

THERMAL ANALYSIS OF THE INTERACTION BETWEEN STEARIC ACID AND PYROPHYLLITE OR TALC. IR AND DTA STUDIES

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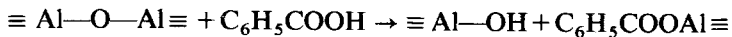
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Pyrophyllite and talc sorb stearic acid on edge surfaces. The grinding of clay-stearic acid associations in the presence of alkali halides converts some of the acid into the ionic form, this occurring more readily with talc than with pyrophyllite. Heating in a closed or semi-closed system causes dissociation of stearic acid adsorbed on talc, but not on pyrophyllite. The infrared absorption frequencies of the adsorbed ionic form vary with the clay mineral and the amount of water present. The thermal stabilities of the clay-stearic acid associations depend on the rate of escape of the acid, which is determined by the strength of bonding to the clay and the nature of the system, and on the degree of dissociation of the acid on the clay surfaces.

The adsorption of fatty acids by clays is of considerable interest because of the possible catalytic effect of these minerals on the conversion of fatty acids to petroleum hydrocarbons. It is to be expected that the nature of the adsorption complexes formed affects the course of thermal decomposition of the organic material. The adsorption of fatty acids may also play a part in petroleum migration by converting organophobic into organophilic pores [1]. A comprehensive study was therefore undertaken to compare the adsorption of fatty acids by a wide range of clay minerals, to establish the nature of the complexes formed and to investigate the thermal decomposition of the clay-fatty acid associations under different experimental conditions [2-5].

Very little is known about the processes which take place during abrasion of minerals in the presence of organic matter (mechanochemical reactions). Yariv et al. [6] established that, when benzoic acid is ground with calcined alumina or calcined kaolinite, benzoate ions are formed and sorbed on the mineral surfaces by the reaction:



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No benzoate ions were formed on grinding benzoic acid with celite, because the functional groups Si—O and Si—OSi exposed on the surfaces of silica are weaker bases than the benzoate ions and do not accept protons from benzoic acid [7].

All clay minerals sorb fatty acids on crystal edges, but pyrophyllite and talc occupy a unique position among the minerals studied, because adsorption is likely to occur predominantly on edge surfaces, due to the negligibly weak basic strength of the siloxane surfaces. As magnesium is less electronegative than aluminium, it may be expected that the edges of trioctahedral clays are more basic than those of dioctahedral ones.

Characterization of the complexes formed with pyrophyllite and talc will help to distinguish edge adsorption from that on different sites of other clay minerals and to determine the contribution of this effect to the thermal stability of the acids. The effect of the environment on the course of the thermal changes must also be considered.

Experimental

Materials

Pyrophyllite, Newfoundland, Canada, HU collection

Talc, Urals, USSR, HU collection

Stearic acid from Merck

Procedure

Clay-stearic acid associations were prepared as follows: mixtures of 1 part clay with 5 parts stearic acid, by weight, were heated in closed vessels at 100° for 72 hours. The molten acid was adsorbed on the clay, ensuring uniform distribution. The samples, after cooling, were washed with hexane to remove non-adsorbed acid. Samples washed once (C-S 1), three times (C-S 3) and five times (C-S 5), respectively, i.e. samples that contained various amounts of stearic acid, were thereby obtained. More exhaustive washing removed the organic material entirely. Unless otherwise stated, experiments were carried out with samples C-S 3, P-S 3 and T-S 3, designating clay in general, pyrophyllite and talc, respectively.

Heating in open systems. a) Samples of C-S 3 in the form of loose powders were heated in open crucibles in air at 190° for 24 hours. b) Mixtures of clay and stearic acid were heated in a CDS 820ZA pyroanalyzer under a stream of N₂ for 1 hour at 250° [5].

Heating in alkali halide pellets. Two series of alkali halide pellets were studied:

For the *first series*, 200 mg of NaCl, KCl or KBr or 150 mg CsCl was ground manually for 5 minutes with 3 mg of the clay-stearic acid association and pelleted. After the IR spectra had been recorded, the disks were crushed, ground for another 5 minutes and pelleted again. This process was repeated another 3 times. The resulting disks were heated for 8 days at 110° and at 190° and 18 hours at 250° and 300°, respectively. After each thermal treatment the disks were cooled, and pressed carefully without crushing, and the IR spectrum was recorded using a Perkin-Elmer 457 IR spectrophotometer.

For the *second series*, KBr pellets of samples of C-S 3 were prepared without grinding. Ground, dry KBr was carefully mixed with the clay organic association without crushing and pelleted. The pellets were heated at 250° for various periods of time. FTIR spectra were recorded on an Analect FX 6100 instrument.

Heating in closed systems. Aliquots of C-S 3 were sealed into ampoules under N₂ and maintained at 250° for 48 hours. The IR spectra of the residues were recorded.

DTA curves were obtained on a Stone instrument, at a heating rate of 10 deg/min, in air. Acid or clay-acid associations were diluted with alumina. Some samples were also mixed with KBr. Weights of samples and diluent are indicated in the Figure captions.

Results and discussion

IR SPECTRA

Samples heated in open systems

Under the conditions of the experiments, no organic matter was retained by the clays after the thermal treatment.

Samples heated in alkali halide disks

Alkali halide disks simulate a closed or semi-closed environment in which the organic material was retained to higher temperatures (250° and above). Abrasion enhanced the interaction between clays and stearic acid, but to reduce the destructive effect on the structure of the minerals, the organo-clays were ground with excess alkali halide [8]. However, the presence of alkali halides may introduce complicating factors, which must be taken into account when the data are interpreted. To facilitate distinction between the effects due to the clay minerals and to the salts, different alkali halides were used (NaCl, KCl, KBr and CsCl). Alkali halide disks containing only stearic acid without any clay were also examined. The spectra obtained with the two clay associations differed significantly from each

other and from those of similarly heated pellets of neat stearic acid. In contrast, only minor differences (see below) were observed in the spectra of either talc or stearic acid associations with the four alkali halides. It was therefore concluded that the spectra obtained after the various heat treatments of the clay-stearic acid associations principally reflect the influence of the clay minerals and were not basically affected by the presence of the alkali halides.

Clay minerals sorb stearic acid in the acidic (RCOOH) and in the anionic (RCOO⁻) form [3, 4, 9–12]. Spectra of disks of pyrophyllite or talc-stearic acid associations which were prepared by gentle mixing showed COOH but no COO⁻ absorptions at room temperature. On regrinding of the disks, COO⁻ absorptions appeared (Table 1). Very minor amounts of stearate ions were also formed when

Table 1 COOH and COO⁻ absorptions in selected spectra of C-S samples in ground KBr disks (cm⁻¹)

	Pyrophyllite			Talc		
	105°	150°	250°	105°	190°	250°
COOH	1660sh	1660sh	1660	1668sh	1668sh	1668sh
	1703	1703		1706	1706	1705
	1730sh	1730sh		1720sh	1720sh	
COO ⁻	1546	1580	1580–1640	1580	1560sh	
	1581				1573	1573br
					1580sh	

Abbreviations: sh — shoulder; br — broad

neat stearic acid was ground with alkali halides, but the shape and position of the corresponding absorption bands differed from those obtained in the presence of clays.

COOH absorptions. With pyrophyllite a broad COOH absorption appeared, maximum at 1703 cm⁻¹, with a shoulder at 1730 cm⁻¹. It disappeared at 250°, indicating that the acid which is represented by this absorption escaped at this stage of the thermal treatment.

The spectrum of the ground KCl disk showed a shoulder at 1660 cm⁻¹ on the H₂O bending absorption at 1635 cm⁻¹. This band was also observed in the spectra of the other alkali halide disks after these were dried at 110°. It persisted when absorptions at 1700–1730 cm⁻¹ were no longer present, which demonstrates that it represents COOH more closely associated with the clay than the rest of the acid.

With talc the COOH absorption occurred at 1695–1710 cm⁻¹, with a weak shoulder at about 1720 cm⁻¹. An absorption at about 1705 cm⁻¹ persisted after

heating of the specimens at 250°, when no absorption band was detected in this region with pyrophyllite.

In addition to the COOH absorption at about 1700 cm⁻¹, a band was observed at 1668 cm⁻¹ in spectra of ground disks, similar to that at 1660 cm⁻¹ with pyrophyllite. It appeared as a shoulder on the H₂O band at 1635 cm⁻¹ in the spectra of the freshly prepared disks, and became more pronounced after water was lost on heating. Like the 1660 cm⁻¹ band in the pyrophyllite samples, the 1668 cm⁻¹ absorption in the talc samples persisted under a thermal regime which caused the absorption in the 1700–1730 cm⁻¹ region to disappear.

COOH groups of neat stearic acid incorporated into alkali halide disks gave rise to an absorption band at 1705 cm⁻¹, which disappeared on heating at temperatures below 190°.

It appears that both pyrophyllite and talc sorb stearic acid through their COOH groups in several forms. According to Yariv and Shoal [3], low frequencies of COOH absorptions are obtained for fatty acids adsorbed by montmorillonite when the acid is directly coordinated to highly polarizing cations. It therefore seems reasonable to assign the absorption at the lower frequency, 1660 cm⁻¹ with pyrophyllite and 1668 cm⁻¹ with talc, to COOH directly coordinated to the edges of the octahedral sheets of the minerals. The fact that the frequencies differ for the two minerals indicates that bonding occurs with the Al and Mg ions of pyrophyllite and talc, respectively, and may be of the type



The intensity of the low-frequency absorption was enhanced on grinding of the samples, when new mineral surfaces were exposed.

The absorptions at higher frequencies, which are slightly variable, probably represent acid molecules trapped in the alkali halide—clay mineral interface. They involve some H-bonding and depend on the amount of water retained in the disks and on the alkali cations, which affects the hydration of the clay surfaces. Association may be through hydrogen bonds to edge functional groups, such as ≡Al—O, ≡Mg—O, ≡Al—OH or ≡Mg—OH, either directly or through water bridges. COOH groups directly coordinated to the clay surfaces are more firmly bound and are therefore lost at higher temperatures.

COO⁻ absorptions. Only the asymmetric stretching vibrations are discussed. The symmetric stretching vibrations of the COO⁻ groups are not considered because they overlap with CH, CO and OH absorptions.

For all the samples examined, grinding of the disks converted some of the stearic acid into stearate ions. This is shown by the appearance of absorptions in the

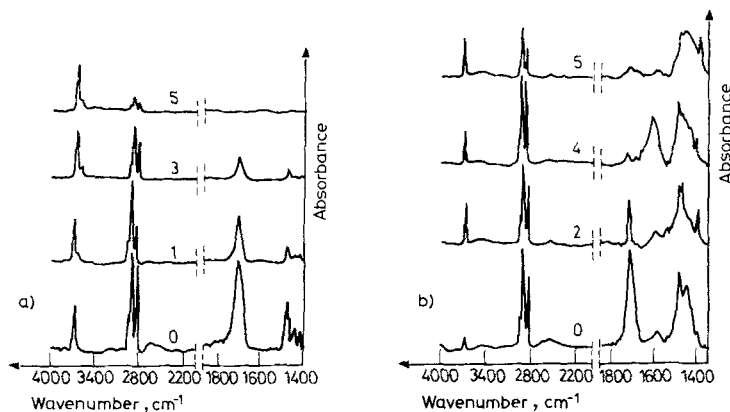


Fig. 1 FTIR spectra of unground KBr disks of a) P-S 3 and b) T-S 3. The numbers on the right indicate the days of heating at 250°

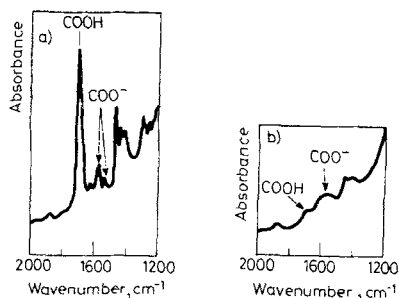


Fig. 2 FTIR spectra of ground KBr disk of P-S 3 a) dried at 105°, b) after heating at 250°

1540–1600 cm^{-1} range, which are very different for talc and pyrophyllite and change on heating of the specimens. Conversion to the ionic form occurs much more readily on grinding in the presence of talc than with pyrophyllite. Moreover, when disks of the pyrophyllite-stearic acid association that had not been ground were heated, no more than traces of ions were detected. In contrast, with unground disks of talc with stearic acid, stearate ions were formed at elevated temperatures. None were observed after heating at 105° for several days, but at 250° the acidic form was gradually converted into the ionic form (Fig. 1).

The spectra of freshly prepared ground disks of P-S showed a tail associated with the 1630 cm^{-1} H_2O absorption, which extended from about 1600 to 1540 cm^{-1} . After dehydration of the disk at 105°, two maxima could be discerned (Fig. 2). On further heating, the absorption became broad. After heating of the disks at 190°, when hydration water still persisted, shoulders appeared at 1590, 1580, 1593 and

1600 cm^{-1} in the spectra of the NaCl, KCl, KBr and CsCl disks, respectively. After heating at 250°, the broad band extended from 1640 to 1580 cm^{-1} . As no absorption band was detected in the 3400 cm^{-1} region, it was inferred that no adsorbed water persisted at this temperature and that the entire 1640–1580 cm^{-1} band must be assigned to adsorbed carboxylate ions.

When stearic acid was ground with talc, ions were formed much more readily than with pyrophyllite. The absorptions were sharper and more intense. Before dehydration of the disks, a band appeared at 1563 cm^{-1} in the spectra, with a shoulder at 1540 cm^{-1} . After partial dehydration of the disks by heating at 105°, the band was shifted and its position depended on the cation of the alkali halide: 1585, 1580 and 1567 cm^{-1} in CsCl, KCl (or KBr) and NaCl, respectively. After further dehydration by heating at 190°, the COO^- band became broad and appeared at 1570–1580 cm^{-1} , at 1582 cm^{-1} with shoulders at 1570 and 1560 cm^{-1} , at 1573 cm^{-1} with shoulders at 1580 and 1560 cm^{-1} , and at 1570–1580 cm^{-1} with a weak shoulder at 1560 cm^{-1} , in the spectra of CsCl, KCl, KBr and NaCl disks, respectively. After heating the ground disks at 250°, the COO^- absorptions were reduced in intensity, but persisted in all the spectra.

The great variability of the frequencies of the COO^- absorptions suggests that the type of bonding depends on the structure of the water layer formed in the mineral—alkali halide interface. This structure depends on three factors: (1) the total amount of water, which decreases with rise in temperature, (2) the size of the alkali cation and halide anion, and (3) the surface acidity of the mineral. The different character of the absorption bands observed for the two minerals may be attributed to the different electronegativities of Mg and Al. The association between the carboxylate group and the less electronegative Mg^{2+} ions is expected to have a more ionic character, giving rise to a relatively sharp band, whereas the more covalent nature of the Al stearate association may lead to surface complexes causing absorption at several frequencies.

CH₂ absorptions. The ratio between the absorbance of the CH_2 band at 2920 cm^{-1} and that of the OH stretching band at 3670 and 3680 cm^{-1} for pyrophyllite and talc, respectively, can be used to estimate the changes in the total amount of organic matter present in samples heated to 110° and above. In unheated samples, adsorbed water interfered in the determination of the intensity of the CH_2 absorbance. A decrease in this ratio on progressive heating of the disks indicates a loss of organic matter. This always occurred at lower temperatures in the presence of pyrophyllite than with talc.

The rate at which the samples were heated also affected the retention of the organic matter when samples of T–S were heated rapidly to 250°. COOH was

converted to COO^- before appreciable amounts of the adsorbed acid escaped. When heating was gradual, much acid was lost before stearate ions were formed.

The unequivocal conclusion from all the experiments is that under similar thermal regimes talc always retained more stearic acid or stearate ions than did pyrophyllite. In the absence of either clay, i.e. with neat stearic acid, loss of the acid occurred at lower temperatures.

Samples heated in closed systems

After heating C-S 3 samples for 48 hours in sealed ampoules at 250° in an inert atmosphere, pyrophyllite did not retain stearic acid or stearate ions, whereas under the same conditions talc did retain both acid and ions. It appears that much of the stearic acid initially adsorbed reacted in the sealed ampoules, but in this system, as in alkali halide disks, talc retained stearic acid and stearate ions more tenaciously than did pyrophyllite.

Differential thermal analysis

Figures 3-5 show DTA curves obtained from clay-stearic acid associations after different treatments, and those of mechanical mixtures of clay and stearic acid. It is apparent that the thermal stability of stearic acid is affected by the presence of the clays. An endothermic peak at 80° is diagnostic of melting of stearic acid. It can be detected in the DTA curves of the clay-stearic acid associations only when the acid is present in large excess, i.e. in sample P-S 1. It was therefore inferred that in samples T-S 1, C-S 3 and C-S 5 all the acid is adsorbed and does not form a separate phase that can be melted. The peak is very weak in the DTA curves of the 1 : 1 mixtures (Fig. 5). This may indicate that adsorption of the acid by the clay occurs in the DTA cell during or before the melting process of the acid.

The exothermic peaks are due to the oxidation of stearic acid. The presence of the clay has a catalytic effect on the oxidation of organic material (Fig. 5). The exothermic peak at 210° , observed with neat stearic acid, does not occur in the DTA curves of samples heated in the presence of the clays. The principal exothermic peak of the neat acid, which has maxima at 373 and 387° , does not appear in any of the pyrophyllite-stearic acid samples and features as a weak peak in the talc-stearic acid mixture only. Comparison of Fig. 5b with 5c shows that the two clays affect the thermal decomposition of stearic acid differently. With pyrophyllite, oxidation of the organic material occurred more abruptly at $325-335^\circ$, while talc retained some of the organic material to higher temperatures, as was also shown by the IR spectra.

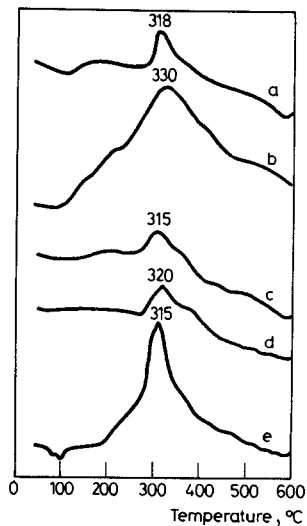


Fig. 3 DTA curves of pyrophyllite-stearic acid associations (recorder range 80 mv). a) Sample P-S 3 [2.5 mg sample + 300 mg Al_2O_3]; b) sample a) ground manually for one minute and together with Al_2O_3 for 4 minutes [2.5 mg sample + 300 mg Al_2O_3]; c) sample a) mixed with KBr and Al_2O_3 [3 mg sample + 150 mg KBr + 150 mg Al_2O_3]; d) sample a) mixed with KBr, pelleted and reground 5 times, then mixed with Al_2O_3 [amounts as in c]; e) sample (P-S 1) [2.5 mg sample + 300 mg Al_2O_3]

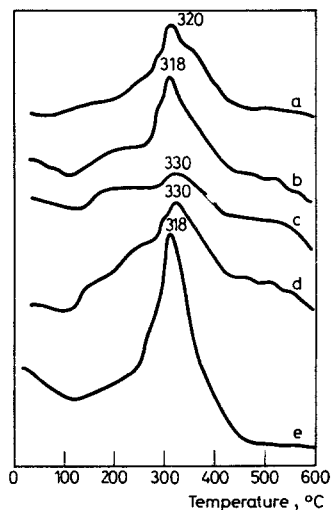


Fig. 4 DTA curves of talc-stearic acid associations (recorder range 80 mv) a)–e) as in Fig. 3

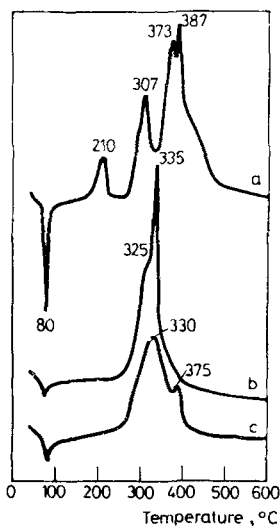


Fig. 5 DTA curves of a) stearic acid (3 mg) + Al_2O_3 (300 mg); b) sample a) + pyrophyllite (3 mg); c) sample a) + talc (3 mg) (recorder range 300 mv)

The area of an exothermic peak depends, in part, on the amount of organic material available for oxidation. As stearic acid has a high vapour pressure, a considerable part of the organic material escaped from the DTA cell before oxidation occurred. The size of the exothermic peaks therefore reflects the amount of organic material retained by the clay.

Grinding of the samples with alumina had a much greater effect on the pyrophyllite than on the talc-stearic acid associations (Figs 3b and 4b). It seems that grinding with the abrasive alumina powder destroyed pyrophyllite more than talc and the product retained more organic material, giving rise to a larger exothermic peak. In general, grinding appears to affect dioctahedral minerals more than trioctahedral ones [7]. In contrast, grinding of the clay-stearic acid complexes with KBr caused a greater increase in the exothermic peak of the talc than of the pyrophyllite complex (Figs 3d and 4d). Infrared spectra showed that the grinding of clay-stearic acid complexes with alkali halides converted some of the acid into the ionic form, and that this occurred more readily with talc than with pyrophyllite. As stearate ions are more firmly retained than stearic acid, an increase in the main exothermic peak of the talc complex was observed.

Conclusions

Talc and pyrophyllite sorb stearic acid in the acid form, but on grinding some of the acid is converted to stearate ions, which are also sorbed by the clays. Conversion to the ionic form occurs more readily in the presence of talc than of pyrophyllite, due to the higher basic strength of the edges of the trioctahedral mineral. Thus, with talc but not with pyrophyllite, conversion to the ionic form also occurs on mere heating of T-S samples in alkali halide disks. Differences in the frequencies of the absorption bands of the clay-stearic acid and stearate associations indicate that the strengths of the bonding to the two clays differ. Both IR spectra and DTA showed that talc retains the organic material to higher temperatures than pyrophyllite in the acid as well as in the ionic form.

These conclusions are compatible with the results of a previous study in which the degree of decarboxylation of stearic acid was determined in the presence of various clay minerals, including talc and pyrophyllite. The experiments were carried out in an open, inert system in which the products were constantly removed from the reagents [5]. The degree of decarboxylation was considerably higher in the presence of talc than of pyrophyllite. This may be due in part to the stronger adsorption of stearic acid by talc observed in the present study, which would cause a longer residence time of the organic material in the pyroprobe chamber, facilitating decarboxylation. However, this is probably not the decisive factor, because the increased residence time of various carboxylic acids caused by the presence of montmorillonite did not increase the degree of decarboxylation [2]. It seems, therefore, that the different type of bonding to the clay surfaces affects the course of the thermal decomposition reaction of stearic acid with the two minerals.

The experiments demonstrate the importance of the environment for the course of the thermal reactions. In an open system, the organic material was lost before strong interaction occurred with the mineral surfaces. In closed ampoules, stearic acid reacted to give various products (unpublished) and only the more basic talc retained some COOH and COO⁻ groups. In the semi-closed environment of alkali halide disks, and under the influence of the adjacent alkali halides, stearic acid and stearate ions were much more strongly retained on the clay surfaces than in either of the other systems and various adsorption complexes were formed.

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Zusammenfassung — Pyrophyllit und Talk adsorbieren Stearinsäure an den Kantenoberflächen. Beim Verreiben von Ton-Stearinsäure-Assoziaten in Gegenwart von Alkalihaliden wird ein Teil der Säure in die ionische Form überführt, und zwar leichter mit Talk als mit Pyrophyllit. Aufheizen im geschlossenen oder halbgeschlossenen System bewirkt eine Dissoziation der an Talk, aber nicht der an Pyrophyllit adsorbierten Stearinsäure. IR-Absorptionsfrequenzen der adsorbierten ionischen Form sind abhängig vom Tonmineral und der anwesenden Wassermenge. Die thermische Stabilität der Ton-Stearinsäure-Assoziate hängt von der Geschwindigkeit der Abgabe der Säure ab, die durch die Stärke der Bindung an das Tonmineral, also der Natur des Systems, und durch den Dissoziationsgrad der Säure an der Tonmineraloberfläche bedingt ist.

Резюме — Пирофиллит и тальк по краям своих поверхностей сорбируют стеариновую кислоту. Размол ассоциатов глина-стеариновая кислота в присутствии щелочногалоидных солей превращает кислоту в ионную форму, причем с тальком более легко, чем с пирофиллитом. Нагревание в закрытой или полужакрытой системе вызывает диссоциацию стеариновой кислоты, адсорбированной на тальке, но не на пирофиллите. ИК полосы поглощения адсорбированной ионной формы стеариновой кислоты изменяются в зависимости от глинистого минерала и присутствующей там воды. Термоустойчивость ассоциатов глина — стеариновая кислота зависит от скорости выделения кислоты, которая определяется энергией связи с минералом и типом системы, а также от степени диссоциации кислоты на поверхности глины.