Clays and Clay Minerals, 1970, Vol. 18, pp. 97–105. Pergamon Press. Printed in Great Britain

ADSORPTION OF SURFACTANTS ON MONTMORILLONITE

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(*Received* 22 *October* 1969)

Abstract—Some authors have stated that anionic surfactants are not adsorbed by montmorillonite while others indicate very minor adsorption. Attempts to quantitatively determine the degree of adsorption have shown that certain problems exist which, unless recognized, will completely mask results. Some of these difficulties have been overcome but exact data have not yet been obtained. However, enough information has been gathered to prove that adsorption of anionic surfactants on montmorillonite is real and substantial. Reliable adsorption data for cationic and nonionic surfactants and one having both nonionic and anionic character have been obtained. It is indicated that 550 mg of these surfactants are adsorbed by 1 g of montmorillonite. X-ray diffraction data for complexes of all surfactants investigated confirm positive adsorption. However, the thickness of the adsorbed surfactant layers cannot always be quantitatively related to the amount of adsorbed surfactant.

INTRODUCTION

A MULTITUDE of organic chemicals are adsorbed by montmorillonite to form what are called organo-montmorillonite complexes. The adsorption mechanism and how strongly the organic molecules are bonded to montmorillonite depend on the structure of the chemical and the type and number of polar functional groups present. Montmorillonite carries a negative charge which attracts the positively charged cationic molecules. Thus, cationic surfactants are adsorbed by montmorillonite primarily by electrostatic forces. Nonionic organic chemicals, such as nonionic surfactants, are also adsorbed by montmorillonite, but the adsorption mechanism here is due to hydrogen bonding and van der Waals' attraction forces. A general opinion has developed that anionic surfactants are not adsorbed by montmorillonite. However, it is known that inorganic anions are adsorbed at the positive sites on the edges of montmorillonite crystals and it could be theorized that anionic surfactants would be similarily adsorbed. The degree of adsorption at these sites would be relatively minor as compared to cationic surfactant adsorption.

Physical evidence has been reported that confirms the opinion that anionic surfactants are not adsorbed by this clay. For example, Law and Kunze (1966) found no evidence of anionic surfactant adsorption based on adsorption studies and X-ray diffraction analysis. Schott (1968) also found a lack of interaction between anionic surfactants and sodium montmorillonite. In another paper, Schott (1968) restates that sodium montmorillonite does not adsorb anionic surfactants but that adsorption does take place with calcium montmorillonite. No quantitative data was given but X-ray spacings for the surfactant-clay complexes were listed. Wayman (1963) detected minor adsorption using alkylbenzene sulfonates that were tagged with radioactive sulfur. Relatively small concentrations of surfactants were used in this work.

The general tone of the above findings are in conflict with observations made in our laboratory several years ago when aqueous solutions of an anionic surfactant were passed through columns of sand that contained small quantities of montmorillonite. The effluent from the columns exhibited a much higher surface tension than the influent solutions indicating that a significant amount of surfactant was being adsorbed. Thus, it was deemed advisable to conduct carefully controlled adsorption tests to determine if anionic surfactants are adsorbed by montmorillonite and, if so, how much. To provide background information, adsorption studies were made with cationic and nonionic surfactants prior to the anionic surfactant investigation.

MATERIALS

The montmorillonite used originated in Wyoming and was considered to be the sodium clay with a small amount of calcium also present. After purification, it still contained very small amounts of quartz and feldspars and 9 per cent water. In all tests, this percentage of water was subtracted from the weight of clay used to designate the quantity of absolutely dry clay. Its cation exchange capacity (CEC) was 94 m-equiv./100 g.

https://doi.org/10.1346/CCMN.1970.0180205 Published online by Cambridge University Press

The surfactants used are coded according to their type. The capital letters C, N, A, and NA designate cationic, nonionic and anionic surfactants and a surfactant having nonionic and anionic functional groups, respectively. Numerals used in conjunction with the letters designate specific structure properties of each surfactant, such as, the number of moles of ethylene oxide in the chemical, carbon chain length, or number of sulfonate groups per molecule. The meaning of each number will be self evident from the description of the chemical.

N-10 is a nonionic surfactant made by reacting octyl phenol with an average of 9–10 moles of ethylene oxide. Its molecular weight is approx. 624. (Triton X-100 from Rohm and Haas Co.).

NA-5 is a surfactant having both nonionic and anionic functional groups. It is made by reacting an alcohol having a carbon chain length of 12 with 4–5 moles of ethylene oxide. This chemical is then sulfated and subsequently converted to the ammonium salt. Its molecular weight is approx. 497.

C-12 is a cationic surfactant. It is an alkyl trimethylammonium chloride where the alkyl group contains an average of 12 carbon atoms. It has an indicated molecular weight of 260·5. (Arquad C from Armour Industrial Chemical Co.).

C-16 is a cationic surfactant. It is a very pure alkyl trimethylammonium bromide where the alkyl group contains 16 carbon atoms. Its molecular weight is 364·5.

A-13-1 is the sodium salt of an anionic surfactant. It is the mono sulfonate of a hydrocarbon having an average chain length of 13 carbon atoms where at least 60 per cent of the hydrocarbon is straight chain. Its indicated molecular weight is 286.

A-13-1·7 is the sodium salt of an anionic surfactant similar to A-13-1 except that each molecule contains an average of 1·7 sulfonate groups. Its indicated molecular weight is 358.

A-18-1·8 is the sodium salt of an anionic surfactant. It is made by sulfonating a hydrocarbon having an average chain length of 18 carbon atoms where at least 60 per cent of the hydrocarbon is straight chain. Each surfactant molecule contains an average of 1·8 sulfonate groups. Its indicated molecular weight is 438.

A-13B-1 is the sodium salt of an alkyl benzene sulfonate where the alkyl group is a straight chain that contains an average of 13 carbon atoms. It is a mono sulfonate and has an indicated molecular weight of 362. This particular surfactant is a solid that contains 40 per cent of the described chemical, 59 per cent sodium sulfate and 1 per cent water. (Santomerse 1 from Monsanto Chemical Co.).

N-10, C-12, and A-13B-1 are commercial products while NA-5, A-13-1, A-13-1·7 and A-18-1·8 are laboratory prepared surfactants. All of the laboratory prepared chemicals were supplied in a diluted form and contained varying quantities of sodium chloride. The point of sulfonation on the hydrocarbon chain for A-13-1, A-13-1·7 and A-18-1·8 could not be controlled and must be considered random. C-16 was recrystallized from acetone, washed with petroleum ether, recrystallized from acetone again and dried to produce a very pure product. In all instances, the amount of surfactant employed in a test is based on the amount of active ingredient present.

METHODS

The concentration of many surfactants in water solutions may be determined by measuring the surface tension of the solutions if surfactant concentrations are below the critical micelle concentration (CMC). Surface tension versus surfactant concentration curves were developed for all of the listed surfactants using a du Nuoy Tensiometer for surface tension measurements. This method of determining surfactant concentration has been used in the past but it has not always been considered to be an ideal method. However, patience, care and the use of a good routine can provide data that are reproducible and meaningful. Each curve was rechecked with solutions of known surfactant concentration using solutions that were aged at least 24 hr. Reproducibility was found in all instances except for the A-13-1, A-13-1·7, and A-18-1·8 solutions. For these exceptions, the aged solutions exhibited tension values that were as much as 5 dynes/cm lower than where fresh solutions were employed. These lower values indicated a significantly higher surfactant concentration than the real concentration and prevented the use of this method of analysis for this group of anionic surfactants. Other methods of analysis, which will be discussed later in this paper, were investigated in an effort to determine anionic surfactant concentration. Reproducible surface tension values were found for alkyl benzene sulfonate A-13B-1 solutions over a period of more than 1 month.

Adsorption studies. Specific weights of montmorillonite (from 0·5 to 2 g) were weighed in 500 ml glass stoppered flasks. 100 ml solutions with varying amounts of surfactant in distilled water, were

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added to the flasks to develop a series of systematic surfactant to montmorillonite ratios. The maximum ratio used was 1500 mg surfactant to 1 g of clay. No effort was made to adjust the pH of surfactant solutions from their naturally developed values which fell in the range of 6·2–7·6. The flasks were shaken periodically over at least a 24 hr period to provide effective contact between the surfactant solutions and montmorillonite. This 24 hr contact period appeared to be adequate as several spot checks after 30 days contact did not indicate additional surfactant adsorption. All mixes were centrifuged at 4000 RPM as long as required to remove clay solids. The resulting supernatant solutions were then tested for residual surfactant concentration by surface tension determinations. Where relatively high surfactant to clay ratios were employed, it was necessary to dilute the supernatant solutions below the CMC to obtain reliable surface tension readings. In some instances, this dilution was as great as 300:1 and reliable values were so obtained. However, a small error in a surface tension determination could result in a greatly magnified error when this value was multiplied by 300 or more to obtain the residual surfactant concentration for the undiluted solution. It is for this reason that adsorption tests were not conducted at ratios greater than 1500 mg surfactant to 1 g of montmorillonite. Once the residual surfactant concentration was determined, it was subtracted from the starting concentration to find the amount of surfactant adsorbed by a specific weight of montmorillonite. In all cases, the quantity of surfactant adsorbed is reported in the ratio of milligrams surfactant to 1 g dry clay.

X-ray diffraction. Before X-raying the surfactant–montmorillonite complexes, X-ray diffractograms were obtained for each surfactant. The most reliable method of sample preparation entailed dissolving the surfactants in distilled water and placing a part of the solutions on glass slides. After drying at room temperature, X-ray diffractograms were obtained by scanning from 0·8°–7°2θ. These diffractograms were compared to those obtained for the surfactant–montmorillonite complexes so that any response due to the surfactant alone would not be confused with that derived from a complex.

The centrifuged clay solids from the adsorption studies were smeared on glass slides for X-ray analysis. Where ratios of surfactant to montmorillonite in excess of 1500 were used, a well dispersed 3 per cent slurry of montmorillonite in distilled water was added to the surfactant solutions to give a total volume of 100 ml. Again, these mixes were centrifuged after 24 hr and the solids smeared on glass slides and dried at room temperature. In every instance, the solids were scanned from 0·8°–7°2θ at 2°/min using copper radiation. Past experience has shown that small amounts of water may be present in organo-montmorillonite complexes, even when the clay has a dry appearance. Heating the clay slide on a hot plate for 15 min at 140°F will remove this water and the resulting 001 response will more accurately depict the true thickness of the organo-montmorillonite complex. Once a stable spacing was developed, the thickness of the dry montmorillonite crystal (9·5 A) was subtracted to obtain the thickness of the adsorbed surfactant layer.

At surfactant to montmorillonite ratios of 4000 mg/g, stable complexes were developed within 24 hr after mixing, However, where ratios of 10,000 mg/g were used it required a longer period of time for a stable spacing to form. These mixes were checked periodically over a period of 162 days to make certain that stable spacings were obtained.

All tests were performed at 75 ± 1°F.

RESULTS

Nonionic Surfactants-NA-5 is included with N-10 since its nonionic character appears to be predominant when exposed to montmorillonite. Montmorillonite dispersed very well in both surfactant solutions and settled slowly with time. However, the resulting solids appeared to be rather gummy and were quite difficult to redisperse, with N-10 showing the greater resistance to redispersion. Table 1 provides adsorption and X-ray data for these two surfactants. Column one designates the ratio of surfactant to montmorillonite used in each test.

When the adsorption data were plotted, smooth curves developed which indicated maximum adsorption to be 550 mg surfactant per gram of dry montmorillonite.

The quality of the X-ray peaks were generally very good, particularly where the higher surfactant to montmorillonite ratios were used. However, with N-10 at the 10,000 ratio the 20·32 A response required 81 days to develop while only 1 day at the 3000 ratio. In addition, a minor 44 A spacing slowly developed at the 10,000 ratio that remained the same after 162 days. This spacing may indicate a complex containing several layers of nonionic surfactant.

Both complexes were washed with large volumes of distilled water. The N-10 spacing dropped from 20·32A to 15·93A and then became stable and the 44A spacing quickly disappeared. After the last washing, the complex remained in 100 ml of distilled water for two years. At the end of this time, the water was separated from the clay and, by surface tension measurement, only a trace of N-10 could be detected. The spacing for NA-5 dropped

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Table 1. Adsorption and X-ray data obtained for nonionic surfactants when exposed to montmorillonite

	N-10		NA-5	
mg surfactant/ g mont.	mg adsorbed/ g mont.	X-ray spacings (A)	mg adsorbed/ g mont.	X-ray spacings (A)
100	99·1	14·74	95·4	13·38
200	192·2	15·33	188·0	13·89
400	321·4	15·94	350·0	14·04
600	412·0	20·07	410·0	17·73
1000	512·0	20·16	518·0	18·13
1500	540·0	20·16	534·0	18·17
2000		20·16		18·17
3000		20·07		18·17
10,000		20·32		18·17
Maximum surfactant layer thickness		10·82		8·67

from 18·17A to 13·71A and then remained stable. Additional washings with calcium chloride and potassium chloride solutions did not change the 13·71A spacing. After 2 yr aging of this washed complex in 100 ml distilled water, only a slight trace of NA-5 could be detected in the water.

The X-ray data discussed above generally agrees with findings reported by Brindley and Rustom (1958) where they found two layers of a nonionic surfactant adsorbed by montmorillonite. Repeated washings with water reduced the two layer to a one layer complex.

Cationic surfactants. Both C-12 and C-16 caused an immediate and severe flocculation of montmorillonite. Table 2 lists adsorption and X-ray data for these surfactants.

The maximum amount of surfactant adsorption noted in Table 2 for the cationic surfactants is quite close to the values reported in Table 1 for nonionics. A plot of the cationic surfactant adsorption data indicates maximum adsorption to be very close to 550 mg/g montmorillonite.

The quick flocculation of montmorillonite may have occluded some of the clay and prevented complete surfactant contact at the higher ratios. This is not evident through the 1500 ratio but the lower spacings found for the 2000 and 10,000 ratios indicate that some of the clay was not treated. The X-ray response for these higher ratios was rather diffuse as compared to the sharp peaks for the lower ratios. The 1000 ratio complex was washed with large volumes of distilled water without significally reducing the X-ray spacing. The same was true when the complex was washed with 2·5 per cent solutions of potassium chloride, calcium chloride, hydrochloric acid, sodium hydroxide

Table 2. Adsorption and X-ray data obtained for cationic surfactants when exposed to montmorillonite

	C-12		C-16	
mg surfactant/ g mont.	mg adsorbed/ g mont.	X-ray spacings (A)	mg adsorbed/ g mont.	X-ray spacings (A)
100	97·6	13·71	99·8	13·59
200	188·0	14·72	198·0	16·05
400	351·0	16·60	331·0	17·70
600	451·0	17·18	460·0	17·95
1000	510·0	17·21	521·0	17·94
1500	528·0	17·20	534·0	17·80
2000		16·98		17·95
10,000		15·77		
Maximum surfactant layer thickness		7·71		8·45

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and ammonium hydroxide. It is interesting to note that the surfactant layer thickness for the longer alkyl chain C-16 is greater than that obtained for C-12. Washing of the C-16 complex with the same solutions used with C-12 did not materially alter the X-ray spacing of the complex. With both C-12 and C-16, no surfactant could be detected in the final wash water.

Anionic surfactants. X-ray diffraction spacings were obtained for the four anionic surfactant–montmorillonite complexes up to the surfactant's limit of solubility in distilled water. In every case, the montmorillonite was well dispersed in the mixtures and the treated clay settled slowly. Redispersion was accomplished very easily in contrast to the difficulty in redispersion noted with nonionic surfactants. Table 3 lists these data with the left column designating the surfactant to clay ratio.

The 2000 ratio complexes were rechecked after 4 months aging with no more than a 0·03A difference being found from the data recorded in Table 3.

The X-ray responses were all quite sharp except for relatively poor peaks found for the 200 ratio. Intensities were generally greater for the lower molecular weight surfactants A-13-1 and A-13-1·7 indicating more efficient ordering of these molecules on the montmorillonite surface. Of interest is the fact that the more highly sulfonated A-13-1·7 develops a thicker complex at lower surfactant concentrations than A-13-1 while the maximum thickness for both surfactant complexes is the same. The effect of carbon chain length on complex thickness is shown where the longer chain A-18-1·8 develops a much thicker complex than the 13 carbon chain A-13-1·7 which has almost the same degree of sulfonation. However, the introduction of the benzene ring to the surfactant molecule (A-13B-1) greatly reduces the thickness of the complex which could indicate less adsorption than with the other anionic surfactants. Washing of the anionic surfactant complexes with distilled water quickly removed all of the surfactants from the clay.

As noted previously, the surface tension of solutions prepared with A-13-1, A-13-1·7 and A-18-1·8 decreased on aging. Thus, the surface tension method of determining residual surfactant concentration with these chemicals could not be employed. However, A-13B-1 solutions showed good surface tension stability and a series of adsorption tests were conducted with this surfactant. The results of these tests indicated that either no adsorption or negative adsorption was taking place. In this case, negative adsorption is where the supernatant solution separated from the clay exhibited a lower surface tension and thus a higher surfactant concentration than the original solution.

Since Schott (1968) had stated that calcium montmorillonite does adsorb anionic surfactants, calcium montmorillonite was prepared and adsorption tests conducted. The results of some of these tests and those conducted with the stock montmorillonite are presented in Table 4. The starting concentration of A-13B-1 was 1 mg/ml of solution and the left column of the table designates the surfactant to clay ratio in mg/g.

It is quite evident that the so called degree of "negative adsorption" was much greater where calcium montmorillonite was used.

It was known from the start of this work that the

Table 4. Indicated negative adsorption of anionic surfactant A-13B-1 with stock and calcium montmorillonite

mg A-13B-1/g mont.	Indicated A-13B-1 solution concentration after contact with	
	Stock mont.	Calcium mont.
100	1 mg/ml	1·14 mg/ml
200	1·11 mg/ml	1·54 mg/ml
400	1·22 mg/ml	2·48 mg/ml

Table 3. X-ray data obtained for anionic surfactants when exposed to montmorillonite

	X-ray spacings (A)			
per gram mont.	A-13-1	A-13-1·7	A-18-1·8	A-13B-1
200	13·34	14·02	13·95	13·89
600	15·02	17·11	17·35	14·77
1000	15·68	17·66	18·02	14·72
2000	17·59	17·80	21·80	14·84
3000	17·66	17·59	22·07	14·77
4000	17·73	17·66	22·18	Not Sol.
10,000	17·80	Not Sol.	Not Sol.	
Maximum surfactant layer thickness	8·3	8·3	12·68	5·34

https://doi.org/10.1346/CCMN.1970.0180205 Published online by Cambridge University Press

stock montmorillonite contained a small amount of calcium as the base exchange cation. Since A-13B-1 contained 59 per cent sodium sulfate, it was thought that sodium ions may be exchanging calcium ions from the clay and thus reducing the surface tension of the A-13B-1 solutions. Analysis of the stock montmorillonite showed that each gram of clay contained 3·07 mg of exchangeable calcium which amounted to 16·3 per cent of its CEC. Table 5 contains data clearly showing that a very small quantity of calcium will greatly lower the surface tension of 100 ml of 2·45 mg/ml A-13B-1 solution. The solutions were diluted 1:10 to reduce surfactant concentrations below the CMC for surface tension determinations.

Table 5. Effect of calcium on the surface tension of a A-13B-1 solution

Amount calcium ions present	Surface tension (diluted 1:10)	Indicated A-13B-1 concn
None	47·8 dynes/cm	2·45 mg/ml
0·9 mg	40·8 dynes/cm	4·28 mg/ml

The sharp decrease in surface tension caused by the very small quantity of calcium ions noted in Table 5, indicates that even a very small release of calcium by cation exchange will completely mask adsorption determinations. This fact may be one of the reasons why Schott (1968), who also used surface tension techniques to determine residual surfactant concentrations, did not detect anionic adsorption on montmorillonite.

An attempt was then made to prepare sodium montmorillonite that was free of calcium. Stock montmorillonite was slurried in distilled water and converted to the acid form by the use of an ion exchange resin. The acid form was then converted to the sodium clay and the clay washed and concentrated by centrifuging. After drying, the clay was pulverized for adsorption studies and labeled sodium montmorillonite No. 1. However, about this time, it was determined that calcium salts are sometimes present in the air in our laboratory and could be concentrated in the clay slurry during centrifuging. Another preparation was made similar to that described above only all containers were covered whenever possible, particularly during centrifuging. This sample was labeled sodium montmorillonite No. 2. Adsorption tests were conducted with both samples using a surfactant to montmorillonite ratio of 1000 mg A-13B-1/1 g clay. The results of these tests are recorded in Table 6.

The data in Table 6 have several interesting implications:

1. The excess sodium ions, from sodium sulfate, in the A-13B-1 do exchange calcium from the stock montmorillonite to reduce surfactant solution surface tension.

2. Trace amounts of calcium ions in air are apparently concentrated in solutions during centrifuging.

3. The anionic surfactant A-13B-1 is adsorbed to a significant amount by montmorillonite. The quantity recorded for sample No. 2 may not represent the total amount adsorbed. In spite of all the observed precautions, a trace of calcium still may have entered the system causing the indicated amount of adsorbed surfactant to be lower than the real value.

As a note of interest, controlled amounts of calcium ions were added to NA-5 solutions and not found to affect the surface tension of these solutions at the calcium ion level that would be derived from the stock montmorillonite.

Anionic surfactants generally have sodium salts mixed with them whether the surfactant is furnished in solid form or in solution. Some of these salts can be removed by special treatment but not sufficiently to develop an inorganic cation free condition. Therefore, the surface tension method of determining residual anionic surfactant concentrations is somewhat limited. This is particularly evident where calcium ions are a part of the CEC of montmorillonite.

There are other methods of determining anionic surfactant solution concentrations. Epton (1948) has successfully applied a titration method using a known concentration of a cationic surfactant as a standard. This method gave excellent results with A-13B-1 where no clay was present. However, where a trace of clay remained in the surfactant solutions, inaccurate data was obtained. Here, the clay suspensions were centrifuged for 8 hr to

Table 6. Adsorption of anionic surfactant A-13B-1 on specially prepared sodium montmorillonite

Clay used	Amount A-13B-1 adsorbed/g montmorillonite
Sodium montmorillonite No. 1	96 mg
Sodium montmorillonite No. 2	232 mg

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develop clear solutions but, evidently, some clay was still present. When these solutions were titrated, the cationic surfactant would displace the anionic from the clay, thus releasing more anionic to be neutralized. Flocculated clay could be detected in the titrated solutions. Weber, *et al.* (1962) described an ultraviolet spectrophotometry method that also gave erratic results with A-13B-1 solutions after they had been exposed to montmorillonite. However, some adsorption was indicated. Two pyrolysis methods of analysis were also investigated. One is the carbon–hydrogen–nitrogen system and the other entailed adsorption by gas chromatography of the pyrolyzed products. Both methods showed some surfactant adsorption but not to the same degree as recorded for sample No. 2 in Table 6.

The possibility of relating X-ray data to the amount of adsorbed surfactant as a means of determining anionic adsorption quantitatively was investigated. Data from Tables 1 and 2 for nonionic and cationic surfactants was combined with that for sodium montmorillonite No. 2 from Table 6 to develop Table 7. In all instances, the 1000 mg surfactant to one gram montmorillonite ratio data was used.

The surfactant layer thickness and adsorption data appears to be fairly consistent for NA-5, C-12 and C-16 while the N-10 data does not correlate. If N-10 is ignored and the NA-5, C-12 and C-16 data averaged, a ratio of 62·6 mg of surfactant for each Angstrom of layer thickness is obtained. Using this figure, an indicated adsorption for A-13B-1 of 327 mg/g montmorillonite is obtained which is significantly greater than the value of 232 mg/g derived from adsorption studies. Adsorption data may also be calculated for the other anionic surfactants listed in Table 3 to provide approximate values. It is rather risky to use such a system of calculation to obtain exact numbers. Configuration of adsorbed molecules on clay, particularly ones having a relatively high molecular weight, is not fully understood. At low surfactant to montmorillonite ratios, it is felt that the carbon chains are adsorbed relatively parallel to the clay surface. Here, the zig-zag carbon chains could be oriented either parallel or perpendicular to the clay under these conditions. The random positioning of sulfonate groups on the anionic surfactants further complicates orientation theory. At high surfactant to montmorillonite ratios, many packing possibilities exist. Double layer adsorption may occur with the carbon chains parallel to the clay surface and even a third layer could be imbedded in this system. Models of surfactant molecules may be made and arranged in a tilted orientation of 56–63 degrees to the clay to account for observed X-ray spacings. In some instances, an orientation vertical to the clay surface may be indicated. Molecular structure of organic molecules combined with functional group repulsion and attraction further complicate orientation predictions. Therefore, it would be virtually impossible to predict molecular packing densities of surfactant molecules on montmorillonite and we must assume that packing densities will vary from one molecular structure to another. From the above discussion, it is felt that any ratio of weight of adsorbed surfactant to thickness of surfactant layer, as determined by X-ray diffraction for one type of molecular structure, cannot be used to quantitatively determine the amount of adsorbed surfactant having a different molecular structure.

It is now evident that anionic surfactants are adsorbed by montmorillonite and X-ray data indicates that adsorption occurs on the face of the clay crystals. Although the sulfonate group of the surfactant exhibits a negative charge, this portion of the molecule is relatively small compared to the hydrocarbon tail. Attraction by van der Waals' forces between the hydrocarbon tail and the clay crystal are possible as well as hydrogen bonding through oxygen in the sulfonate group. The positioning of the negatively charged sulfonate group would logically be at a point remote to the negative charges in the crystal lattice.

CONCLUSIONS

1. Adsorption data has been obtained for some nonionic and cationic surfactants with up to 550

Table 7. Comparison of adsorption data and X-ray spacings found for the 1000 mg surfactant/gram montmorillonite ratio

Surfactant	mg adsorbed/ g mont.	X-ray spacings (A)	Surfactant layer thickness (A)
N-10	512	20·16	10·66
NA-5	518	18·13	8·63
C-12	510	17·21	7·71
C-16	521	17·94	8·44
A-13B-1	232	14·72	5·22

https://doi.org/10.1346/CCMN.1970.0180205 Published online by Cambridge University Press

mg of surfactant being adsorbed by 1 g montmorillonite.

2. Anionic surfactants are adsorbed by sodium montmorillonite and the amount adsorbed is significant. Although exact quantities have not been determined, it may be estimated that anionic adsorption can, in some instances, approach that of nonionic and cationic surfactants.

3. The surface tension method of measuring residual surfactant concentration is reliable for nonionic and cationic surfactants but is limited for anionic surfactants where traces of calcium ions may be present.

4. The maximum X-ray 001 spacings obtained for surfactant–montmorillonite complexes indicate some type of surfactant double layer configuration. One exception is the alkylbenzene sulfonate A-13B-1 where either a tilted monolayer or a deeply imbedded double layer orientation is indicated. Another exception is a minor response of around 44A for nonionic N-10 which may indicate many layers of adsorbed surfactant. These data were obtained, where surfactant solubilities permitted, with surfactant to montmorillonite ratios as high as 10,000 mg/g. The surfactant concentration under these conditions represent a 5 per cent solution.

5. The thickness of adsorbed surfactant layers on montmorillonite, as determined by X-ray diffraction, cannot be quantitatively used to determine the weight of adsorbed surfactant. Only estimated values can be so obtained. However, it is strongly felt that X-ray diffraction can be used to detect positive adsorption of surfactants by montmorillonite.

6. Since only a limited number of surfactants have been investigated in this study, it would be hazardous to accurately predict maximum X-ray 001 spacings for other surfactant–montmorillonite complexes.

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Résumé—Certains auteurs ont établis que les surfactants anioniques ne sont pas adsorbés par le montmorillonite, tandis que d'autres indiquent une adsorption très petite. Des essais pour déterminer quantitativement le degré d'adsorption ont montré qu'il existe certains problèmes qui, à moins d'être reconnus, masqueront complètement les résultats. Certaines de ces difficultés ont été surmontées, mais les donnés exactes n'ont pas encore été obtenues. Toutefois, on a rassemblé suffisamment d'informations pour prouver que l'adsorption des surfactants anioniques sur le montmorillonite est réelle et substantielle. Des données d'adsorption extrêmement sûres pour les surfactants cationiques et nonioniques, et l'une ayant à la fois un caractère nonionique et anionique, ont été obtenues. Il est indiqué que 550 mg de ces surfactants sont adsorbés par un gramme de montmorillonite. Des données de diffraction de rayons X pour des complexes de tous les surfactants étudiés confirment une adsorption positive. Toutefois, l'épaisseur des couches de surfactants adsorbés ne peut pas toujours être quantitativement reliée â la quantité de surfactant adsorbé.

Kurzreferat—Verschiedene Autoren haben angegeben, dass anionische Tenside an Montmorillonit nicht adsorbiert werden, während andere eine sehr geringfügige Adsorption festgestellt haben. Versuche den Grad der Adsorption quantitative zu bestimmen haben gezeigt, dass gewisse Probleme bestehen, die wenn nicht erkannt, die Resultate vollkommen verschleiern werden. Einige dieser Schwierigkeiten sind überwunden worden doch sind bis jetzt noch keine exakten Messwerte erhalten worden. Es ist jedoch bereits genügend Information vorhanden um beweisen zu können, dass die Adsorption anionischer Tenside an Montmorillonit ganz beträchtlich ist. Es sind verlässliche Adsorptionswerte für kationische und nichtionische Tenside sowie eines von nichtionischen sowie anionischem Charakter erhalten worden. Es zeigt sich, dass 550 mg dieser Tenside durch ein Gramm Montmorillonit adsorbiert werden. Die Röntgenbeugungswerte für Komplexe aller der untersuchten Tenside bestätigen positive Adsorption. Die Dicke der adsorbierten Tensidschichten kann jedoch nicht immer quantitativ mit der Menge an adsorbiertem Tensid in Beziehung gebracht werden.

Резюме—Некоторые авторы полагают, что анионные поверхностно активн е вещества не поглощаются монтмориллонитом, в то время как другие отмечают очень незначительное поглощение. Попытки количественного определения степени поглощения показали, что

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здесь имеют место определенные трудности, которые, не будучи полностью разрешенными, препятствуют правильной интерпретации результатов. Некоторые из этих трудностей были преодолены, однако точных данных пока еще не получено. Тем не менее были получены достаточные сведения для доказательства того, что поглощение анионных поверхностно активных веществ монтмориллонитом действительно имеет место и является существенным. Были получены надежные данные по поглощению катионных и неионных поверхностно активных веществ, а также поверхностно активных веществ, обладающих как неионным, так и анионным характером. Показано, что 550 мг этих поверхностно активных веществ поглощается одним граммом монтмориллонита. Рентгеновские данные для комплексов со всеми используемыми поверхностно активными веществами подтвердили факт несомненного поглощения. Однако, толщина поглощенных слоев поверхностно активных веществ не может быть всегда количественно связана с количеством поглощенного поверхностно активного вещества.

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