

DETERMINATION OF SURFACE AREA BY SURFACTANT ADSORPTION IN AQUEOUS SUSPENSION—I. DODECYLAMINE HYDROCHLORIDE*

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Abstract—Conductometric titrations of clay suspensions with surfactant solutions offer a rapid method of surface area determination of clay particles suspended in aqueous media. A cationic surfactant, dodecylamine hydrochloride, was used in this investigation. This surfactant was adsorbed by electrostatic bonding at cation exchange sites and by van der Waals forces. A monomolecular or bimolecular layer of the surfactant coats the particle and the completion of the layer is determined from a change in slope of the conductometric titration curve due to the formation of micelles. Good agreement between this method and BET determined values were obtained for kaolinite. The bentonite suspensions had a strong tendency to flocculate after the initial stage of adsorption causing the results to vary considerably. This method of surface area measurement of clay particles offers many advantages over the present techniques: (1) a dry particle is not required; (2) the equipment is inexpensive and available in many laboratories; (3) the method is rapid; (4) vacuum and high temperature are not required, and (5) the method measures the internal as well as external surface area.

INTRODUCTION

A COLLOIDAL suspension contains particles that are large compared to simple molecules, but sufficiently small that both interfacial and inertial forces influence the system's behavior. Clay particles, ranging in size from a fraction of a micron to several microns, behave as a colloidal system when dispersed in an aqueous media. Thus, many of the physical properties observed in a clay suspension are a function of interfacial forces. These observed properties are related to both the nature and extent of the clay-media interface. Because of this the surface area of clay particles is a very important property influencing much of the particles' behavior.

There have been many methods devised for determining the surface area of clays, including

both direct and indirect procedures. The direct method of surface area determination consists of measuring the parameters of the particle, usually by electron or optical microscopy. Indirect measurements are based on observations of properties that are influenced by the surface area. These methods are numerous and are more commonly used to determine the surface area.

Gas, water, ethylene glycol, and glycerol adsorption have been the most commonly used indirect methods. They all involve the use of a dry particle. It is questionable if a dry particle is representative of a solvated suspended particle. The amount of electrolyte in a colloidal suspension affects the thickness of the double layer, which influences the rate of coagulation and flocculation. These factors affect the surface area of the suspension. Therefore, the measurement of the surface area of a dry particle is not necessarily a measure of the surface area of a suspended particle. Since surface area is a primary property influencing the behavior of a suspended particle, a method is needed by which to measure it in aqueous suspension.

The objectives of this investigation were to

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study the adsorption mechanism of surfactants by suspended clay particles. The experimental work consisted of conductometrically measuring the amount of adsorption of dodecylamine hydrochloride by kaolinite and bentonite suspensions. Surface area values were calculated from the adsorption isotherms and compared to BET determined values. Specific acknowledgement is made to Dr. Q. van Winkle of the Ohio State University Chemistry Department for his many suggestions during the study.

LITERATURE REVIEW

The adsorption of surfactants from aqueous solutions by clay particles has been investigated by a few people for the determination of surface area. Orr and Bankston (1952) investigated the adsorption of a monomolecular layer of stearic acid on clays. Due to the insolubility of stearic acid in aqueous suspension, the clay was suspended in anhydrous methanol. The anhydrous methanol also eliminated competitive adsorption with the solvent and cation exchange reactions. The completed monolayer was determined by conductometrically back titrating the excess stearic acid with sodium hydroxide. This method was compared to BET determined surface areas for several kaolinites and good agreement was obtained.

Burford, Greenland, and Quirk (1963) investigated the adsorption of cetyl pyridinium bromide from aqueous solution. Cetyl pyridinium bromide formed a bimolecular layer and gave good agreement with BET determined surface areas on a large number of clays with nonexpanding lattices. They used this method for the determination of the surface area in the interlamellar regions where the bimolecular layer is shared by the opposite face.

Maron and Elder (1954) developed a method of determining the surface area of synthetic latex by adsorption of laurylamine hydrochloride in aqueous suspension. A monolayer of the surfactant formed on the surface, and its completion was determined by either a conductometric or tensionmetric titration of the latex with the surfactant solution.

The use of surfactants for the determination of surface areas of clay particles has the advantage that the determinations are fast and may be done in aqueous suspension. The principle of adsorption from solution is similar to gas adsorption in that a multimolecular layer is formed on the surface of the particle. Adsorption from solution has the added advantage that it will measure the internal as well as external surface area of expandable clay particles. Haynes (1961) lists three major disadvantages encountered with adsorption from

solution: (1) the solvent as well as the solute is adsorbed especially in the case of water on polar solids; (2) large adsorbate molecules can adopt different orientations on the surface; and (3) the adsorption of cationic materials on clays is complicated by cation exchange reactions. For accurate determinations of the surface areas these handicaps must be overcome. The first problem may be solved by using a solute that is much more strongly adsorbed than the solvent. A large ion such as methylene blue accomplishes this. Cation exchange reactions can be minimized, if desired, by choosing the appropriate adsorbate: cationic, anionic, or nonionic. Even with these existing problems, excellent relative surface areas may be obtained by multimolecular adsorption of surfactants.

ADSORPTION MECHANISM

The detergent type of surface active agents consist of a hydrophilic or water-loving polar group and a hydrophobic or water-repelling group. The hydrophobic group consists of an aliphatic or aromatic hydrocarbon chain. The hydrophilic group may be ionic or nonionic in nature. These surfactants are characterized by the following properties:

- (1) interface or surface tension depression in dilute solution,
- (2) micelle formation above a certain concentration,
- (3) the uptake by micelles of solvent-insoluble substances,
- (4) the low concentration of molecularly dispersed molecules.

The solution mechanism consists of the initial ionization of the counter ion if it is an ionic species. The negative charge carried by the solid ionic surfactant particles resulting in a strong repulsive force between the particles, increases the solvency of the hydrocarbon chain and hydrophilic group. A strong repulsive force between the water molecules and the hydrophobic tails does not exist, but there is a strong cohesive force between the water molecules. The cohesive force is much stronger than that between the hydrocarbon-water groups and the hydrocarbon-hydrocarbon groups causing the mixed phase state to have higher energy than the separate two-phase state. The hydrophilic group counterbalances this effect permitting some of the surfactant to dissolve. The degree of solubility decreases with increasing carbon chain length. The surfactants that do not dissolve form micelles which are spherical aggregates of both the ionized and nonionized surfactant particles. These micelles form because of an affinity between the hydrocarbon tails due to

van der Waals forces. The concentration at which the micelles form is known as the critical micelle concentration (CMC). The CMC decreases with decreasing temperature and increasing hydrocarbon chain length.

Solvation occurs on both the clay particles and the surfactant molecules. The charge on the cationic detergent can reorient the water molecules around the hydrophilic portion of the surfactant molecule. This may cause desolvation of the clay particle when the surfactant coats the particle.

The coating of the surfactant on the clay particle consists of a combination of three mechanisms. If an ionic surfactant is used, it will adhere to the clay particle by electrostatic bonding—charge neutralization—at cation exchange locations. The polarity of the clay particle aids in the coating mechanism. These methods would normally consist of the hydrophilic-ionic group adjacent to the clay particle with the hydrocarbon tail perpendicular to the surface. If these mechanisms are not sufficient to form a monolayer on the surface of the particle additional coating may occur by van der Waals forces. This adsorption mechanism is predominant on the positive edges of the clay particle. Since these surfactant molecules are held by van der Waals forces, the longer the surfactant the greater the binding force. These surfactant molecules would orient on the surface of the clay with their hydrophilic groups away from the surface of the particle. Hendricks (1941) originally suggested that the larger cationic surfactants were held on the surface by van der Waals forces in addition to electrostatic forces. Grim, Alaway, and Cuthbert (1947) verified Hendricks study and found that larger surfactants could be adsorbed in excess of the cation exchange capacity. Greenland and Quirk (1960) found that 1-*n*-alkyl pyridinium bromides with alkyl chains longer than eight carbons were adsorbed in excess of the cation exchange capacity

on sodium montmorillonite. Law and Kunze (1966) found that kaloinite adsorbed distearyl-dimethyl ammonium-chloride and cetyl pyridinium-chloride in excess of the cation exchange capacity, while the shorter dodecyl dimethyl-benzyl ammonium-chloride was adsorbed just slightly in excess of the cation exchange capacity.

A bioriented monomolecular layer may occur when there is adsorption due to van der Waals forces and also due to either electrostatic bonding or polar characteristics of the clay particle. The first orientation consists of electrostatically bonded molecules with the hydrophilic groups adjacent to the clay particle. The second orientation forms due to van der Waals forces with the hydrocarbon tails either adjacent to the hydrocarbon tails of the first orientation or attached perpendicular to the surface of the clay particle. With the initial adsorption the particle becomes hydrophobic and tends to flocculate. The final adsorption causes the particle to become hydrophilic again. A monomolecular and a bioriented monomolecular layer are illustrated in Fig. 1.

The adsorption mechanism is temperature dependent. With increasing temperature there is a corresponding increase in the CMC. This effect is more pronounced with the ionic than with the nonionic surfactants. At lower temperatures gelling may occur. Gelling is related to the hydrocarbon chain length with increased gelling occurring with longer chains. Garcia, Cano-Ruiz, and MacEwan (1964), and del Pino, Ramirez, and Cano-Ruiz (1966) have shown that the adsorption of surfactants perpendicular to the interlamellar surfaces is temperature dependent. Their study showed that the lower the temperature the greater the basal spacing. It is suggested that the perpendicular orientation is an ideal state and is never completely obtained. X-ray diffraction data presented by Law and Kunze (1966) on montmoril-

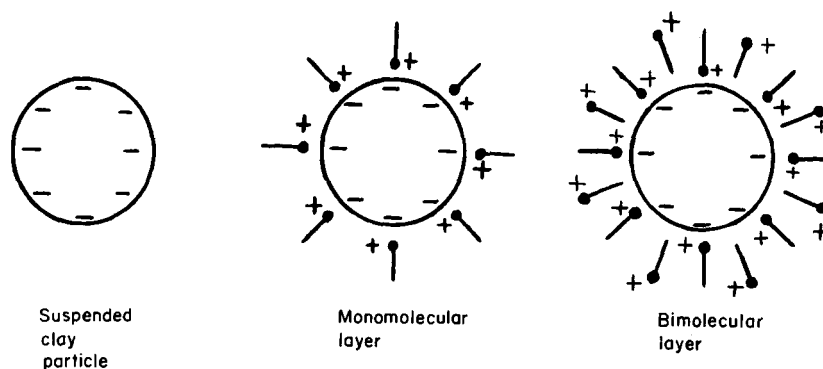


Fig. 1. Adsorption mechanism on suspended clay particle.

lonite treated with surfactants show that the interlamellar spacings do not consistently contain the surfactant molecules perpendicular to the surfaces.

DETERMINATION OF THE COMPLETED LAYER

The completed surfactant monolayer or multilayer may be determined by several methods. Shinoda *et al.* (1963, p. 217) lists three methods:

- (1) The soap antagonist method—the concentration of the surfactant ion in excess of the multilayer is determined by titration with another surfactant of opposite charge, using certain colored materials as indicators.
- (2) The soap titration method—the amount of adsorption is determined from the displacement of the CMC before and after adsorption.
- (3) The radiotracer method—the surfactant is tagged with a radioactive tracer, and the concentration of the isotope is determined before and after adsorption.

The soap titration procedure is the most commonly used. The displaced CMC may be measured by two titration procedures: conductometric and tensiometric. The conductometric titration is the simplest and works satisfactorily as long as an ionic surfactant is used. The endpoint consists of a break in the rising conductivity due to the formation of the low conductivity micelles. Tensiometric titrations offer a very sensitive method, but extreme care must be taken to be certain that no foreign material is present in the system. The surface area is calculated from the number of moles of surfactant between the CMC's before and after adsorption by knowing the effective coverage area of the surfactant molecule on the particle surface.

EXPERIMENTAL

The surface area determination investigated in this study consisted of measuring the displacement of the CMC with the addition of clay to an aqueous system. The surfactant used was dodecylamine hydrochloride. It is a cationic surfactant that forms a bioriented monomolecular layer on the surface of the clay particle. Adsorption occurs in excess of the cation exchange capacity by van der Waals forces. The initial micelle formation in the clay suspensions was detected by conductometric titrations of the suspensions with a standardized dodecylamine hydrochloride solution. The micelles have a lower conductivity than the ionized surfactant in solution causing a change in slope of the titration curve at the initial formation of micelles. The difference between the CMC of the surfactant in plain water and that in an aqueous clay suspension represents the adsorption on the clay surface.

Harkins *et al.* (1946) reported that each dodecylamine hydrochloride molecule has an effective surface coverage of 26 \AA^2 . The surface area of the clay is then calculated from these data. This investigation consisted of conductometrically titrating two clays, a kaolinite and a bentonite, at six concentrations of suspension and five temperatures.

Material

The dodecylamine hydrochloride was prepared by mixing equal molar amounts of dodecylamine and 0.1 N hydrochloric acid, following the procedure of Maron *et al.* (1954). The mixture was heated to aid solution. Additional hydrochloric acid or dodecylamine was added until the solution maintained a pH of 7. The dodecylamine hydrochloride was standardized for amine content by adding chloroform and phenolphthalein, and then titrated to a colorimetric endpoint with standard sodium hydroxide. The chloride content of the solution was determined by a potentiometric titration with standard silver nitrate. Less than a 1 per cent variation between chloride and amine content was maintained. The surfactant solution was diluted to the desired concentration and restandardized before the conductometric titrations.

The kaolinite used was "Georgia Kaolin Hydrite UF," furnished by the Georgia Kaolin Company, with a particle size range of $0.1\text{--}1.0 \mu$, equivalent spherical diameter. At each temperature investigated, 6-100 ml suspensions containing 0.2, 0.5, 1.0, 2.0, 3.0 and 4.0 g of kaolinite were prepared by adding the weighed clay to 100 ml of deionized water and placing the suspensions in an ultrasonic generator for 10 min.

The bentonite used in this study was a sodium saturated Wyoming bentonite provided by the American Colloid Company under the trade name "KWK Volclay." A 2 per cent suspension of the bentonite was sedimented three times to remove large particles of foreign material. The bentonite was prepared like the kaolinite with the exception that the samples contained 0.02, 0.05, 0.1, 0.15, 0.25 and 0.50 g of bentonite in 100 ml of deionized water.

Procedure

At each temperature the 6-100 ml kaolinite suspensions, the 6-100 ml bentonite suspensions, and 3-100 ml samples of deionized water were conductometrically titrated with the standardized surfactant solution to determine the point of initial micelle formation. One replication was made on each suspension. The five temperatures at which the suspensions were titrated were 3.0, 12.5, 20.0, 28.0 and 43.0°C. The temperatures of the

suspensions were maintained within $\pm 0.1^\circ\text{C}$ in an alcohol-water bath with a refrigeration unit and a constant temperature circulator. The concentrations of surfactant at which micellization occurred for the plain water (CMC) and for the suspensions were determined from graphs of the specific conductivity vs. moles/l. of surfactant in the titrated suspension. Moles/l. of surfactant in the titrated suspension were used instead of milliliters of surfactant solution added during titration, because the surfactant is in an aqueous solution and the water added during the titration affects the CMC causing a dilution effect. The number of moles of surfactant required to form a bioriented monolayer on the suspended clay was determined by subtracting the number of moles required before micelles form in plain water from the number of moles required before micelles form in the clay suspension. A bioriented monomolecular adsorption layer was used because the suspensions showed strong hydrophobic-hydrophilic changes during the titrations suggesting both orientations and a complete bimolecular adsorption layer would double the surface area values obtained which would be in disagreement with calculations determined from particle size. By knowing that one molecule of dodecylamine hydrochloride will occupy 26 \AA^2 , the surface area of the suspended clay was calculated. The surface area per gram was

determined from the number of grams of clay in suspension. Ideally, the surface area/g of clay should be independent of the concentration of the clay.

RESULTS AND DISCUSSION

Initial conductometric titrations of deionized water with various concentration of surfactant solution showed a variation of the CMC with the concentration of the surfactant used in the titration. The CMC decreased with decreasing surfactant concentration. Therefore, all the titrations were done with a surfactant solution of approximately 0.1 molar. Conversely, the CMC did not show a significant dependence on temperature. Theoretically, the CMC should decrease with decreases in temperature. This effect could have been masked, since at the lower temperatures the observable endpoint appeared to reflect supersaturation of the system before micelles formed.

The titration curves obtained for the kaolinite suspensions at 12.5 , 20.0 , 28.0 and 43.0°C were similar in form. Figure 2 shows the titration curves of two of the kaolinite samples and the water sample done at 12.5°C . The endpoints, representing the initial micelle formation, are located due to the concave nature of the curve before the micelles form. Ideally, the curve would be straight in this region representing a Freundlich or Langmuir

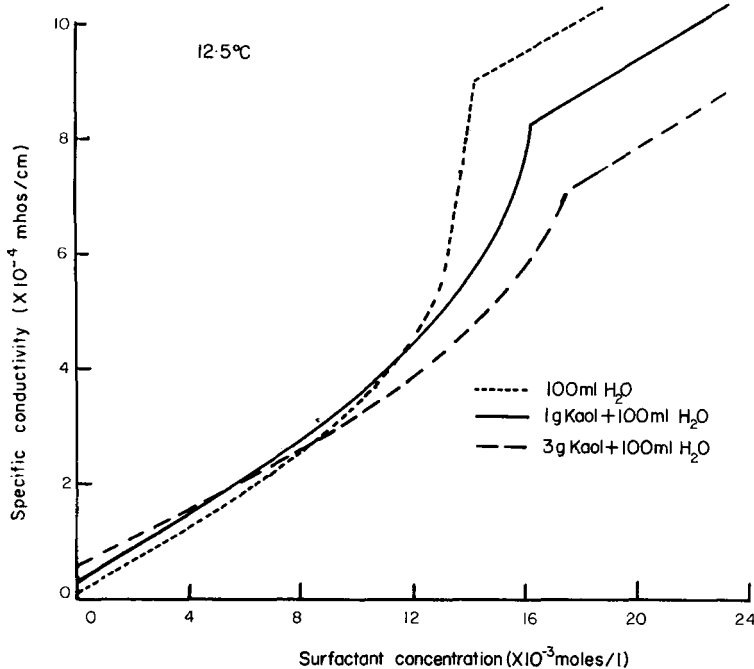


Fig. 2. Conductometric titration curves for kaolinite suspensions at 12.5°C titrated with 0.1 M dodecylamine hydrochloride solutions.

type adsorption curve. The observed curvature appeared to be related to the age of the surfactant solution. (The curvature increased with the age of the surfactant solution.) The slope of the curve after the initial micelle formation was the same for each concentration of kaolinite titrated at all the temperatures but 3.0°C . The slope of these lines is dependent upon the concentration of the surfactant solution. Figure 3 summarizes the surface

Figure 4 contains the titration curves of three different concentrations of bentonite and one water sample at 12.5°C . The curves are similar in nature to those obtained for kaolinite with the exception that at the higher concentrations a pronounced deviation occurs near the start of titration. Where the curve reassumes the basic Freundlich-Langmuir shape, flocculation occurs, which is so severe that at the highest concentration investigated

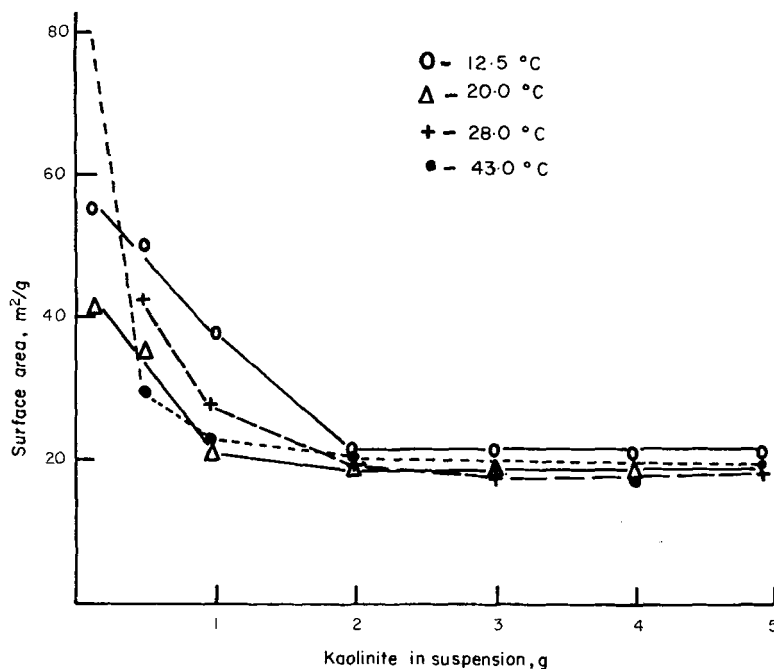


Fig. 3. Surface area values of kaolinite determined from the conductometric titration curves showing a dependence on the concentration of kaolinite.

area data obtained for kaolinite. At concentrations of kaolinite in excess of $1.5\text{ g}/100\text{ ml}$ of water, the surface areas of the clay show no dependence on the concentration of the clay. BET determined surface areas of this kaolinite prepared by the Georgia Kaolin Company varied from 20 to $21\text{ m}^2/\text{g}$, which is in good agreement with the experimental data obtained in this investigation. Differences between the isotherms in the linear section of the graph were not sufficiently large to permit conclusions to be drawn on temperature dependent relationships. In the region below 1.5 g of kaolinite/ 100 ml of deionized water multimolecular layering occurred. It can be concluded that when working in the linear section of Fig. 2 ($>1.5\text{ g}/100\text{ ml}$ of water) a good approximation of the surface area of kaolinite may be obtained at temperatures between 12.5 and 43.0°C .

(0.50 g of bentonite in 100 ml of deionized water) it was impossible to keep the bentonite in suspension. This deviation represents the replacement of the exchangeable sodium by the surfactant ion. The abnormal increase in the specific conductivity is due to the additional sodium ions entering the system. This represents the completion of the first surfactant layer on the particle.

Flocculation following the first stage of adsorption is due to either the high affinity between the hydrocarbon tails or the hydrophobic properties of the suspended particles. Deflocculation occurs with the second stage of adsorption due to van der Waals forces. Figure 5 summarizes the surface area data for the bentonites at the four higher temperatures. The four isotherms have average surface areas between 300 and $380\text{ m}^2/\text{g}$, with the average surface areas increasing proportionately

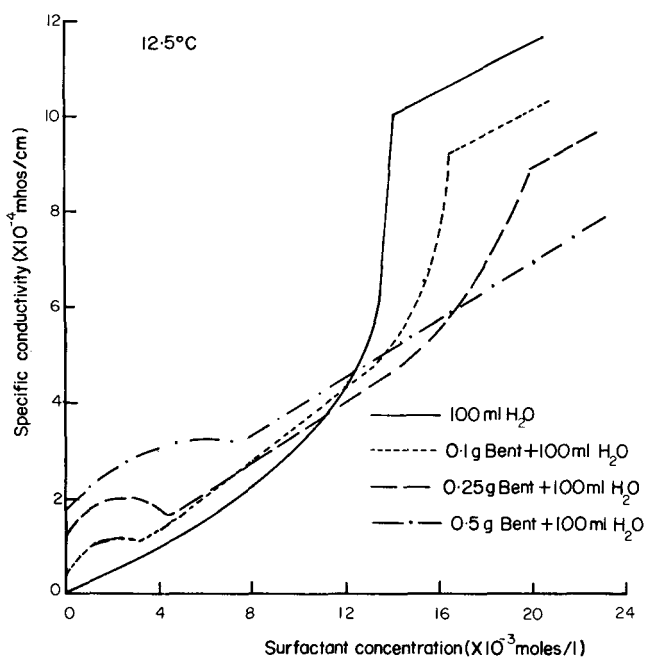


Fig. 4. Conductometric titration curves for bentonite suspensions at 12.5°C titrated with 0.1 M dodecylamine hydrochloride solution.

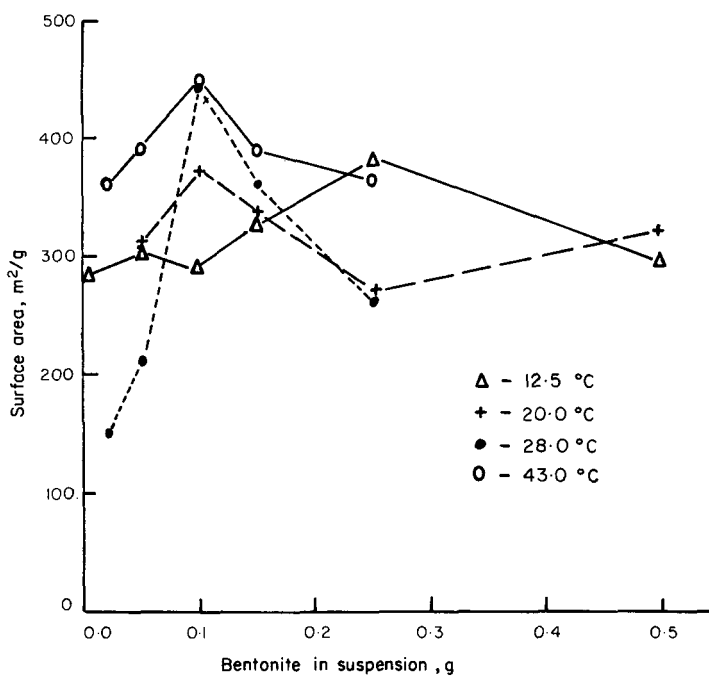


Fig. 5. Surface area values of bentonite determined from the conductometric titration curves.

with the temperature. Adsorption is in excess of the external surface area of bentonite showing some coating in the interlamellar areas. There is no multilayer formation at the lower bentonite concentrations as was apparent with the kaolinite samples. The fluctuations in the isotherms are probably due to the flocculation that occurs after the initial stage of adsorption and would be a function of the cation exchange capacity. The average surface area values are all above the methylene-blue adsorption determined surface area of $295 \text{ m}^2/\text{g}$. The BET determined exterior surface area of this clay prepared by Battelle Memorial Institute, Columbus, Ohio was $12.57 \text{ m}^2/\text{g}$. If it is assumed that the bioriented monomolecular layer is shared by the two faces in the interlamellar area, the surface areas calculated from the experimental data, considering the $12.57 \text{ m}^2/\text{g}$ of exterior surface area to contain a nonshared molecular layer, would be in the range of $700 \text{ m}^2/\text{g}$. This agrees with the calculated theoretical surface area for bentonite of $750 \text{ m}^2/\text{g}$. Due to the large fluctuations in the calculated surface areas for each temperature, it is highly improbable that this surfactant can be used to determine surface areas of bentonitic clays in suspension.

Figure 6 shows the conductometric titration curves for kaolinite and bentonite at 3.0°C . It is proposed that these curves reflect supersaturation

of the ionized form of the surfactant in the solution before micellization occurs. The correct endpoints may be obtained by extrapolating the curve after it has leveled off beyond the initial micelle formation.

From the results of this study the laboratory technique is only recommended for use with kaolinite. The recommended laboratory procedure is:

- (1) Prepare an approximately 0.1 M solution of dodecylamine hydrochloride as outlined in the section on materials.
- (2) Prepare 3-100 ml suspensions of kaolinite in the range of $2 \text{ g}/100 \text{ ml}$ to $6 \text{ g}/100 \text{ ml}$.
- (3) Conductometrically titrate the three suspensions with the standardized dodecylamine hydrochloride at any temperature between 12.5 and 43.0°C .
- (4) The specific conductivity is plotted against the molar concentration of surfactant in the suspension as is shown in Figs. 2, 4, and 6. The endpoints will give the molar concentration of surfactant at which the initial micelle formation occurs.
- (5) The CMC of the surfactant in deionized water is obtained by plotting the grams of kaolinite in each sample vs. the concentration of surfactant at which the micelles start to form. A line through these three points is

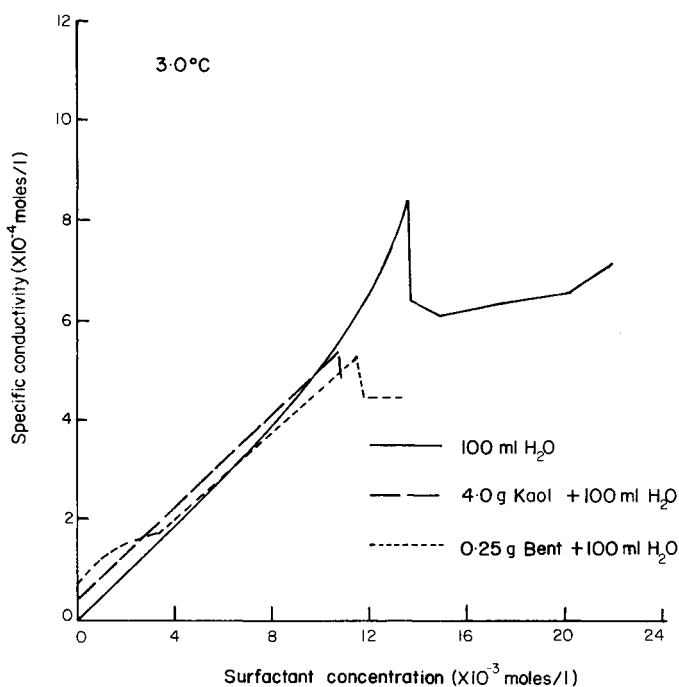


Fig. 6. Conductometric titration curves observed at 3.0° .

extrapolated to zero kaolinite concentration. The intercept on the surfactant concentration axis represents the CMC. This procedure is illustrated in Fig. 7. This technique is recommended in place of titrating 100 milliliters of water because the clay acts as a

SUMMARY

Conductometric titrations have been used to study the adsorption of dodecylamine hydrochloride on the surfaces of bentonite and kaolinite in aqueous suspensions. The surface areas of the clays were calculated from the adsorption iso-

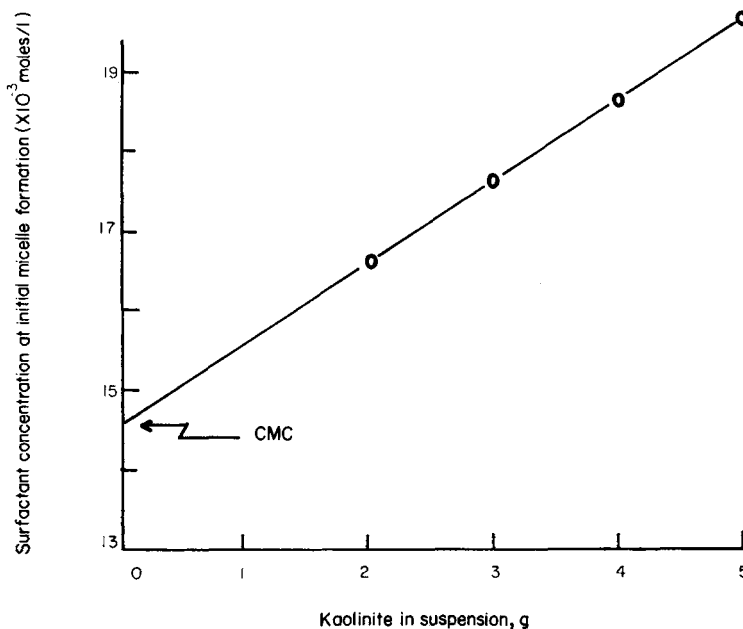


Fig. 7. Extrapolation procedure for determining the CMC of 100 ml of water.

catalyst decreasing the time involved for equilibrium to be obtained after each increment has been added.

- (6) The number of moles of surfactant required to form the bioriented monolayer on the clay surface is obtained by multiplying the difference between the surfactant concentration representing micelle formation for each of the three samples and the CMC obtained from the extrapolation, by the sum of the number of milliliters in the suspension at the endpoint for each of the clay samples. The surface area is calculated by multiplying the number of moles required to form the monolayer by the surface area covered by one mole of surfactant ($26 \text{ \AA}^2/\text{molecule} \cdot 6.024 \times 10^{23} \text{ molecules/mole}$). The surface area/g is obtained by dividing the surface area for each sample by the number of grams in sample. The surface area values should be reproducible to within $\pm 0.50 \text{ m}^2/\text{g}$.

therms realizing that one molecule of dodecylamine hydrochloride covers 26 \AA^2 of surface. The advantages with this method are that a solvated sample is measured and the procedure is relatively simple and fast.

The surface area values obtained for the kaolinite samples in excess of 1.5 g per 100 ml of deionized water showed no dependence on the concentration of the suspended clay and were in good agreement with BET determined surface areas. In this region there was no noticeable temperature dependence between 12.5 and 43°C. The surface areas for the kaolinite samples below this concentration were much higher than expected and illustrated multimolecular layering on the surfaces. The surface areas calculated from the bentonite adsorption isotherms showed considerable instability and are not considered suitable for surface area determinations. Both the bentonite and kaolinite samples titrated at 3°C showed supersaturation of the ionized surfactant before the

initial micellization occurred. These adsorption isotherms could be extrapolated back to the approximate endpoint, but the time involved for equilibrium to be obtained was excessive.

A procedure was given for the surface area determination of kaolinites. It differs from the procedure used by the investigator in that the CMC of deionized water is obtained by extrapolation of the moles per liter of surfactant required before micellization occurs to zero concentration of suspended clay. This study determined the CMC by titrating 100 ml of deionized water containing no clay. When this procedure is used the surface area values obtained should be reproducible to within ± 0.50 m²/g.

This procedure has been used with several kaolinite and bentonites containing different counter ions with results in agreement with the data presented. In this initial investigation only one surfactant was thoroughly investigated. For more accurate results with kaolinites a surfactant with a lower critical micelle concentration and a lower micelle conductivity should be used. The authors also believe that the problems involved with the bentonite suspensions can be solved with the choice of another surfactant.

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Résumé—La titration conductométrique des suspensions d'argile avec des solutions surfactantes offre une méthode rapide de détermination de la superficie des particules d'argile en suspension dans un milieu aqueux. On a employé dans cette étude un surfactant cationique, l'hydrochlorure de dodecylamine. Ce surfactant a été adsorbé par liaison électrostatique aux endroits de l'échange cationique ainsi que par les forces de van der Waals. Une couche monomoléculaire ou bimoléculaire de surfactant enrobe la particule et l'achèvement de la couche est déterminé par une modification de la pente de la courbe de titration conductométrique en raison de la formation de micelles. On a obtenu un bon accord entre cette méthode et les valeurs BET pour le kaolinite. Les suspensions de bentonite montraient une tendance marquée à la flocculation après l'étape initiale de l'adsorption; par conséquent il y avait une variation importante dans les résultats. Cette méthode de mesure de la superficie des particules d'argile offre de nombreux avantages par rapport aux techniques actuelles: (1) une particule sèche n'est pas nécessaire; (2) le matériel est peu coûteux et disponible dans beaucoup de laboratoires; (3) il s'agit d'une méthode rapide; (4) le vide et une température élevée ne sont pas nécessaires, et (5) la méthode mesure la superficie intérieure aussi bien que la superficie extérieure.

Kurzreferat—Leitfähigkeitstitrationen von Tonsuspensionen mit oberflächenaktiven Lösungen stellen ein Schnellverfahren zur Messung des Oberflächeninhaltes von Tonteilchen, die in wässrigen Medien suspendiert sind, dar. In dieser Arbeit wurde ein kationisch wirksames Mittel, Dodecylamin Hydrochlorid verwendet. Das oberflächenaktive Mittel wurde durch elektrostatische Bindung an Kationenaustauscher-Stellen sowie durch van der Waals Kräfte adsorbiert. Eine monomolekulare oder bimolekulare Schicht des oberflächenaktiven Mittels bedeckt das Teilchen, und die Komplettierung der Schicht wird mit Hilfe einer Änderung in der Neigung der Leitfähigkeitstitrationskurve infolge der Bildung von Mizellen festgestellt. Für Kaolinit wurde gute Übereinstimmung zwischen dieser Methode und BET-bestimmten Werten erhalten. Die Bentonit-Suspensionen neigten stark dazu nach der ersten Adsorptionsstufe auszuflocken wodurch die Ergebnisse starken Schwankungen

unterworfen waren. Diese Methode der Messung des Oberflächeninhalts von Tonteilchen bietet eine Reihe von Vorteilen gegenüber den gegenwärtig angewendeten: (1) trockene Teilchen sind nicht erforderlich; (2) die Ausrüstung ist billig und in den meisten Laboratorien vorhanden; (3) die Methode ist schnell; (4) Vakuum und hohe Temperatur sind nicht erforderlich, und (5) die Methode misst den inneren sowie den äusseren Flächeninhalt.

Резюме—Кондуктометрическое титрование глинистых суспензий поверхностно-активными растворами предоставляет быстрый метод определения площади поверхности глинистых частиц, которые суспендированы в водных средах. Катионное поверхностно-активное вещество, додециламинированный гидрохлорид, применялось в настоящем исследовании. Это поверхностно-активное вещество адсорбировалось электростатической связью в местах катионного обмена, а также вандерваальсовыми силами. Мономолекулярный или бимолекулярный слой поверхностно-активного вещества покрывает частицу, а завершение покрытия определяется по изменению в наклоне кривой кондуктометрического титрования вследствие образования мицелл. Хорошее согласование между этим методом и значениями, определенными по системе BET, получено было для каолинита. Суспензии бентонита обладают сильной склонностью к флокуляции после исходной фазы адсорбции, вызывая крупные различия в результатах. Настоящий метод измерения площади поверхности глинистых частиц предоставляет много преимуществ, по сравнению с применяемыми теперь методами: (1) не надо иметь сухой частицы; (2) оборудование гешевое и имеется в распоряжении во многих лабораториях; (3) метод этот быстрый; (4) нет нужды в вакууме и в высоких температурах и (5) методом этим измеряется как внутренняя, так и внешняя площадь поверхности.