SPE
Society of Petroleum Engineers of AIME

SPE 11800

Adsorption of Asphaltenes and Water on Reservoir Rock Minerals

by S.H. Collins and J.C. Melrose,* *Mobil Research & Development Corp.*

*Member SPE-AIME

This paper was presented at the International Symposium on Oilfield and Geothermal Chemistry held in Denver, CO, June 1-3, 1983. The material is subject to correction by the author. Permission to copy is restricted to an abstract of not more than 300 words. Write SPE, 6200 North Central Expressway, Drawer 64706, Dallas, Texas 75206 USA. Telex 730989 SPEDAL.

ABSTRACT

New data relating to the adsorption of asphaltenes on reservoir rock minerals are reported. The data were obtained by contacting samples of several different clay mineral types, as well as of Berea sandstone, with toluene solutions of a petroleum asphaltene fraction. This material was recovered from a deposit on the tubing string of a producing well. It was characterized with respect to molecular weight and elemental composition. Adsorption isotherms were determined and found to be of the Langmuir type, indicating monolayer adsorption. For each of the samples an independent surface area measurement was made. This permitted the probable size of the adsorbed asphaltene particles to be estimated. The effect of water on the adsorption of asphaltenes on kaolinite was also determined. It was found that adsorption was reduced but not eliminated by the presence of water. In these experiments the water was either pre-adsorbed on the clay or simply dissolved in the solvent. The amount of co-adsorbed water corresponded to 30-50 monolayers, indicating the probable formation of liquid bridges of water between clay particles. Estimates were obtained for the magnitude of the microscopic toluene/water contact angles which characterize these liquid bridges.

INTRODUCTION

Various problems arising in petroleum reservoir exploitation involve the interaction of pore-filling fluids with the minerals which are exposed at the pore surfaces in reservoir rock. For example, the wettability of a reservoir is believed to be strongly dependent on the extent of heavy ends adsorption[1-5]. Although the nature of this dependence has yet to be expressed in quantitative terms, it appears that heavy ends adsorption will affect, in the first place, the relative proportions of the total pore surface area which are in contact with each of the two fluid phases, oil and brine. If the fluid in question is the oil phase, the fractional surface area for this fluid may be termed the surface oil saturation. Thus, a general objective of much research on wettability has been to develop a method for measuring the surface oil saturation of reservoir rock samples[6,7].

Another phase of wettability research has been directly focused on the process of heavy ends adsorption. This has involved the quantitative determination of the extent and nature of the adsorption of a well-characterized asphaltene fraction on various rock and mineral surfaces[1,2]. The present paper reports the results of further work of this kind. A specific objective was to determine whether thin films of water on the surface of a mineral would prevent or modify the subsequent adsorption of asphaltenes. The fact that adsorbed water affects the adsorption of petroleum heavy ends has been alluded to in the literature[1,3]. However, it is believed that the present study is the first to attempt to quantify the effect by means of adsorption measurements on clay mineral surfaces.

The manner in which heavy ends adsorption determines the magnitude of the surface oil saturation of reservoir rocks is not known at present It has been proposed[5] that a complex interplay of capillary forces[8,9], thin film forces[10-12], and adsorption forces[13-16] is involved. Other studies on wettability suggest that in many instances this type of interplay gives rise to a state of mixed wettability[17,18]. In the present paper, attention is restricted to the question of how asphaltene adsorption is affected by the presence of adsorbed water. Isotherms are reported for various amounts of pre-adsorbed water on a kaolinite surface. Also, oil/water contact angle data are reported for several solid surfaces which had been prepared by compacting a sample of asphaltene-covered clay.

The principal constituents of petroleum which adsorb on clay minerals have been identified in previous work[2-4] as asphaltenes and resins. These fractions comprise the most polar class of compounds

---

References and illustrations at end of paper.

in petroleum and are concentrated in what has been termed the heavy ends[19]. In the present work a sample of asphaltenes from a single source was chosen as representative of a heavy ends fraction.

EXPERIMENTAL

The asphaltene sample used in this work was a tubing string deposit from a well in an Alberta, Canada, light oil reservoir. The elemental analysis and molecular weight data for this sample are shown in Table 1.

A particular clay sample was used in most of the experiments. This clay was a kaolinite obtained from Fisher Scientific Company. The BET surface area was 19.3 m^2/g, and the cation exchange capacity was 2.97 meq/100 g. From these data the calculated surface charge density was 0.15 C/m^2. Data obtained by various methods for measuring surface area and cation exchange capacity are compared in a recent review paper[20]. In the present work cation exchange capacity (CEC) was measured by a modified ammonium acetate method.

Adsorption experiments were also carried out using several other clay mineral and rock samples. Surface areas and cation exchange capacities for these samples are listed in Table II. Calculated surface charge densities are also given. Densities in excess of 0.5 C/m^2 are unrealistic. Thus, the surface area for the Berea sandstone sample is probably too low and does not represent the actual value of the surface area when a sample is exposed to a bulk aqueous phase, as in the CEC determination. However, the asphaltene adsorption studies with the Berea sample involved exposure to water vapor only at low relative humidities. Therefore, the surface area listed in Table II is believed to be applicable to these experiments.

Mallinckrodt spectrophometric grade toluene dried through a silica gel column was used in all experiments. The clay samples were dried overnight at 120°C and kept in a dessicator. Two samples of the dry Fisher kaolinite were placed in dessicators at constant relative humidities. One sample was kept at a relative humidity of 83 percent with a saturated solution of KBr. The other sample was kept at a relative humidity of 97 percent with a saturated solution of K_2SO_4. The clay sample at 83 percent relative humidity adsorbed 2.3 weight percent water while the sample at 97 percent relative humidity adsorbed 6.6 weight percent water.

The adsorption isotherms of asphaltene on clay were determined by contacting approximately 0.1 g of clay with 20 ml of a solution of asphaltene in toluene and shaking overnight. The asphaltene solutions were prepared by dilution of a stock solution to give a concentration range from 50 mg/l to 1,000 mg/l. The solutions used with the clays containing water were saturated with water before contacting the clays. The concentrations of the asphaltene solutions after contact with the clay were determined spectrophotometrically with a Beckman model 25 spectrophotometer. The samples were centrifuged and the absorbance determined at 400 nm. Since an asphaltene in toluene solution does not have an absorbance peak at any wavelength, the 400 nm wavelength was chosen because it gave a better least squares fit of absorbance vs. concentration than other wavelengths.

The amount of asphaltene adsorbed on the clay was determined directly on a few samples using a Perkin Elmer 240B Elemental Analyzer. The samples were air dried, and the amount of carbon on the clay was then determined. Since the clay itself contained no carbon, all the carbon found was due to the asphaltene adsorbed on the clay.

The water content of the toluene solutions was determined by Karl Fischer titration. The solubility of water in toluene is shown in Table III as a function of asphaltene concentration. The average water solubility was 496 mg/l, there being no effect of asphaltene concentration.

Contact angles between water and toluene were also measured on several surfaces. These included a graphite surface and the surface of a kaolinite sample with 25.7 mg/g of asphaltene adsorbed. The graphite surface was prepared by polishing a small piece with 600 grit wet sandpaper, and then with wet crocus cloth. This produced a smooth, flat surface. Two methods were used to prepare a clay/asphaltene surface. One method was to press asphaltene-covered clay into a pellet, using a pellet press. Two pellets were prepared, a large pellet pressed at 20,000 psi in an aluminum cup, and a small pellet pressed at 10,000 psi. The other method of preparing a clay/asphaltene surface was to slurry the clay/asphaltene in isooctane and pour it quickly over a clean quartz or limestone plate and allow the isooctane to evaporate. This produced a relatively uniform but rough surface.

Both the pressed surface and the layered surface were stable when immersed in toluene containing 40-50 mg/l of asphaltene. Neither surface was stable when immersed in water. The layered surface separated from the plate and fell to the bottom of the container. The pressed surface buckled and cracked after several hours of immersion in water. However, the pressed surface remained stable for several days after the initial deformation, and contact angles were obtained for several toluene drops. The layered surface did not remain stable overnight, and therefore, contact angles were obtained after 5 to 10 minutes.

Contact angles were measured using the semimicro sessile drop technique[21]. The advancing angles were determined using a water drop in toluene while the receding angles used a toluene drop in water. Pure toluene and water were used for the graphite system. The clay/asphaltene system used a toluene solution of 50 mg/l asphaltene for the advancing case and the equilibrium solution of the clay/asphaltene for the receding case. The contact angles were determined by photographing the drop and measuring the angles with a protractor. Where possible both sides of the drop were measured and the results averaged.

RESULTS

Asphaltene Adsorption on Various Mineral Surfaces

Asphaltene adsorption isotherms were determined on dry samples of kaolinite, illite, and chlorite obtained from Ward's Natural Science Establishment and on a sample of Berea sandstone, as well as on the Fisher Kaolinite. The results are given in Figure 1 and Table IV. Figure 1 shows that typical Langmuir type 1 adsorption isotherms were obtained. The maximum adsorption for the four clays studied ranges from 20 mg/g for the Georgia kaolinite to 30 mg/g for the Fisher kaolinite. However, as indicated in Table IV, if the isotherms are expressed as mg/m^2 instead of mg/g, a different order appears.

The asphaltene adsorption isotherm for the dry Berea sand is not shown in Figure 1. When expressed in mg/m^2, the isotherm for the Berea sand was similar to that of the Fisher kaolinite. It should be noted that the clays associated with Berea sand include both kaolinite and illite.

The isotherms for several of the clays showed a decline in adsorption at the highest asphaltene concentration. This is attributed to scatter in the data and may be a reflection of the inhomogeneity of the solids.

Plots of the ratio of asphaltene concentration to amount of adsorbed asphaltene versus the asphaltene concentration indicated some deviation from simple Langmuir isotherm behavior. This deviation occurred at the lowest concentrations. Consequently, only approximate values of the initial slopes of the isotherms shown in Figure 1 could be determined. Within the accuracy of the data, the same value of the initial slope appeared to represent the results for each clay. This value, 0.1 l/m^2, is related to the equilibrium constant for the adsorption of asphaltenes at low concentrations. Hence, it is also related to the standard Gibbs free energy change for the adsorption process.

Effect of Water on Asphaltene Adsorption

The isotherm data for the adsorption of asphaltenes on Fisher kaolinite under various conditions are summarized in Table V and shown in detail in Figure 2. The dry clay adsorbed a maximum of about 30 mg asphaltene per gram of clay. The addition of 2.3 percent water to the clay reduced the maximum adsorption to 22 mg/g. The addition of 6.6 percent water reduced the adsorption to 13 mg/g. Dry clay adsorbed 24 mg/g of asphaltenes from water-saturated toluene solution. It is seen that the presence of a thin film of water adsorbed on the kaolinite surface reduces but does not eliminate the adsorption of asphaltenes.

Again, the initial slopes of the isotherms shown in Figure 2 could be determined only approximately. It appeared that within the accuracy of the data, the initial slopes were essentially the same as those found when dry clays were used.

Related work had led to the conjecture that the adsorption of asphaltenes on clay might depend on the equilibration time, especially in those cases where water was present. However, as shown by the solid symbols of Figure 2 and the data of Table V, no significant change in the adsorption of asphaltenes occurred after one month equilibration both for the dry clay and for the sample containing 6.6 weight percent water.

Co-Adsorption of Water

The purpose of using toluene solutions saturated with water was to prevent the desorption of water from the clay. However, the final water concentration (Column 3 of Table V) shows that the clay adsorbed water from the toluene solutions. Table VI shows that the clay sample containing 2.3 percent water adsorbed an average of 4.75 percent water on the clay. The clay containing 6.6 percent water adsorbed an average of 2.9 percent water from the toluene solution for a total of 9.5 percent water on the clay.

Using a packing area per water molecule of 10.8 x 10^{-2} nm^2, as given in the literature[20], the amount of water required to form a monolayer on the clay surface is found to be 0.535 percent. This means that the number of monolayers of water on the clay increased from 4.3 monolayers to 13.2 monolayers and from 12 monolayers to 18 monolayers for the clays originally containing 2.3 percent water and 6.6 percent water, respectively. The dry clay adsorbed an average of 4.6 percent water from water saturated toluene solutions. This corresponds to 8.7 monolayers of water.

Contact Angles

The contact angle data are shown in Table VII. There was considerable hysteresis on all surfaces tested. Both methods of preparing the clay/asphaltene surface produced approximately the same contact angles even though the layered surface was much rougher than the pressed surface. Contact angles were measured on quartz and limestone to determine if the support influenced the contact angle on the clay/asphaltene layer. Water advancing angles of 35° on quartz and 80° on limestone, contrasted with water advancing angles of 155° for clay/asphaltene on quartz and 130° for clay/asphaltene on limestone, indicate that the substrate exerted no influence on the contact angles. A comparison of the contact angles reported here and literature values was not possible because no contact angle data for clay/asphaltene systems have been reported.

DISCUSSION

Maximum Adsorption Values for Dry Clay

In assessing the validity of the results given in Table IV, it is of interest first to compare these data with previous work. As noted, the isotherms shown in Figure 1 are of the Langmuir type 1, indicating monolayer adsorption. The maximum values of the adsorption are similar to the values obtained by Clementz for the adsorption of petroleum heavy ends on dry montmorillonite[2]. Thus, for example, the adsorption of asphaltenes on both Fisher kaolinite and montmorillonite is about 30 mg/g. A more realistic comparison is that based on the surface areas of the clays. This comparison is not possible, however, because the surface area of the montmorillonite used by Clementz is not known. Data reported by Brooks[22] suggest that surface areas for dry montmorillonite are probably in the range of 10-30 m^2/g. On this basis the adsorption per unit area for montmorillonite would be expected to be in the same range as for the clays studied here. A similar level of adsorption for asphaltenes on silica and on kaolinite has been reported by Fritschy and Papirer[23].

Another way to evaluate the significance of the maximum adsorption values given in Table IV is to attempt to relate these values to the size and shape of the asphaltene particles as they exist in the adsorbed state. Since the adsorption appears to be of the monolayer type, it can be assumed that the size and shape are not altered by the process of adsorption. Various studies suggest that such particles are sheet-like in structure (see Figure 3) and hence can be roughly modeled as having a disk-like shape. Thickness values ranging from 1.8 to 2.3 nm[24] and from 1.0 to 1.4 nm[25] have been reported. The equivalent diameter can then be calculated if values of the molecular weight and the density are known or can be assumed. Measurements reported by Parkash et al[26] suggest that a density of about 1.6 g/cm^3 is appropriate for an asphaltene fraction with a carbon content of 86 percent. Using this value, a molecular weight of 4000, and a thickness of 1.1 nm, a diameter of 2.2 nm is obtained. This is just within the reported range of 2.2 to 3.7 nm[24].

In applying these estimates of particle thickness and density to the adsorption data, several assumptions are required. The first is that the asphaltene particles are adsorbed with the disk or sheet faces in contact with the planar faces of the clay particles. Two further assumptions which must be made involve the values of (1) the packing density of the particles on the clay surface, and (2) the fraction of the total clay surface which corresponds to the planar surface of the clay particles, as distinguished from the edge surface. Neither of these quantities is known very precisely but can be estimated as 0.8 and 0.9, respectively. With these assumptions, a thickness of 1.1 nm and a density of 1.6 g/cm^3 give a value for the maximum adsorption of 1.27 mg/m^2. This value is surprisingly close to the average for the two kaolinite samples given in Table IV. It is concluded that the adsorption data for this clay are not inconsistent with what is currently known about the size and shape of asphaltene particles and their probable configuration on the surface of clay minerals.

The results given in Table IV for the other clays and for Berea sandstone are also roughly consistent with the simple model used to interpret the data for the two kaolinites. For the Georgia kaolinite and illite samples, it is possible that not all of the water was removed from the adsorption system by the drying procedures used. The high value of the maximum adsorption which was observed with the chlorite sample may be an indication of an erroneously low value of the surface area in this case. Further experiments, with systems more closely controlled with respect to traces of water, will be required to test the applicability of the model in a more rigorous fashion.

Co-adsorption of Water and Asphaltenes

One of the first observations that pre-adsorbed water films do not prevent the adsorption of asphaltenes was reported by Devereux[27], who showed that NMR proton relaxation times were altered by asphaltene adsorption. In the work reported by Clementz[2], reference was made to a number of Russian papers dealing with asphaltene adsorption. One of these papers, by Lyutin and Burdyn[1], indicates that asphaltene adsorption is reduced by about 60 percent when the water saturation in an unconsolidated sand pack increases to 30 percent. This agrees qualitatively with the results reported in the present study (Table VI).

Clementz[3] also studied the sensitivity of Berea cores to fresh water. It was found that asphaltenes adsorbed on the pore surfaces stabilized the clays and eliminated the sensitivity. However, adsorption of the asphaltenes in the presence of water did not stabilize the clays. It is evident that the detailed mechanism by which asphaltene adsorption can take place, even though several molecular layers of water are preadsorbed on the clay surface, is not understood. A number of possible mechanisms for the asphaltene/clay mineral interaction are mentioned by Czarnecka and Gillott[28].

It is likely that further insight into the mechanism of asphaltene adsorption could be obtained if adsorption measurements were to be carried out at various temperatures and over a wider range of pre-absorbed water content. A thermodynamic analysis of the data would then permit values for the enthalpy and entropy of adsorption to be calculated. Comparison of such values with related data in the literature would enable the molecular interactions involved the asphaltene adsorption process to be identified.

In this conection the evidence reported by Clementz[2] for the dependence of asphaltene adsorption on both the type of exchangeable cation and the type of solvent is significant. It appears that magnesium clay adsorbs asphaltenes most strongly from aromatic solvents, but potassium clay adsorbs most strongly from nitrobenzene. Effects such as these suggest that the molecular interactions involved in asphaltene adsorption are quite specific in nature and are closely connected with detailed features of asphaltene chemical structure, as yet poorly understood.

One feature of the results obtained in the present study should be discussed further. This feature relates to the fact that the calculated number of monolayers of co-adsorbed water varies from about 9 to about 18, as the maximum value of the asphaltene adsorption decreases. These water monolayer values should, however, be adjusted upwards, in order to take into account the coverage of only a fraction of the total surface area by the asphaltene layer (as indicated in Table VI). Thus, the actual value of the number of monolayers of water is of the order of 30-50 and is only weakly dependent on the level of asphaltene adsorption.

If now this adjusted value of the thickness of the co-adsorbed water layers is regarded as approximating the true value, an important conclusion may be drawn. This conclusion is that capillary forces, rather than true adsorption forces, are responsible for the major part of the water which is retained by the clay. Thus, the bulk of the water is almost certainly in the form of liquid bridges between individual clay particles. The role of such liquid bridges in stabilizing agglomerates of fine particles, suspended in a non-wetting fluid, is well known[29]. Unfortunately, in the present case, the geometrical shapes of these liquid bridges cannot easily be predicted. This is, in part, due to the highly asymmetric shapes of the clay particles and to the differences in the adsorptivity for water on the faces and edges of the particles.

With respect to a possible quantitative relationship between asphaltene adsorption and the quantity of co-adsorbed water, it should be pointed out that the data given in Table VI do provide evidence for such a relationship. Thus, when the final amount of water on the clay is plotted against the maximum asphaltene adsorption, a smooth curve results. Unfortunately, insufficient data are available to indicate whether or not the amount of asphaltene adsorption decreases to zero with a very large excess of water. Various studies reported in the literature[6,15,27,28] suggest that, at least in many cases of practical interest, an excess of water does not completely inhibit asphaltene adsorption.

Significance of Contact Angle Measurements

Contact angle data are particularly useful in cases in which two immiscible liquids interact competitively with a solid substrate. The data reported in Table VII show that the presence of an adsorbed layer of asphaltenes alters the wetting characteristics of the kaolinite surface to a very significant degree. The data also indicate that with respect to both advancing and receding angles the resulting surface is somewhat comparable to that of graphite. The hysteresis which is observed is very likely due in part to the heterogeneity of the asphaltene/clay surface[30]. Whether or not this heterogeneity is the result of incomplete monolayer coverage is not known. It should be noted that in these experiments the water advancing angles observed with clean solid surfaces were also significantly greater than the receding angles.

The interpretation of the contact angle data in terms of a detailed molecular model of the surface formed by asphaltene adsorption on clay has not been attempted. Nevertheless, the data clearly indicate that, even in the presence of bulk water, the adsorbed asphaltene layers in the clay surfaces are not immediately displaced. It is believed that to the extent that the solid surfaces used in these experiments were observed to be unstable, this effect was due to the penetration of water into pores which were not covered by adsorbed asphaltenes. A similar affect was observed by Czarnecka and Gillott[28]. Thus, the contact angle data are believed to be consistent with the adsorption results, indicating that water and asphaltenes co-adsorb on clay mineral surfaces.

SUMMARY AND CONCLUSIONS

1. Under water-free conditions the clay minerals kaolinite, chlorite, and illite adsorb asphaltenes in a manner similar to that of dry montmorillonite.
2. The maximum adsorption of asphaltenes on the surfaces of the various clays studied in the dry state approximates a full asphaltene monolayer.
3. The adsorption of asphaltenes on Berea rock is similar, on an equivalent surface area basis, to that on clay minerals.
4. Water pre-adsorbed on kaolinite reduces but does not eliminate the subsequent adsorption of asphaltenes from toluene solution.
5. Kaolinite adsorbs additional water from water-saturated asphaltene/toluene solutions.
6. On the basis of the surface area not covered by asphaltenes, the thickness of the co-adsorbed water on kaolinite corresponds to about 30-50 monolayers, indicating the formation of liquid bridges between clay particles.
7. Oil/water contact angle measurements support the concept that water and asphaltenes can co-adsorb on clay mineral surfaces.

ACKNOWLEDGEMENTS

Appreciation is expressed to the Mobil Research and Development Corporation for permission to publish this paper. Appreciation is also expressed to J. E. Baker, T. H. Bushaw and S. R. Faris for assistance in carrying out chemical analyses.

REFERENCES

1. Lyutin, L. V., and Burdyn, T. A., "Adsorption of Asphaltenes in a Stratum and Its Effect on Permeability and Oil Production," Tr., Vses. Neftegazov Nauch. - Issled. Inst. (1970) 53, 117-130.
2. Clementz, D. M., "Interaction of Petroleum Heavy Ends with Montmorillonite," Clays and Clay Minerals (1976) 24, 312-319.
3. Clementz, D. M., "Clay Stabilization in Sandstones Through Adsorption of Petroleum Heavy Ends," J. Pet. Tech. (September, 1977) 1061-1066.
4. Clementz, D. M., "Alteration of Rock Properties by Adsorption of Petroleum Heavy Ends: Implications for Enhanced Oil Recovery," Paper SPE 10683 (April, 1982), Third SPE/DOE Joint Symposium on Enhanced Oil Recovery, Tulsa, Okla.
5. Melrose, J. C., "Interpretation of Mixed Wettability States in Reservoir Rocks," Paper SPE 10971 (September, 1982), 57th Annual Fall Technical Conference, New Orleans, Louisiana.
6. Holbrook, O. C., and Bernard, G. G., "Determination of Wettability by Dye Adsorption," Trans. AIME (1958) 213, 261-264.
7. Shankar, P. K. and Dullien, F. A. L., "Experimental Investigation of Two-Liquid Relative Permeability and Dye Adsorption Capacity versus Saturation Relationships in Untreated and Dri-film Treated Sandstone Samples," in Surface Pheonomena in Enhanced Oil Recovery, ed. by D. O. Shah, Plenum Press, New York (1981), 453-477.

8. Leverett, M. C., "Capillary Behavior in Porous Solids," Trans. AIME (1941) 142, 152-169.

9. Melrose, J. C., "Interfacial Phenomena as Related to Oil Recovery Mechanisms," Can. J. Chem. Eng. (1970) 48, 638-644.

10. Verwey, E. J. W., and Overbeek, J. T. G., Theory of the Stability of Lyophobic Colloids, Elevier, New York (1948).

11. Takamura, K., "Microscopic Structure of Athabasca Oil Sand," Can. J. Chem. Eng. (1982) 60, 538-545.

12. Hall, A. C., Collins, S. H., and Melrose, J. C., "Stability of Aqueous Wetting Films in Athabasca Tar Sands," Paper SPE 10626 (January, 1982), Sixth International Symposium on Oil Field and Geothermal Chemistry, Dallas, Texas.

13. Brooks, C. S., "Free Energies of Immersion for Clay Minerals in Water, Ethanol, and n-Heptane," J. Phys. Chem. (1960) 64, 532-537.

14. Van Olphen, H., "Clay-Organic Complexes and the Retention of Hydrocarbons by Source Rocks," Intern. Clay Conf., Proc. Conf., Stockholm (1963) 1, 307-317.

15. Reed, M. G., "Retention of Crude Oil Bases by Clay Containing Sandstone," Clays and Clay Min. (1968) 16, 173-178.

16. Van Olphen, H., An Introduction to Clay Colloid Chemistry, 2nd ed., Wiley, New York (1977), Chapters 10 and 11.

17. Salathiel, R. A., "Oil Recovery by Surface Film Drainage in Mixed-Wettability Rocks., J. Pet. Tech. (October, 1973), 1216-1224.

18. Swanson, B. F., "Rationalizing the Influence of Crude Wetting on Reservoir Fluid Flow with Electrical Resistivity Behavior," J. Pet. Tech. (August, 1980), 1459-1464.

19. Tissot, B., "Connaissance Actuelles sur les Produits Lourds du Petrolie, "Rev. de l'Inst. Fr. du Petrole (July-August, 1981) 36, 429-446.

20. Faris, S. R., Woessner, D. E., and Melrose, J. C., "Significance of Surface Area Data to Sandstone Petrophysical Analysis," ACS Div. of Geochemistry (March, 1983).

21. Dunlap Wilson, P. M., and Brandner, C. F., "Aqueous Surfactant Solutions which Exhibit Ultra-Low Tensions at the Oil-Water Interface," J. Colloid and Interface Sci. (1977) 60, 473-479.

22. Brooks, C. S., "Nitrogen Adsorption Experiments on Several Clay Minerals," Soil Sci. (1955) 79, 331-347.

23. Fritschy, G., and Papirer, E., "Interactions Between a Bitumen, Its Components, and Model Fillers," Fuel (1978) 57, 701-704.

24. Dickie, J. P. Haller, M. N., and Yen, T. F., "Electron Microscopic Investigations on the Nature of Petroleum Asphaltics," J. Colloid and Interface Sci. (1969) 29, 475-484.

25. Speight, J. G., "On the Molecular Nature of Petroleum Asphaltenes," in Chemistry of Asphaltenes, ec. by J. W. Bunger and N. C. Li, Advances in Chemistry Series 195, ACS, Washington, D.C. (1981), 1-15.

26. Parkash, S., Moschopedis, S., and Speight, J., "Physical Properties and Surface Characteristics of Asphaltenes," Fuel (1979) 58, 877-882.

27. Devereux, O. F., "Effect of Crude Oil on the Nuclear Magnetic Relaxation of Water Protons in Sandstone," Nature (1967) 125, 614-615.

28. Czarnecka, E., and Gillott, J. E., "Formation and Characterization of Clay Complexes with Bitumen from Athabasca Oil Sand," Clays and Clay Min. (1980) 28, 197-203.

29. Kawashima, Y., and Capes, C. E., "Some Experiments on the Effect of Contact Angle in Agglomeration from Liquids," Ind. Eng. Chem. Fundam. (1980) 19, 312-314.

30. Dettre, R. H., and Johnson, R. E., Jr., "Contact Angle Hysteresis IV. Contact Angle Measurements on Heterogeneous Surfaces," J. Phys. Chem. (1965) 69, 1507-1515.

TABLE 1

ELEMENTAL ANALYSIS AND MOLECULAR WEIGHT OF ASPHALTENE SAMPLE

	Composition, Weight Percent		
Element	Analysis I[a]	Analysis II[a]	Analysis III[b]
C	85.84	86.16	85.93
H	6.41	6.11	6.62
N	0.48	0.44	0.76
S	5.01	4.76	4.51
O	2.16	-	2.77
Ash	-	-	1.97

Molecular Weights[c]

Solvent	Temperature	MW
Tetrahydrofuran	37°C	3,983
Benzene	37°C	4,019
Nitrobenzene	96°C	1,538

a) Galbraith Laboratories, Inc., Knoxville, Tennessee.

b) Clark, Means and Perkins Microanalytical Laboratory, Inc., Urbana, Illinois.

c) ARRO Laboratories, Inc., Joliet, Illinois.

TABLE II

PROPERTIES OF ADSORBENTS

Sample	Surface Area, m^2/g	Cation Exchange Capacity, meq/100 g	Calculated Charge Density, C/m^2
Kaolinite[a]	19.3	2.97	0.15
Kaolinite, Macon, Ga.[b]	18.0	3.52	0.19
Illite, Rochester, N.Y.[b]	24.0	8.64	0.35
Chlorite, Calaveras Co., Calif.[b]	13.0	3.75	0.28
Berea Sandstone	1.26	0.93	0.71

a) Purchased from Fisher Scientific Company.

b) Purchased from Ward's Natural Science Establishment, Inc.

TABLE III

CONCENTRATION OF WATER IN TOLUENE SOLUTIONS

Asphaltene Concentration, mg/l	Final Water Concentration, mg/l
0	484 ± 11[a]
50	477 ± 15
76	472 ± 9
102	479 ± 7
203	465 ± 13
305	505 ± 15
406	523 ± 4
508	513 ± 8
809	491 ± 3
1,015	547 ± 19

a) Water concentration = 151 ± 3 mg/l for sample dried over silica gel.

TABLE IV

ADSORPTION OF ASPHALTENES ON VARIOUS DRY SURFACES

Sample	Surface Area, m^2/g	Maximum Adsorption, mg/g	Maximum Adsorption, mg/m^2
Kaolinite[a]	19.3	30	1.55
Kaolinite[b]	18.0	20	1.11
Illite[b]	24.0	26	1.08
Chlorite[b]	13.0	24	1.85
Berea Sandstone	1.26	1.8	1.43

a) Purchased from Fisher Scientific Co.

b) Purchased from Ward's Natural Science Establishment, Inc.

TABLE V

ADSORPTION OF ASPHALTENES ON KAOLINITE FROM WATER-SATURATED TOLUENE

Pre-adsorbed Water on Clay, wt. percent	Average Clay Concentration, g/l	Average Final Water Concentration, mg/l	Max. Asphaltene Adsorption, mg/g of clay
		Overnight Shaking	
0[a]	5.14	-[b]	30.3
0	5.14	258	23.9
2.3	5.64	228	21.5
6.6	5.99	327	12.8
		One Month Shaking	
0[a]	5.26	85	29.4
6.6	5.20	337	12.4[c]

a) Nominally dry toluene used, initial water concentration assumed to be 151 mg/l, see Table III.

b) Measured water concentration greater than initial, results rejected as invalid.

c) Adsorption determined by analyzing the clay directly, using a Perkin Elmer Elemental Analyzer.

TABLE VI

CO-ADSORPTION OF WATER AND ASPHALTENES FROM WATER-SATURATED TOLUENE

Pre-adsorbed Water on Clay, wt. percent	Avg. Final Water Water on Clay, wt. percent	No. of Water Monolayers	Max. Asphaltene Adsorption, mg/m^2	Surface Oil Saturation, percent[a]
0[b,c]	1.25	2.3	1.52	97
0	4.63	8.7	1.24	79
2.3	7.05	13.2	1.11	71
6.6	9.42	17.6	0.66	42
6.6[c]	9.66	18.1	0.64	41

a) Monolayer density assumed to be 1.57 mg/m^2.

b) Assuming initial water saturation of 151 mg/l.

c) One month equilibration time.

11800

TABLE VII

CONTACT ANGLES BETWEEN WATER AND TOLUENE
ON VARIOUS SURFACES

Surface	Contact Angle Through Water, Degrees	
	Receding	Advancing
Graphite, polished	76	134
Clay/asphaltene, pressed	37	146
Clay/asphaltene, layered on quartz	26	155
Clay/asphaltene, layered on limestone	-	130
Quartz	-	35
Limestone	-	80

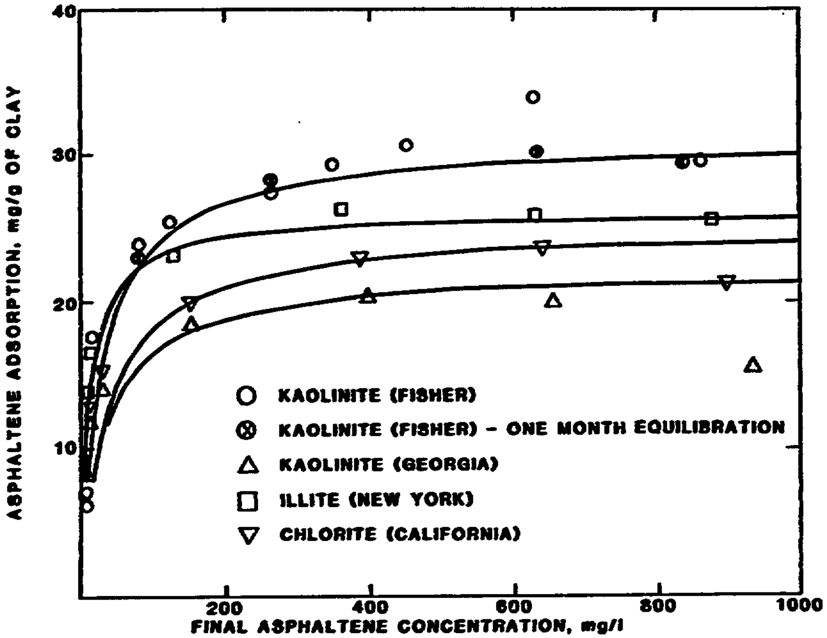

Fig. 1—Adsorption of asphaltenes on various clays.

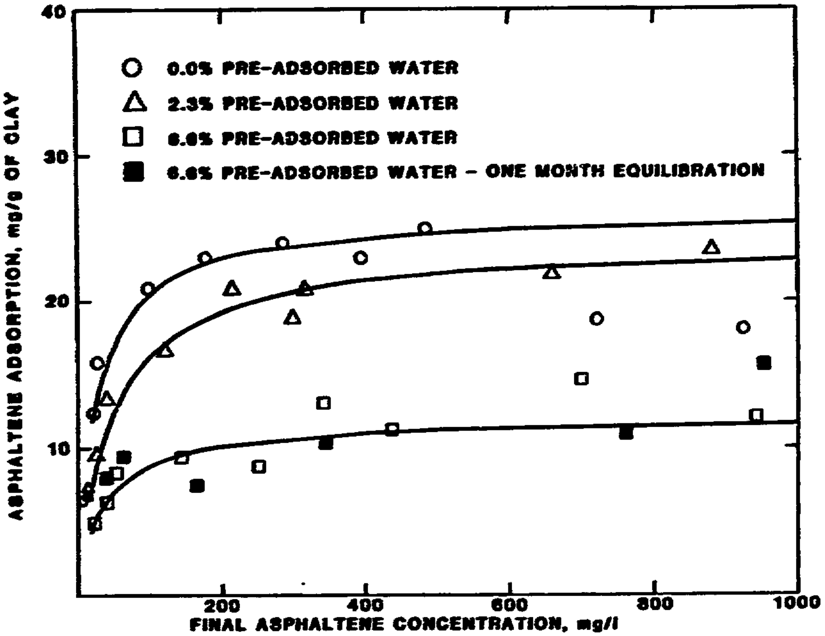

Fig. 2—Adsorption of asphaltenes on kaolinite from water-saturated toluene.

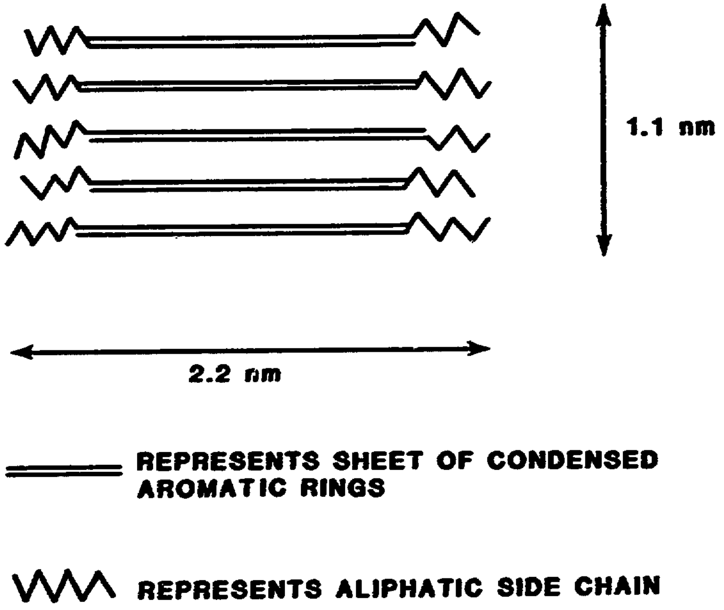

Fig. 3—Structure and dimensions of asphaltene particle.

11800