decrease with increaseing distance separating the carboxy groups in the DAs across the series $C_{17-3} > C_{21-7} >> C_{19-11}$ and $C_{18-2} > C_{18-4}$ because of weakening of the hydrophobic interaction of the hydrocarbon radicals in the adsorption layer; (3) the length of the hydrocarbon radical R in α-position of the DA molecule, like in monocarboxylic acids, is of deciding importance for the hydrophobization effect; and (4) despite the saturated hydrocarbon chains they comprise, the DAs with the optimal composition exhibit a hydrophobization effect identical to that of oleic acid.

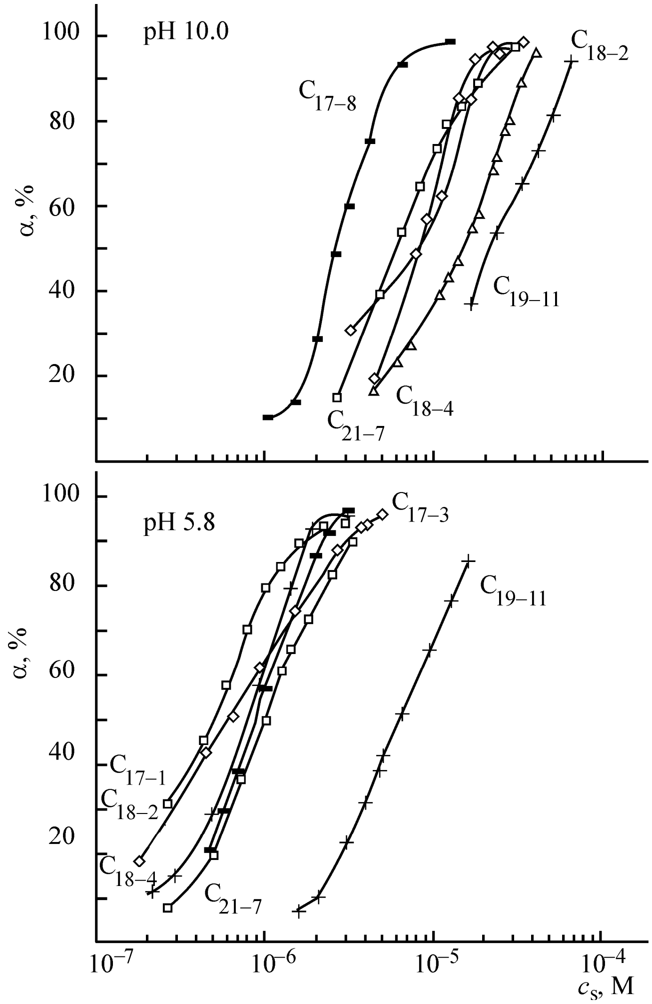


Fig. 3. Flotabiliy of apatite by sodium salts of C_{17}–C_{21} dicarboxylic acids.

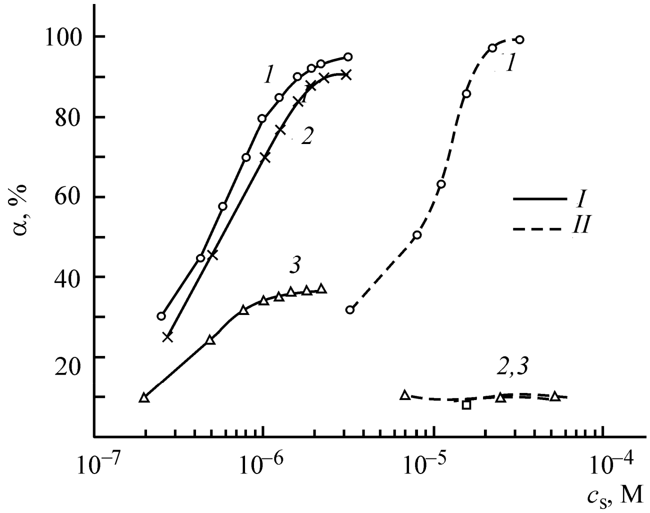


Fig. 4. Influence of Ca^{2+} on the flotability of apatite by sodium salt of C_{17-1}-DA. pH: (*I*) 5.8 and (*II*) 10.0; the same for Figs. 5, 7.

In acid media (Fig. 3, pH 5.8) the composition and structure of the DAs are of lesser significance for the hydrophobization effect; it is close to that of oleic acid for all the DAs. A slightly higher flotation activity, especially at low concentrations, is exhibited by DAs with 1,1 and 1,2 position of carboxy groups. These acids are characterized by higher dissociation constants because of the inductive effect exerted by the second carboxy group [6].

We examined the hydrophobization effect of the acids in the presence of calcium cations. Saturated C_{11}–C_{17} carboxylic acids are known to be highly sensitive to hardness salts. This fact was validated by our data concerning the influence of Ca^{2+} ions in alkaline media on the flotation activity of these acids: The most active among the salts of examined monocarboxylic acids, Na salt of palmitic acid, at pH 9.8 (Fig. 1, pH 9.8) in the presence of the equivalent amount of calcium cations (mode I) exhibit negligible flotation of apatite. This is associated with the formation of poorly soluble (2.8×10^{-6} M) calcium palmitate [8]. In acid media (Fig. 1, pH 5.3–5.8) the highest flotation activity is exhibited by lauric acid, and calcium cations render negligible effect till their content in the liquid phase of the suspension is increased 10-fold.

Oleic acid exhibits a similar effect in acid media in the presence of calcium ions (Fig. 2, pH 5.8). A certain decrease in the yield of apatite with increasing oleic acid concentration is associated with major flocculation of the mineral. In alkaline media (Fig. 2, pH 10) the equivalent amount of calcium causes certain activation of the apatite flotation by oleic acid. A reason can be found in calcium adsorption on the apatite surface and formation of additional reactive centers [8]. Whatever the mode of introduction of Ca^{2+} into suspension, an increase to 10 in the ratio of the number of equivalents of Ca^{2+} to sodium oleate did not cause an appreciable decrease in the apatite flotability. This fact contradicts the available practical data on a lower flotation activity of calcium oleate compared to sodium oleate. The reason is that the actual calcium oleate concentrations under microflotation conditions, $(6–8)\times10^{-6}$ M, do not exceed its solubility, $(0.94–1.34)\times10^{-5}$ M, i.e., calcium oleate occurs in the dissolved and dissociated state.

Examination of the hydrophobization effect exerted by the DAs in the presence of Ca^{2+} showed that it depends on the positional relationships of carboxy groups in the DA molecule, most strongly in alkaline

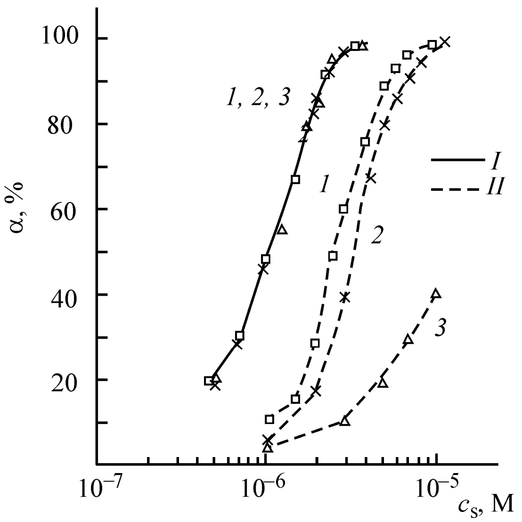


Fig. 5. Influence of Ca^{2+} on the flotability of apatite by sodium salt of $C_{17–3}$-DA.

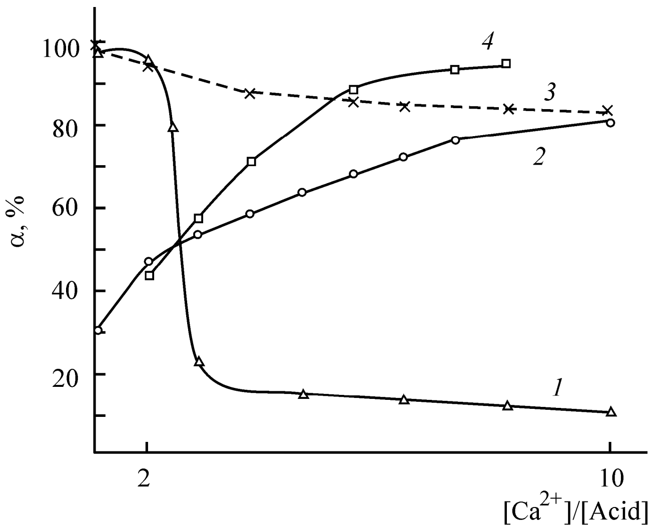
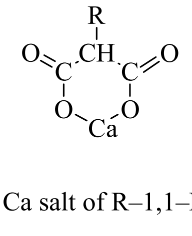


Fig. 6. Influence of the $[Ca^{2+}]$/[Acid] equivalent ratio on the flotability of apatite at pH 10.0. Concentration of Na salt of acid, M: (*1*) 4.5×10^{-6} $C_{17–3}$-DA, (*2*) 7.2×10^{-6} $C_{18–4}$-DA, (*3*) 6.3×10^{-6} oleic acid, and (*4*) 4.5×10^{-6} $C_{21–7}$-DA.

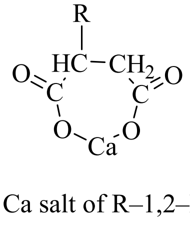
media. Based on the revealed properties, the examined DAs can be subdivided into three groups, namely, those with carboxy groups in 1,1-1,2-, 1,3-, and 1,4-1,11-positions.

Figures 4–7 show the characteristic concentration dependences of the flotability of apatite, with representatives from each of these groups taken as examples. Figure 4 suggests negligible flotation of apatite by DAs with close positions of carboxy groups (1,1-, 1,2-) in alkaline media in the presence of the equivalent amount of calcium cations in the liquid phase of the suspension. The same is true of the DAs supplied in the form of a calcium salt. Our data are consistent with the earlier established fact that, at pH 10–11, the calcium salts of these acids do not exhibit surface activity at the water–air interface [3].

This is evidently due to formation of poorly soluble chelates in the liquid phase of suspension. They are similar to the cyclic compounds formed by unsubstituted 1,1–1,3-DAs (malonic, succinic, glutaric) with strontium cation [9]:



Ca salt of R–1,1–DA



Ca salt of R–1,2–DA

Figure 5 presents the concentration dependences for $C_{17–3}$-DA with the carboxy groups separated by three carbon atoms. By contrast to DAs with carboxy groups in 1,1-1,2 positions, $C_{17–3}$-DA exhibits flotation of apatite in the presence of equivalent amount of calcium cations, but its activity is strongly dependent on the mode of supply of $CaCl_2$. In mode I, the activity of $C_{17–3}$-DA is close to that without calcium cations (Fig. 5, curves *1, 2*). When Ca salt of $C_{17–3}$-DA is supplied (mode *II*), the flotability of apatite is much lower (Fig. 5, curve *3*). This specific behavior of $C_{17–3}$-

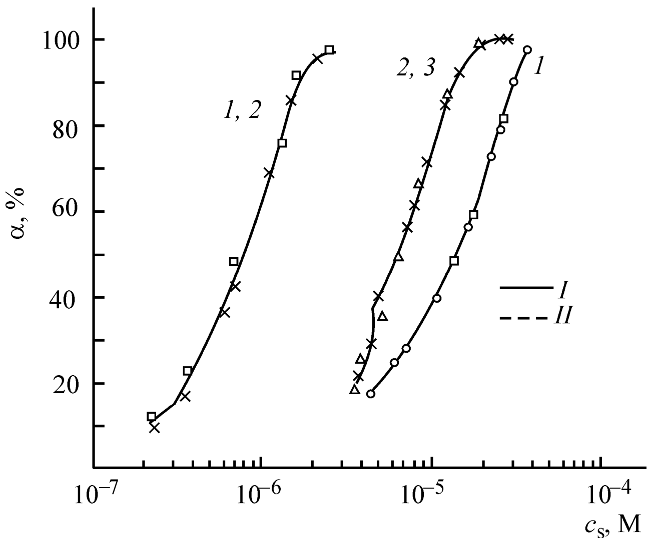


Fig. 7. Influence of Ca^{2+} on the flotability of apatite by sodium salt of $C_{18–4}$-DA.

DA in alkaline media is explained as follows. Despite hardly probable formation of strong eight-membered cyclic compounds with calcium, the resulting calcium salt is characterized by low solubility. This conclusion is supported by the fact that an increase in the calcium cation concentration in suspension beyond the equivalent level (mode *I*) results in a sharp decrease in the flotability of apatite (Fig. 6, curve *1*).

Figure 7 shows the typical concentration dependences for DAs with the carboxy groups separated by ≥4 carbon atoms ($C_{18–4}$, $C_{21–7}$, $C_{19–11}$), with $C_{18–4}$-DA as an example. These data suggest that, in alkaline media, calcium ions in solution cause the hydrophobization effect exerted by DAs with this composition to increases, specifically, to an extent exceeding that in the case of oleic acid (Fig. 2). By contrast to the latter (Fig. 6, curve *3*), with calcium cations in amount exceeding their equivalent concentration by a factor of up to 8, the DAs exhibit an enhanced hydrophobization effect on apatite (Fig. 6, curves *2, 4*). This can be associated with lower cmc values for them [3], as well as with interaction of both carboxy groups with the mineral surface activated by calcium ions and acyclic structure of the resulting calcium compounds [9].

The data on apatite flotation by DAs of different composition in acid media (pH 5.8) suggest that, in the presence of calcium ions, these acids behave differently (Figs. 4, 5, 7). In mode *I*, calcium cations have no influence on the hydrophobization effect of DAs, in particular, when in amounts up to 10 times exceeding the equivalent concentrations. The hydrophobization effect of calcium salts of DAs (mode *II*) with the COOH groups separated by three carbon atoms is identical to that of the sodium salts (Figs. 5, 7), with excess calcium cations having no influence as well. The calcium salts of DAs with COOH groups in 1,1- and 1,2-positions (mode *II*), by contrast to their behavior in alkaline media, exhibit flotation of apatite, but their flotation activity is lower than that of the sodium salts (Fig. 5). This is associated with the stability of the preliminary obtained calcium complexes and their low solubility. Our data on the hydrophobization effect in the presence of calcium cations of DAs with different compositions in acid media and the determined stability constants of calcium complexes for α,ω-DAs with carboxy groups in identical positions [10] suggest low stability of the calcium compounds of all the DAs, formed in acid media. The established pH-dependence of complexing is consistent with the known ability of alkaline-earth cations to form stable complexes in solutions at pH > 7 [11].

Comparison of the hydrophobization properties exhibited in alkaline media by mono- and dicarboxylic acids in the presence of calcium ions shows the following. Introduction of a second carboxy group into the molecule of saturated monocarboxylic acid into position in which the COOH groups are separated by more than three carbon atoms renders an effect considerably surpassing that in the case of unsaturated bond (oleic acid) and increases the flotation activity of DAs in the presence of calcium cations. Earlier [3], we derived a similar conclusion about the surface activity at the gas–liquid interface and micelliazation powers of solutions of the compared acids.

CONCLUSIONS

(1) The deciding role in the hydrophobization of the surface of a mineral (with apatite as an example) by α-alkyldicarboxylic acids is played by the alkyl radical length and the positional relationships of the carboxy groups. At identical total lengths of the hydrocarbon chains, the hydrophobization effect is the weaker, the larger the distance separating the COOH groups.

(2) The α-alkyldicarboxylic acids with odd numbers of carbon atoms separating the COOH groups exert a stronger hydrophobization effect than do the corresponding acids with even numbers.

(3) The hydrophobization effect of α-alkyldicarboxylic acids is much stronger than that of monocarboxylic acids with identical numbers of carbon atoms in the hydrocarbon chain. This is due to a higher solubility of the former and a weaker tendency for association in solution, as well as possible interaction of both carboxy groups with the mineral surface.

(4) The calcium cations have a negligible impact on the hydrophobization effect exerted by dicarboxylic acids of different composition in acid media. However, in alkaline media they affect significantly the behavior of dicarboxylic acids because of formation of calcium compounds with different structures and solubilities.

(5) In the presence of calcium ions, the second carboxy group introduced into the saturated monocarpboxylic acid molecule affects hydrophobization much more stronger than do unsaturated bond (oleic acid).

(6) The data obtained will be helpful in choosing dicarboxylic acids with compositions and structures

best suited for application as collecting reagents, as well as in providing theoretical substantiation of their suitability for ore flotation in water characterized by increased content of hardness of salts.

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