

## INTERACTION OF PETROLEUM HEAVY ENDS WITH MONTMORILLONITE

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**Abstract**—Adsorption of asphaltenes and resins onto montmorillonite occurs rapidly and to a large extent irreversibly under near-anhydrous laboratory conditions. Factors which influence the adsorption are the exchangeable cation on the clay, the basic nitrogen components of the molecules, and the solvent. As a result of this adsorption, the physical and chemical properties of the clay are drastically altered. The fundamental principles revealed in this study lead to a better understanding of the physical and chemical behavior of clays in petroleum reservoirs.

### INTRODUCTION

During migration of crude oil into a reservoir and again as production is under way, the molecular components of the oil must encounter many and varied mineral surfaces. The clay minerals, due to their high surface area and charge density, are among the most reactive of these minerals. Thus, the probability is high that molecular interactions will occur between petroleum components and the clays within a petroleum reservoir. The consequences of this interaction can be significant. Aside from causing chromatographic alteration of crude oil composition (Reed, 1968), this interaction can drastically alter the mineral surfaces. Both of these phenomena can affect oil production.

This report describes the nature of the interaction between the most polar class of compounds in the crude, which are concentrated in the heavy ends, and a model clay mineral montmorillonite.

#### *The heavy ends*

Of the many and varied molecular species in the complex liquid called petroleum, one class of compounds is most likely to interact with mineral surfaces. This is the nonvolatile, high molecular weight fraction of crude oil known as the heavy ends. Although this term generally refers to heavy oil, waxes, resins, asphaltenes, carbenes, carboids, and

other bitumens, the components of most interest are the resins and asphaltenes.

The resins and asphaltenes are a complex mixture of organic compounds which cannot be distilled without thermal cracking. Their properties have been reviewed by a number of authors (Dickie and Yen, 1967; Girdler, 1965; Nicksic and Jeffries-Harris, 1968; Sergienko, 1965; Witherspoon and Winniford, 1967; Yen, 1972). The individual molecules are large polyaromatic and polycyclic condensed ring structures which contain hetero-atoms (N, S, O) and hence polar functional groups. These properties cause them to interact readily with rock surfaces.

The differentiation between resins and asphaltenes is based on their solubility in normal paraffins. Resins are soluble in *n*-pentane while asphaltenes are not. Although their structures are similar, asphaltenes are more aromatic, more polar, and of higher molecular weight than resins.

The sample of heavy ends used in this study is from a typical batch of solvent deasphalted bottoms (SDAB), a mixture of resins and asphaltenes produced from an Arabian crude residuum via propane precipitation at the Social-Richmond refinery. A typical analysis of the material is presented in Table 1. Infrared spectra of the two fractions are shown in Figure 1 with tentative band assignments in Table 2.

Table 2. I.r. band assignments for Figure 1 (after Yen and Erdman, 1962)

Frequency (cm <sup>-1</sup> )	Tentative assignment
3050	C-H stretch (Arom)
2960	C-H stretch (CH <sub>3</sub> )
2930	C-H stretch (CH <sub>2</sub> )
2860	C-H stretch (CH <sub>2</sub> & CH <sub>3</sub> )
1700	C=O stretch (Aryl ketone)
1600-1620	C=C stretch (Arom), Some C=O
1460	C-CH <sub>3</sub> Assym. bending
1380	C-CH <sub>3</sub> Sym. bending
1020-1040	C-O-C Stretching
865	
815	C-H (Arom) out-of-plane bending
750	

Table 1. Analysis of SDA bottoms

	% wt	
	Bulk sample	Pentane insolubles
C	84.9	85.0
H	9.3	8.5
N	1.7	2.1
O	1.7	
Pentane insoluble	41	
Molecular wt*	1300	

\* From the empirical relationship of Markhasin *et al.* (1969).

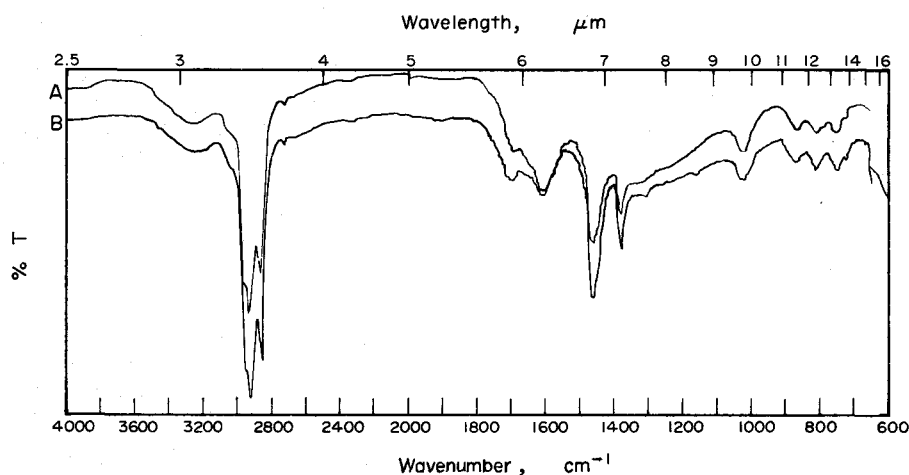


Figure 1. I.r. spectra of pentane insoluble (A) and pentane soluble (B) fractions of SDAB.

There is an important distinction between this material and commercially used road asphalt. While the starting materials are essentially the same, the latter is highly oxidized and often contains additives such as surfactant binders and emulsifiers. Material used in this study was freshly precipitated from the native crude and not exposed to air until ready for use. In this way observations could be made under conditions which more closely model the molecular state of the adsorbing species in a reservoir.

#### Previous studies

Although the adsorption of asphaltic materials on pure quartz sand is rather low (Gerber, 1957; Lyutin and Oleinik, 1962, 1965; and Tumasyan *et al.*, 1964), significant quantities of these materials are adsorbed and retained by natural sandstones, carbonates, and clay minerals (Abdurashitov *et al.*, 1966; Adylova and Ryabova, 1969; Genkina *et al.*, 1970; Gulati and Sagar, 1965; Guseinov and Tairov, 1970; Lyutin and Burdyn, 1970; Milesheina *et al.*, 1968; Tumasyan and Babalyan, 1964). Up until this time, however, little has been known about the adsorption mechanisms.

The adsorption of asphaltenes is clearly dependent upon the amount of water in association with the clay mineral surfaces (Lyutin and Burdyn, 1970; Genkina, 1970). The more water in association with the clay, the less asphaltenes will be adsorbed. This is because the asphaltenes are not soluble in water and they cannot easily penetrate adsorbed water layers to approach the surface. If the adsorption energy is strong enough, however, and the adsorbed water film is a few molecular layers thick then adsorption may indeed take place as noted by Devereux (1967). The importance of adsorbed water was accepted at the outset of this study and not investigated further. All experiments were conducted under anhydrous laboratory conditions.

This study was divided into two general areas. First, an attempt was made to understand what major variables influenced the adsorption of heavy ends onto

montmorillonite. Second, the physical chemical nature of the heavy end/ $\text{Na}^+$ -montmorillonite complex was examined.

#### EXPERIMENTAL METHODS

##### Materials

The montmorillonite (Upton, WY) was from the Clay Minerals Society source clay repository and of structural formula  $\text{M}_{0.64}^+[\text{Al}_{3.06}\text{Fe}_{0.32}\text{Mg}_{0.66}](\text{Al}_{0.10}\text{Si}_{7.90})\text{O}_{20}(\text{OH})_4$  (Ross and Mortland, 1966). The heavy ends were obtained from Chevron Research Company, Richmond, California, in the form of solvent deasphalted bottoms (SDAB). This shiny, black, crystalline material was ground in a mortar and pestle for further use.

Several ion exchange forms ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) of montmorillonite were prepared from sedimented  $<2\ \mu\text{m}$  fractions by washing the fraction 3 times with aqueous 1 N chloride salt solutions and then washing with distilled water until a negative  $\text{Cl}^-$  test was observed with  $\text{AgNO}_3$ . Samples were then dried with methanol, air dried, and ground to pass a 100 mesh screen.

Suspensions of SDAB were prepared by adding the ground material to various solvents to yield  $\sim 1\%$  by weight suspensions. These were stirred for 4–5 hr and then passed through a filter paper to insure complete dissolution. Samples of the resulting suspension were withdrawn and the exact concentration of SDAB (mg/ml) was determined by evaporating and weighing. Stock solutions of SDAB in reagent grade benzene, toluene, xylenes (mixture of isomers), chloroform, and nitrobenzene were prepared.

Two fractions were separated from the SDAB by mixing the sample in 200:1 volumes of *n*-pentane, stirring, and decanting the pentane soluble portion which was reclaimed by evaporating the pentane. The pentane insoluble portion remained. This procedure was repeated 3 times. Suspensions of these fractions in benzene were prepared as described above.

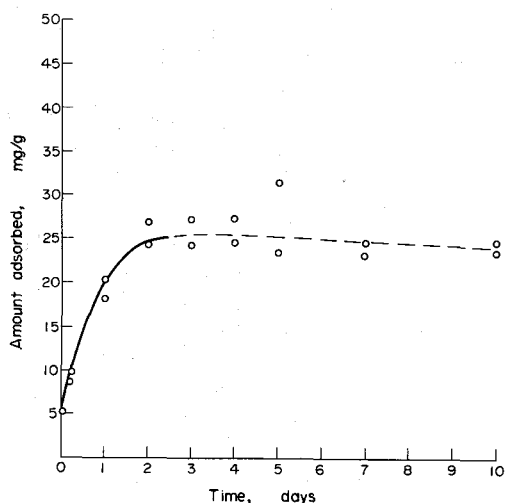


Figure 2. Adsorption of SDA bottoms onto  $\text{Na}^+$ -montmorillonite in benzene as a function of time at 1 mg/ml initial concentration.

#### Adsorption studies

Samples of clay were dried in an oven at  $110^\circ\text{C}$  for 4–6 hr and weighed ( $\sim 0.1$  g) into 50 ml volumetric flasks. The clay was quickly covered with  $\sim 25$  ml of solvent, mixed, and allowed to equilibrate for 24 hr at room temperature. An aliquot of SDAB in the solvent was then added to the flask to give the desired initial concentration. The flask was filled to volume with solvent and shaken well. The proper equilibration time was determined by preparing a series of samples of the  $\text{Na}^+$ -form in benzene and following the adsorption as a function of time. The data, plotted in Figure 2, show that the adsorption was complete after two days at 1 mg/ml initial concentration. This was the minimum amount of time used in obtaining the adsorption isotherms. Equilibrium concentrations of SDAB were determined colorimetrically with a Bausch and Lomb Spectronic 70 set at 625 nm using standard curves for each solvent prepared with various cell path lengths to cover the concentration range of interest.

#### Other physical methods

Samples of the heavy end/ $\text{Na}^+$ -montmorillonite complexes were prepared by allowing the clay to equilibrate with an excess of the SDAB solution ( $\sim 1$  mg/ml) and then solvent washing the clay until the supernatant was colorless. The resulting clay was then air dried and further tests were conducted.

Cation exchange capacity measurements on the treated and untreated  $\text{Na}^+$ -montmorillonite were made via conductimetric titration as described by Mortland and Mellor (1954). Separate electron spin resonance experiments using a Varian E-3, x-band spectrometer at 100 kHz modulation showed that  $\text{Cu}^{2+}$ -montmorillonite treated with SDAB in an identical manner to the above was washed free of  $\text{Cu}^{2+}$  by aqueous 1 N  $\text{CaCl}_2$  and 1 N  $\text{NaCl}$ . It was concluded that the ions remaining on the clay would

be exchangeable with the  $\text{Ba}^{2+}$  and  $\text{Mg}^{2+}$  during conductimetric titration.

X-ray powder diffractograms of treated clays were obtained by depositing a small amount of material from benzene suspension on a glass slide and allowing the sample to dry in air. Another batch of treated clay was suspended in water by sonifying a vial of clay/water mixture for 15 min in an ultrasonic bath. This gave a reasonable suspension which could be deposited on glass slides, dried, then studied via the usual methods. Samples of untreated  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  clays were deposited on glass slides from aqueous suspension, dried in an oven at  $110^\circ\text{C}$  for 4 hr, then placed in solvent for 24 hr. These slides were mounted on the diffractometer and a few drops of excess solvent added prior to scanning. Measurements were made on a Philips/Norelco diffractometer using  $\text{Cu K}\alpha$  radiation and a Ni filter.

Infrared spectra were obtained on a Beckman 4250 i.r. spectrophotometer. SDAB spectra were obtained by depositing a few drops of a chloroform suspension onto an IRTRAN-2 window and evaporating all solvent. IRTRAN-2 as a substrate blank was placed in the reference beam. Spectra of the material adsorbed on the clay were obtained differentially by preparing KBr pellets containing equal amounts of treated and untreated clay which were placed in the sample and reference beams respectively (Chester and Elderfield, 1971). Ordinate scale expansion was used to amplify the areas of interest. Infrared studies of water adsorbed in the presence of solvent were conducted on thin clay films of the various exchange forms of montmorillonite, which had undergone identical heat and solvent treatments as the X-ray slides.

#### Chemical methods

The stability of the complex was studied via soxhlet extraction. Due to the large amounts of clay required for this study, the naturally occurring clay ( $< 100$  mesh) was used without further preparation. 25 g quantities were equilibrated with excess SDAB/benzene and prepared as described above. These samples were soxhlet extracted with various solvents for  $\sim 6$  hr. The remaining samples were analyzed for percent total carbon on a Leco carbon analyzer. Similarly, large amounts of the natural clay were equilibrated with dilute solutions of SDAB/benzene and the amount of basic N remaining in solution was determined by evaporating the solvent and conductimetrically titrating a known quantity dissolved in toluene with acetic/perchloric acids as described by Nicksic and Jeffries-Harris (1968).

#### DISCUSSION OF RESULTS

The adsorption of SDAB onto montmorillonite is rapid and, to a large extent, irreversible. Immediately upon exposure to the dark benzene solution of SDAB, the normally white clay takes on the dark appearance

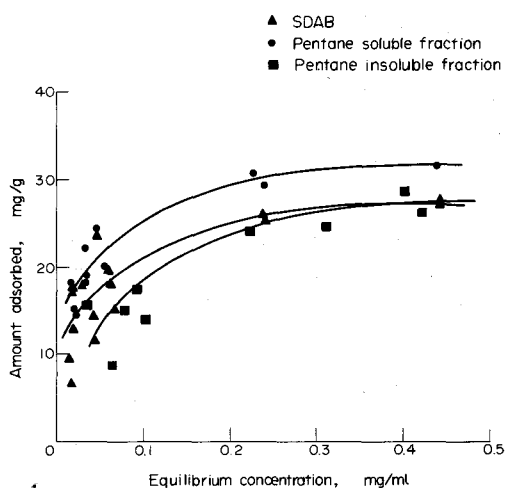


Figure 3. Adsorption of SDAB and component fractions onto  $\text{Na}^+$ -montmorillonite from benzene solution.

of the heavy ends, becomes quite hydrophobic, and will not disperse readily in distilled water.

#### Factors influencing the adsorption

The adsorption of SDAB and its component fractions onto  $\text{Na}^+$ -montmorillonite from benzene is depicted in Figure 3. The native clay is flocculated in this solvent. Notice that while the adsorption curve for the asphaltene fraction (pentane insoluble) is nearly identical to that of the bulk SDAB, the curve for the resin fraction (pentane soluble) lies significantly above the other two. The data yield linear Type I Langmuir plots.

Similar results have been reported for dye and polymer adsorption (Adamson, 1967). In many cases the expected mass action model, which requires that a certain number of solvent molecules are displaced per polymer molecule, does not hold. Solvent molecules are not readily displaced but are entwined in the polymer molecule. In the case of dye adsorption the solvent may be re-adsorbed on the dye-covered surface. Asphaltenes and resins are structurally very similar to many organic dyes (Nicksic and Jeffries-Harris, 1968). Their large, condensed ring structures have a high affinity for aromatic hydrocarbons. Re-adsorption or inclusion of the solvent at the surface is highly probable and likely results in Langmuir Type I adsorption. Admittedly, the process is complicated by the wide variability in molecular weights of the adsorbate and this may not be the most accurate model but it allows useful comparisons.

The difference in the adsorption curves may be due to the smaller molecular size of the resin fraction. This would allow better packing on the flocculated clay surfaces and possibly some interlamellar penetration. In spite of the differences between these materials the order of magnitude of the amount of material required to form a monolayer is essentially the same.

Several adsorption mechanisms may be operating in these systems. Ion exchange is most obvious. Like many organic dyes, the asphaltenes have basic

nitrogen groups in their structures (Nicksic and Jeffries-Harris, 1968). Attraction of the positively charged nitrogen to the negatively charged clay surface is expected. When a benzene solution of SDAB was exposed to  $\text{Na}^+$ -montmorillonite the amount of basic N in the remaining solids was  $0.27\% \pm 0.01$  as compared to 0.31% before exposure. This  $\sim 15\%$  reduction is consistent with observations of preferential retention of crude oil bases in cores made by Reed (1968). One can conclude that the basic nitrogen does play a role in the adsorption and may be involved in the long-range interaction between asphaltenes and surface. However, there are other factors which become important as the molecules approach the surface.

Once these large molecules get close to the surface, van der Waal's attractive forces will become large. Also significant  $\pi$  interactions of the disk-like aromatic molecules with exchangeable cations and surface oxygens are expected. The infrared data of Figure 4 substantiate this prediction. Spectra A and B are for the resin and asphaltene fractions of SDAB, respectively, as shown in Figure 1. These are compared to a spectrum of the material adsorbed on  $\text{Na}^+$ -montmorillonite from an SDAB/benzene solution (C). Notice that the relative intensity of the aromatic C=C stretch at  $\sim 1600 \text{ cm}^{-1}$  compared to the asymmetric C-CH<sub>3</sub> stretch at 1460 is significantly higher in the asphaltene fraction than in the resin fraction. The relative intensity of aromatic C=C stretch in the adsorbed material is greater still, implying selective removal of the asphaltenes. The slight but significant upward shift in the wavelength of this band also indi-

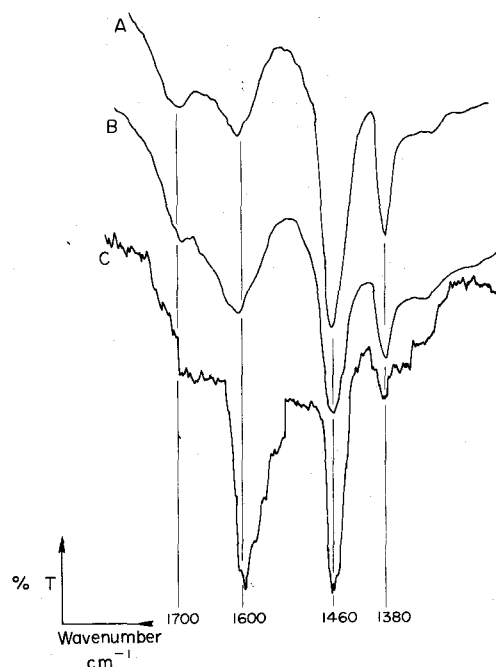


Figure 4. I.r. spectra of: A—pentane soluble SDAB fraction, B—pentane insoluble SDAB fraction, C—adsorbed SDAB on  $\text{Na}^+$ -montmorillonite.

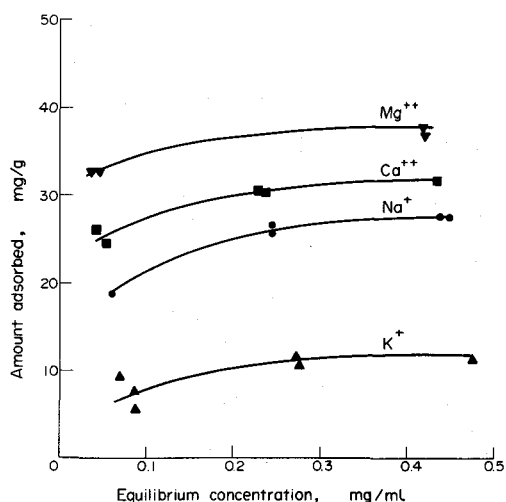


Figure 5. Adsorption of SDAB onto montmorillonite from benzene solution as a function of exchangeable cation.

icates some binding interaction between the aromatic carbons and the clay surface. One could conceive of these large, flat molecules oriented parallel to the clay surface in a manner analogous to adsorbed methylene blue (Huang and Brindley, 1970).

Another factor which influences the adsorption, depicted in Figure 5, is the exchangeable cation. Clearly, there is a significant increase in the amount of SDAB adsorbed in the order  $K^+ < Na^+ < Ca^{2+} < Mg^{2+}$ . There are two reasons for this. The most important undoubtedly is related to the hydration energy of these ions. The amount of water coordinated to the exchangeable ions can influence expansibility of the silicate structure in aromatic solvents (Theng, 1974). Those ions which are most energetically hydrated will resist structural collapse during the drying process at  $110^\circ C$  and then will be able to absorb more solvent into the interlayer. On the other hand, those ions with the lowest hydration energy will lose water upon drying and the layers will collapse and resist expansion by the solvent. The enthalpy of hydration of these ions is in the order  $Mg^{2+} > Ca^{2+} > Na^+ > K^+$ . From Table 3 one can see that the interlamellar spacing of these various exchange forms of montmorillonite in benzene does seem to increase in the same series as the hydration energy. Infrared spectra of the clays in benzene show adsorbed water (coordinated to the cations) present in all cases but much more in the  $Ca^{2+}$  and  $Mg^{2+}$  cases. Thus, the calcium and magnesium clays may

have more interlamellar surface available for adsorption in a given solvent than the sodium and potassium systems.

Specific interaction between the heavy end molecules and the exchangeable cations also may give rise to differences in adsorption. Polar functional groups of sulfur, nitrogen, carboxyls, and aromatic structures within the molecules are known to coordinate with metal ions in the above series. This effect should be small, however, in comparison to the changes in available surface described above.

The asphaltenes are largely solvent stabilized, the extent and sign of charge on the molecules being controlled by the solvent (Wright and Minesinger, 1963; Eldib, 1962). The results of Figure 6, which show the amount of heavy ends adsorbed at a given concentration as a function of solvent used and exchangeable cation, reveal that the solvent carrier for the heavy ends is undoubtedly the most important factor controlling the adsorption. These solvents stabilize the asphaltenes in suspension and keep them from precipitating. Even within a particular ion exchange form of clay, however, there is a wide variability in the amount adsorbed.

A partial explanation of this result is obtained from Table 3. The basal spacings determined are given for various exchange forms in the different solvents used. Most of the 001 reflections for the  $Na^+$  and  $K^+$  forms, unfortunately, are quite broad while those of  $Ca^{2+}$  and  $Mg^{2+}$  are sharp. It is therefore difficult to determine the percent expanded layers for  $Na^+$  and  $K^+$ . For the  $Ca^{2+}$ , however, there is a distinct reduction of the interlayer spacing in chloroform which corresponds to a significant decrease in the amount adsorbed. Also, there is a noticeable increase in interlayer spacings in nitrobenzene. These changes in interlayer spacing undoubtedly influence the amount of material which can be adsorbed in the interlayer.

Another contribution to this solvent effect may be found in the work of Eldib (1962) and Penzes and Speight (1974). They found the specific conductance of asphaltenes was highest in solvents of high dielectric constant. The higher the dielectric constant, the lower the interaction between positive and negative sites on the molecules, and the greater is the molecular dissociation. In solvents of high dielectric constant, such as nitrobenzene, asphaltenes and resins actually become ionized. This may account for the

Table 3. Average basal spacings ( $\text{\AA}$ ) of various cation exchange forms of montmorillonite in different solvents

Cation	45% r.h.	Benzene	Toluene	Xylenes	Chloroform	Nitrobenzene
$Na^+$	11.5	14.4 (b)	10.7 (b)	11.6 (b)	12.2 (b)	15.2 (s)
$K^+$	11.3	13.5 (b)	10.6 (b)	11.3 (b)	11.9 (b)	15.2 (s)
$Ca^{2+}$	15.0	15.2 (s)	15.2 (s)	15.2 (s)	13.7 (s)	15.4 (s)
$Mg^{2+}$	15.0	15.4 (s)	14.9 (s)	14.9 (s)	14.2 (s)	15.4 (s)

b = broad, s = sharp.

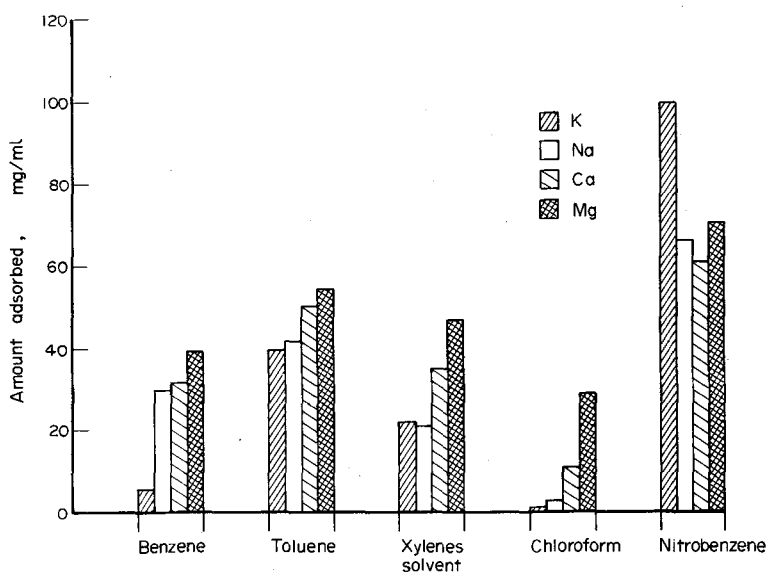


Figure 6. Adsorption of SDAB onto montmorillonite as a function of solvent and exchangeable cation at 0.5 mg/ml initial concentration.

large increase in the amount adsorbed from nitrobenzene, in which case ion exchange can become the dominant mechanism. On the other hand, in chloroform the molecules will not be ionized but will be effectively solvated. Also, it can be seen from Figure 6 that the relative effect of the exchangeable ion on adsorption is essentially the same for all solvents except nitrobenzene. In that solvent, the potassium clay adsorbs significantly higher amounts of heavy ends. This may be related to an interaction of the heavy ends with the strong  $K^+$ -nitrobenzene coordination complex which is known to form under these conditions (Yariv *et al.*, 1966).

#### The nature of the heavy end montmorillonite complex

The physical and chemical properties of montmorillonite are drastically altered after adsorption of the asphaltenes and resins. A better understanding of the adsorption phenomenon and a feeling of its importance to practical problems can be achieved by studying the altered clay.

As demonstrated by Table 4 the adsorption of asphaltenes is largely irreversible. Only the powerful solvent combination of the azeotropic chloroform/acetone mixture can remove some of the adsorbed material. The observation is similar to those made with polymer/clay systems and implies that there are many binding sites which "anchor" these large molecules to the surface. It is likely that those molecules which are removed by extraction are the lower molecular weight resins.

Results from X-ray powder diffractograms of the treated and untreated  $Na^+$ -montmorillonite are listed in Table 5. The untreated clay gives the usual sharp (001) reflection at 12.4 Å under air dry conditions, and collapses to 9.8 upon heat treatment. The treated clay, however, shows a broad peak centered at 11.5 Å. After heating, the treated sample yields a 9.8 Å peak which is asymmetrical on the high side. This indicates that some of the layers are "propped" open by partial interlayer penetration of the adsorbed heavy ends. After extensive sonification, the clay shows a broad 12.4 Å

Table 4. Solvent extraction of adsorbed heavy ends from  $Na^+$ -mont. (raw)

Sample	Extraction procedure	LECO carbon % ( $\pm 0.01\%$ )
$Na^+$ -mont.	None	0.78
$Na^+$ -mont.	Benzene wash	0.78
SDAB/ $Na^+$ -mont.	Benzene wash	1.81
SDAB/ $Na^+$ -mont.	Soxhlet	1.81
	$CS_2$ extracted	
SDAB/ $Na^+$ -mont.	Soxhlet	1.32
	chloroform/acetone extracted	
SDAB/ $Na^+$ -mont.	Soxhlet chloroform/acetone extracted in $N_2$ atm	1.31

Table 5. X-ray powder diffraction study of SDAB-treated Na<sup>+</sup>-montmorillonite

	Untreated	Treated	Treated sonified
Air dry	12.4 (s)	11.5 (b)	12.4 (b)
Heated	9.8 (s)	9.8 (b)	9.8 (s)
Glycol	17.2 (s)	17.0 (b)	17.1 (s)
Glycerol	17.8 (s)	12.0 (b)	18.0 (s)
Trihexylamine	17.0 (s)	13.7 (b)	17.5 (s)

b = broad, s = sharp.

Table 6. Effect of adsorbed heavy ends on cation exchange capacity of Na<sup>+</sup>-montmorillonite

Sample	CEC (m-equiv./g)	% Reduction
Untreated	0.62	—
SDAB treated	0.30	52
Asphaltene treated	0.45	27

peak. Evidently, prior to disruption by the ultrasonic energy, particles are bridged together by the heavy end molecules and partial interlayer penetration may exist. Positioning of the adsorbed molecule in this way greatly reduce the accessibility to the interlayer. Glycerol will not wet the sample at all prior to sonification and the spacing remains essentially unchanged, whereas, ethylene glycol will expand the clay as usual. However, exposure of the treated clay to an aqueous solution of tri-*n*-hexylamine, which normally causes expansion of the layers, does not result in significant expansion until after sonification.

Cation exchange capacity (CEC) data are consistent with the above X-ray results. Table 6 shows the effect of heavy end adsorption on the cation exchange capacity of Na<sup>+</sup>-montmorillonite. The CEC is reduced by 27% when the asphaltene fraction is adsorbed and by 52% when the total mixture is used. Undoubtedly, the larger asphaltene molecules adsorb primarily on external surfaces and are not too effective at blocking interlamellar sites. On the other hand, the mixture contains the smaller resin molecules which may also cover, or block entrance to, interlamellar sites. The fact that the clay surface becomes somewhat hydrophobic after the heavy end adsorption might also reduce contact by aqueous solutions.

#### SUMMARY AND CONCLUSIONS

Several important observations have been made during this study. Adsorption of asphaltenes and resins from hydrocarbon solutions under near-anhydrous conditions is rapid, and irreversible. The dehydration need not be accomplished by heating but may occur via solvent action which can displace bulk water from the clay surface. Nor does it have to remove all water from the surface. Water molecules coordinated to exchangeable cations do not restrict the adsorption. Thus, it is conceivable that under certain circumstances heavy ends are adsorbed onto

clays in petroleum reservoirs and lead to alterations in rock properties. This may add to the explanation of how similar clay minerals can behave in entirely different ways in different rocks.

Some important physical and chemical consequences of this result have been observed. For example, an adsorbed layer of heavy ends has been demonstrated to prevent kaolinite from damaging Berea sandstone cores under conditions of fresh waterflooding (Clementz, unpublished data).

Measurements of rock properties also may be affected by this result. Any measurement which is based on the charge of the clay, its expansibility, or the nature of its surface will be altered. The effect that the adsorbed material has on X-ray diffraction patterns of the pure clay has already been shown. Broadening of 001 reflections and alteration of expandability could cause an underestimate of the amount of expandable clay in a rock sample. Likewise, the measured CEC can be significantly reduced by the adsorbed material. Devereux (1967) showed that adsorbed asphaltenes cover paramagnetic centers on rock surfaces and thereby alter the proton NMR measurements of water relaxation in the system. In effect, the water "sees" less of the surface and relaxes more like bulk. Similarly when solvent benzene is in contact with clay which has adsorbed heavy ends, the benzene relaxes more like bulk (Clementz, unpublished data). This causes an underestimate of the amount of surface "seen" by the solvent protons.

Laboratory procedures for handling core samples also may lead to alterations of clay properties. For example, flushing a core with an aromatic solvent can disperse or solvate asphaltenes and resins and also displace water from the clay surface. This will favor adsorption of these heavy ends and result in the alteration of clay properties. Certain oil recovery schemes, such as solvent flooding, may cause the same thing to happen on a larger scale.

Although seemingly insignificant, the interactions of an adsorbed layer of petroleum heavy ends with reservoir clays can have far-reaching effects. This interaction is influenced by the type of exchangeable cation on the clay, the amount of basic nitrogen on the heavy end molecules, and on the solvent system which transports these molecules.

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