HYDROPHOBIC NATURE OF ORGANO-CLAYS AS A LEWIS ACID/BASE PHENOMENON

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Abstract—The surface thermodynamic properties of a series of *n*-alkylammonium and quaternary ammonium treated clay films were determined by contact angle measurement of drops of test liquids using the Young equation for polar materials. The two clays were a Wyoming montmorillonite (SWy-1) and Laponite RD. For a series of primary *n*-alkyl ($6 \leq n \leq 15$) and several quaternary organic cations, the organo-clay (both SWy-1 and Laponite RD) showed very little change in the value of γ^{LW} compared to the equivalent ammonium-saturated clay. Also, $\gamma^{\oplus}$ remained small or increased slightly compared to the ammonium-saturated clay. For SWy-1 exchanged by both quaternary ammonium and primary *n*-alkylammonium cations, the value of $\gamma^{\ominus}$ was smaller ($0.1 \leq \gamma^{\ominus} \leq 15.8$ mJ/m^2) than for the ammonium-saturated clay ($\gamma^{\ominus} = 36.2$ mJ/m^2) and decreased linearly with the number of carbon atoms. The $\gamma^{\ominus}$ values for the organic cation-exchanged Laponite RD samples ($24.2 \leq \gamma^{\ominus} \leq 31.2$ mJ/m^2) were smaller than or comparable to the ammonium saturated clay ($\gamma^{\ominus} = 30.7$ mJ/m^2), and were relatively insensitive to the number of carbon atoms in the organic cation. Thus, for both clays the increased adsorption of organic molecules resulting from replacement of inorganic cations by organic cations is due primarily to the decrease in the value of the Lewis base parameter, $\gamma^{\ominus}$.

Key Words—Organo-clay, Surface tension, Lewis acid/base.

INTRODUCTION

The adsorption and intercalation of organic molecules by smectites is a subject that has attracted much attention since the work of Hofmann *et al.* (1934) and Smith (1936). Much of this work has centered on examining the intercalation of different organic species and how they interact with the clay surface. In order to achieve intercalation, it was often necessary to treat the smectite with pure organic material either as a liquid or a vapor. More recently, interest has grown in studying the adsorption of organic species, particularly toxic materials, from solution in water or in organic solvents. This latter effort has shown that for many organic molecules, particularly non-polar or weakly polar ones, the adsorption on untreated smectite surfaces is small. For these materials, the surface of a typical smectite immersed in water is "organophobic." It was shown quite some time ago that the surface properties of smectites could be modified by replacing the exchangeable inorganic cations with organic cations (Cowan and White, 1962). Increasing the organophilicity of the smectite surface is typically done by replacing the exchangeable inorganic cations with an alkyl ammonium cation to form an organo-clay. Examination of a number of alkyl ammonium treated clays has shown that there is both a chemical and a shape selectivity for the adsorption of organic molecules from a solvent, typically water. The driving force

for the adsorption of organic molecules by an organo-clay (in water) has been described rather vaguely as a "hydrophobic binding" in the sense that hydrophobic parts of the adsorbate react with the hydrophobic alkyl groups covering the organo-clay surface (Mortland *et al.*, 1986). In spite of much experimental effort, little progress has been made in understanding the changes in surface properties which take place when the surfaces of a smectite are partially or completely covered by organic cations. In those instances where the surface thermodynamic properties of clay-organic complexes have been examined, an incomplete thermodynamic theory was employed (Jouany and Chassin, 1987; Jouany, 1991). The purpose of this communication is to explore the surface thermodynamic properties of two organo-clay minerals with different types and complexities of organic cation replacement.

BACKGROUND

In a general sense, a molecular species, dissolved or suspended in a liquid, adsorbing onto a solid surface is an interfacial phenomenon, and the energetics of the process can be described in surface thermodynamic terms. The theory of surface and interfacial thermodynamic interactions was recently reviewed by van Oss *et al.* (1988) and only those aspects which are essential to the present discussion will be mentioned here. The surface thermodynamic properties have been deter-

mined for a number of phyllosilicate minerals: hectorite (van Oss *et al.*, 1990), talc and pyrophyllite (Giese *et al.*, 1991), Ca-montmorillonite (Chassin *et al.*, 1986), a group of natural smectite minerals (Giese *et al.*, 1989), illite (Li *et al.*, 1991) and kaolinite (Chibowski and Staszczuk, 1988; Murphy *et al.*, 1991). In addition, the role of interfacial interactions, and especially the importance of the Lewis acid/base contribution to the flocculation of hectorite has been examined (van Oss *et al.*, 1990); the thermodynamics of adsorption of human serum albumin on several clay minerals has been studied (Costanzo *et al.*, 1991b); and the changes in surface properties of humic-clay complexes have been reported (Jouany, 1991).

The surface free energy of a condensed medium is composed of two different types of interaction; one is apolar resulting from a combination of dipole-dipole, dipole-induced dipole, and fluctuating dipole-induced dipole phenomena similar to van der Waals interactions of gas atoms. The macroscopic theory for condensed media was developed by Lifshitz; hence, these interactions collectively are referred to as Lifshitz-van der Waals, or LW, interactions. The second interaction is polar and results from interactions between electron acceptor and electron donor sites (Lewis acids and bases) and are designated AB (van Oss *et al.*, 1988). For the AB component, two parameters must be specified, one describing the electron donor character, $\gamma^{\ominus}$, and the other describing the electron acceptor character, $\gamma^{\oplus}$. These parameters are related to the polar AB surface tension component by:

$$\gamma_i^{AB} = -2\sqrt{\gamma_i^{\oplus}\gamma_i^{\ominus}}. \tag{1}$$

Whilst the apolar interfacial surface tension component, γ_{ij}^{LW}, between materials i and j is related to the surface tension of each material by a geometric mean combining rule, the polar interfacial tension component takes a completely different form, consisting of the sum of four different geometric means (van Oss *et al.*, 1988). The total interfacial tension is the sum of the apolar and the polar interfacial tensions.

$$\gamma_{ij} = \left(\sqrt{\gamma_i^{LW}} - \sqrt{\gamma_j^{LW}}\right)^2$$
$$+ 2\left(\sqrt{\gamma_i^{\oplus}} - \sqrt{\gamma_j^{\oplus}}\right)\left(\sqrt{\gamma_i^{\ominus}} - \sqrt{\gamma_j^{\ominus}}\right). \tag{2}$$

The Young-Dupré equation describes the relation between the contact angle, θ, formed at the edge of a drop of liquid in contact with a smooth, non-porous solid surface and the surface tensions and interfacial tensions of the solid and liquid. It can be written as:

$$(1 + \cos\theta)\gamma_L = \gamma_S + \gamma_L - \gamma_{SL} \tag{3}$$

where S refers to the solid and L to the liquid. The Young equation for polar materials then is:

$$\frac{(1 + \cos\theta)}{2}\gamma_L = \sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^{\oplus}\gamma_L^{\ominus}} + \sqrt{\gamma_S^{\ominus}\gamma_L^{\oplus}}. \tag{4}$$

In applying the Young equation in this form to the determination of the surface tension components of the solid, there are three unknowns, γ_S^{LW}, $\gamma_S^{\oplus}$, and $\gamma_S^{\ominus}$. These can be determined by solving a set of simultaneous equations, one for each kind of liquid used, with the restriction that at least two of the liquids must be polar. For the measurements reported here, five liquids were used: the apolar diiodomethane and α-bromonaphthalene, and the polar liquids water, formamide, and glycerol. The values of the surface tension components and parameters for these liquids are given in van Oss *et al.* (1990).

A different approach to the determination of the surface free energy of clay minerals was taken by Jouany (1991), Janczuk and Bialopiotrowicz (1988), Chassin *et al.* (1986) and Chibowski and Staszczuk (1988). These workers reported that drops of water spread when placed on the surfaces of clay minerals either in the form of compressed powders or as films. This was interpreted as an indication of the very high energy of the clay surface. Their approach was to measure the contact angle of a drop of water in contact with a surface of pressed clay in the presence of different liquid alkanes. A second difference between the present study and those mentioned above is the treatment of the polar part of the surface tension. Jouany (1991), for example, treated the polar component of the surface tension as a single quantity, γ^P, with a value of 51 mJ/m² for water. Thus, in this case only, γ^P is equivalent to γ^{AB} in Eq. (1). However, as seen in Eq. (1), γ^{AB} is determined by the Lewis acid and base parameters, $\gamma^{\oplus}$ and $\gamma^{\ominus}$, a feature not accounted for in the work of Chassin *et al.* (1986), Jouany and Chassin (1987), Chibowski and Staszczuk (1988), and Jouany (1991). Further, the relation between the polar component of the interfacial tension, I_{12}^P, in the work of Jouany (1991), is related to the individual surface tensions, γ_1^P and γ_2^P, by the harmonic mean:

$$I_{12}^P = \frac{4\gamma_1^P\gamma_2^P}{(\gamma_1^P + \gamma_2^P)}, \tag{5}$$

rather than by the geometric mean. In view of all of these differences, a comparison of the present measurements with those of Jouany (1991), Chassin *et al.* (1986), Jouany and Chassin (1987), and Chibowski and Staszczuk (1988) cannot be made. The use of γ^P is not only arbitrary with no theoretical or practical basis, it also leads to grossly aberrant results (see van Oss and Good, 1992). It is of interest to note that at least one of these research groups has ceased using γ^P and has adopted the methodology used in this paper (Holysz and Chibowski, 1992).

EXPERIMENTAL

Materials

For this study, two smectite clays were used. One was the <2 μ fraction of Wyoming montmorillonite

Table 1.　The quaternary ammonium cations used in this study.

Organic cation	Code	Formula
trimethyl	TRMA	$CH_3-\overset{\overset{\displaystyle CH_3}{\|}}{\underset{\underset{\displaystyle CH_3}{\|}}{N}}-H$
tetramethyl	TMA	$CH_3-\overset{\overset{\displaystyle CH_3}{\|}}{\underset{\underset{\displaystyle CH_3}{\|}}{N}}-CH_3$
hexadecyltrimethyl	HDTMA	$CH_3-\overset{\overset{\displaystyle CH_3}{\|}}{\underset{\underset{\displaystyle CH_3}{\|}}{N}}-(CH_2)_{15}CH_3$
trimethylphenyl	TMPA	$CH_3-\overset{\overset{\displaystyle CH_3}{\|}}{\underset{\underset{\displaystyle CH_3}{\|}}{N}}-\langle\!\bigcirc\!\rangle$
tetraethyl	TEA	$CH_3CH_2-\overset{\overset{\displaystyle CH_2CH_3}{\|}}{\underset{\underset{\displaystyle CH_2CH_3}{\|}}{N}}-CH_2CH_3$

(SWy-1 from the Clay Minerals Repository) and the second was a synthetic smectite, Laponite RD as supplied by Laporte Industries, Ltd. Both easily form films suitable for contact angle measurements, but differ in that SWy-1 easily intercalates organic molecules and a variety of organic cations while Laponite RD is not nearly as reactive.

The exchange of inorganic cations for organic cations has been studied extensively in two contexts: for the determination of the layer charge (by intercalation of primary n-alkylammonium cations; Lagaly and Weiss, 1969), and to increase the adsorption of a variety of organic molecules (particularly toxic materials) by smectites treated with quaternary ammonium cations. The present study utilized both types of organic ammonium salt. Primary n-alkylammonium compounds (C_6 to C_{15}) were obtained either from Eastman Kodak as the pure amine salt or the n-alkyl ammonium chloride was synthesized by treating the appropriate amine (from Eastman Kodak) with hydrogen chloride gas while the amine was dissolved in methanol (Norris, 1987). After reaction, the solvent was removed by filtration, the salt was washed repeatedly with acetone at $-20°C$, dried, and then stored in a sealed container. The quaternary ammonium compounds were obtained from Eastman Kodak. The organic cations are listed in Table 1.

Table 2.　Average contact angles for drops of the test liquids (Table 1) on films of organo-Wyoming montmorillonite (SWy-1). For the primary alkyl ammonium cations, the C = 0 point represents the clay saturated with ammonium cations. Values in parentheses are the standard deviations in the contact angle measurements.

Primary alkyl ammonium cations

C =	0	6	7	8	9	10	11	12	13	14	15
ABROM	20.1 (1.3)	26.0 (2.0)	28.0 (2.9)	26.1 (2.7)	27.2 (3.8)	25.5 (2.4)	26.4 (1.5)	27.0 (3.7)	23.0[1] (1.8)	25.4 (1.7)	34.7 (1.7)
DIM	37.4 (2.5)	36.3 (1.9)	39.5 (3.4)	42.0 (6.1)	43.3 (4.6)	39.1 (5.5)	38.8 (1.4)	42.3 (3.0)	48.8 (2.7)	43.6 (3.3)	44.2 (2.2)
WATER	38.4 (2.9)	68.0 (3.0)	69.5 (2.7)	71.0 (7.5)	72.5 (4.6)	63.4 (4.8)	74.1 (1.7)	77.0 (3.1)	75.2 (2.4)	77.4 (5.7)	95.0 (3.2)
FO	15.0 (3.4)	36.2 (2.4)	39.2 (2.3)	41.9 (4.4)	42.4 (3.6)	39.7 (2.8)	44.0 (2.0)	45.1 (4.4)	43.8 (2.4)	43.4 (4.0)	55.6 (3.7)
GLY	46.2 (2.9)	60.2 (1.8)	58.0 (2.5)	58.6 (4.7)	62.8 (3.7)	61.0 (2.7)	66.7 (1.4)	69.8 (3.5)	69.5 (2.4)	69.1 (2.8)	78.8 (2.5)

Quaternary ammonium cations

	TMA	TRMA	HDTMA	TMPA	TEA
ABROM	24.9 (3.0)	21.4 (2.9)	29.8 (3.2)	24.9 (2.9)	23.0 (1.8)
DIM	34.6 (3.4)	28.7 (2.9)	37.7 (3.2)	35.8 (2.9)	37.5 (2.1)
WATER	55.7 (3.5)	49.8 (2.9)	71.6 (2.0)	59.9 (2.4)	52.5 (1.8)
FO	12.8 (3.7)	7.3 (3.3)	46.2 (3.4)	14.4 (3.3)	16.7 (2.9)
GLY	38.2 (3.1)	31.4 (2.4)	61.5 (2.5)	41.0 (2.4)	47.7 (2.7)

[1] Omitted from the Young equation calculation.

Table 3. Average values for the contact angles of drops of the test liquid on Laponite RD films after exchange by different organic cations as described in Table 2.

	Amm	C = 8	C = 10	C = 12	HDTMA
ABROM	18.5 (1.2)	21.4 (2.8)	22.9 (3.2)	19.4 (3.1)	20.5 (2.8)
DIM	31.5 (2.1)	31.6 (3.1)	33.5 (2.6)	34.3 (3.0)	29.0 (2.8)
WATER	39.3 (2.2)	49.2 (2.4)	51.0 (3.0)	50.2 (3.4)	50.2 (3.9)
FO	26.8 (1.7)	37.1 (3.2)	42.0 (3.6)	42.4 (3.0)	37.2 (2.8)
GLY	28.9 (3.1)	38.1 (2.5)	40.5 (2.5)	37.8 (3.2)	43.1 (2.7)

Organo-clay film preparation

Phyllosilicate minerals present experimental difficulties not encountered when measuring contact angles of test liquids on smooth, non-porous solid surfaces. These difficulties have largely been overcome either by fabricating thin films of smectite minerals for direct contact angle measurements (van Oss *et al.,* 1990; Giese *et al.,* 1989) or indirectly by determining the value of $\cos \theta$ from measurements of the rate of capillary rise of the test liquid through a thin layer of powdered sample supported on a glass substrate (Costanzo *et al.,* 1991c; Giese *et al.,* 1991; van Oss *et al.,* 1992). The measurements reported here relied exclusively on contact angle measurements.

While many natural smectites form either self-supporting films or films cast on glass slides, once the smectite is converted into an organo-clay by treatment with an organic cation, film formation is no longer possible. This is undoubtedly due to the change in the surface thermodynamic properties and the surface electrostatic potential, both of which are important for film formation. As a consequence, a different approach was adopted for this study. The clay film was first formed by covering a clean glass slide with a 2% aqueous dispersion by weight of the untreated smectite. The slide was allowed to dry slowly under ambient conditions and then the slide with the clay film attached was immersed in an aqueous solution of an organic *n*-alkylammonium salt contained in a culture dish for a period of 2 m. For the longer chain lengths (i.e., C_{13-15}), the solutions were mildly heated to ensure dissolution of the ammonium salt. After the first exposure, the slide was removed and placed in a fresh solution for a second 2 m period after which the surface of the slide was thoroughly washed in running deionized water to remove excess ammonium salt. Finally, the slide was dried overnight under ambient conditions and the contact angles were then measured. The concentration of the organic cation in aqueous solution was 0.5 M for the C = 6 and 7, and 0.1 M for the longer chains (Ruehlicke and Kohler, 1981). The quantity of the organic cation was well in excess of the cation exchange capacity of the exposed surface of the clay film. For the contact angle measurement, no attempt was made to fully intercalate the clay films because the contact angle liquids interact only with the external surfaces.

Contact angle measurements

For each slide, at least 5 drops of each test liquid were placed on the surface using a Gilmont Teflon microsyringe and the advancing contact angles at both edges of each drop were measured with a Gaertner telemicroscope equipped with an eyepiece goniometer. Normally 2 slides for each smectite and organic cation combination were examined for a total of twenty contact angle measurements for each test liquid. In a few cases, extra slides were measured. All the contact angles were averaged and these values were used to solve the set of Young equations. The average observed contact angles and associated standard deviations are listed in Table 2 for the SWy-1 samples and in Table 3 for the Laponite samples. The standard deviations are larger than would be expected for contact angle measurements of liquid drops on a molecularly smooth, non-porous surface (1–2°). This greater variability probably resulted from a greater variability in the fabrication of the clay slides. These angles were measured on a potentially rough surface, and there is the possibility that the angles reported here are somewhat greater than if the drops were in contact with a smooth cleavage surface (Johnson and Dettre, 1964). Nonetheless, the changes in contact angles resulting from the treatment of the clay surface with different alkylammonium are independent of the surface roughness.

RESULTS AND DISCUSSION

The surface tension components and parameters for the organo-smectites of this study are shown in Tables 4 and 5. At present it is not possible to calculate a standard deviation for these values because of the non-linear nature of the Young equation. Repeated measurements of related surfaces suggest that the value of γ^{LW} probably has an error of 1–2% at most, while the Lewis acid/base parameters may be uncertain by 5%.

As the work progressed, it became clear that the surface properties of the SWy-1 (Table 4) were dramatically changed by the treatment. The amine-treated Laponite RD samples (Table 5) showed only a modest change, compared to the ammonium saturated sample that was relatively constant for the different amines. For this reason, the Laponite was not treated with all of the organic cations.

Table 4. Values of the surface tension components and parameters for Wyoming montmorillonite (SWy-1) after exchange by different organic cations. For the primary alkyl ammonium cations, the C = 0 point represents the clay saturated with ammonium cations. The value of γ^{AB} was calculated from the electron donor and electron acceptor parameters using Eq. (1). All values are in mJ/m².

Primary alkyl ammonium cations C =	0	6	7	8	9	10	11	12	13	14	15
γ^{LW}	41.7	41.2	39.9	39.4	39.1	40.5	40.5	39.6	40.4	39.5	37.7
$\gamma^{\oplus}$	0.7	0.7	1.0	1.0	0.7	0.3	0.3	0.3	0.2	0.4	0.3
$\gamma^{\ominus}$	36.2	9.8	8.4	7.7	7.5	15.8	7.5	6.0	7.2	5.3	0.1
γ^{AB}	10.1	5.2	5.7	5.4	4.6	4.7	3.0	2.7	2.5	3.0	0.4

Quaternary ammonium cations	TMA	TRMA	HDTMA	TMPA	TEA
γ^{LW}	41.5	43.2	40.0	41.3	41.3
$\gamma^{\oplus}$	3.0	2.8	0.5	3.1	1.5
$\gamma^{\ominus}$	12.9	16.9	8.7	9.7	19.5
γ^{AB}	12.4	13.8	4.0	11.0	10.8

TMA = tetramethyl ammonium. HDTMA = hexadecyltrimethyl ammonium. TMPA = trimethylphenyl ammonium. TEA = tetraethyl ammonium. TRMA = trimethyl ammonium.

Montmorillonite

Taking the contact angle of water as a measure of "hydrophobicity" of a solid surface, examination of Table 2 indicates that the surface exchange of the primary n-alkylammonium cations increased the hydrophobicity, as expected. What is interesting is that the contact angles of the other polar liquids also changed as the result of the treatment while the contact angles with the apolar liquids were relatively constant for all samples. The general aspect of the data suggests that as the surface of the montmorillonite is covered by progressively larger amounts of n-alkyl organic material, the surface properties change in a continuous manner.

On the other hand, the ammonium clay is less hydrophobic than would be predicted assuming that it could be treated as the C_0 member of the series. The extrapolation to the ammonium clay is large because the shortest chain in this study had 6 carbon atoms. It is likely that the change in properties from an ammonium clay to a clay covered with, e.g., methylammonium (C_1) cations represents a discontinuous step rather than part of a continuum. At the other extreme, the C_{15}-treated clay is much more hydrophobic than predicted by the trend of values. At this chain length, the solubility of the ammonium salt in water decreases to the point where it was necessary to mildly heat the solution in order dissolve the salt. It was difficult to maintain the temperature while the clay film was immersed in the solution so it is possible that excess ammonium salt was also present on the film surface in spite of attempts to wash off all excess material. A second set of slides was prepared in the same way and a combined water and ethanol washing was employed. The contact angles for this set were not sensibly different so these data were not incorporated in the results reported here. An apparent anomaly in the contact angle values is seen for the C_{10}-sample where the water

contact angle is observed to be distinctly below the fitted straight line. The C_{10} measurements were repeated many times to verify the correctness of the apparently anomalous water contact angle.

The quaternary amines are more complex than are the primary n-alkylamines because they involve replacement of 3 or 4 of the hydrogens of the ammonium cation and, in one case, some of the carbons are involved in a ring (the phenyl group) rather than in a chain. Hence the coverage of the external surface of the organo-clay may not be directly related to the number of carbon atoms in the quaternary moiety. Nonetheless, the trends in the values of Table 2 suggest that this is a useful measure of the organic nature of the treated clay surface. Here, as for the primary alkyl amines, the trend is for increasing hydrophobicity, i.e., increasing contact angle, as the number of carbon atoms in the amine increases. As with the n-alkylamines, the contact angles for the apolar liquids are relatively invariant for the quaternary amines of the study. The contact angles for the polar liquids on ammonium-montmorillonite also are smaller than for the treated clay, but the ammonium clay is less hydrophilic than predicted by a simple linear extrapolation to zero carbon.

While the trends in the contact angles are clear, they are not directly useful in elucidating which aspects of the surface thermodynamic properties are changing. Examination of the values of γ^{LW} (Table 4) for the ammonium montmorillonite and the montmorillonite treated with both the primary alkyl amines and the quaternary amines shows that the organo-clay does not differ substantially from the ammonium clay. This is a striking result of the present study because the γ^{LW} for the n-alkanes, that part of the primary ammonium cations which are covering the surfaces of organo-montmorillonite, range from 18.40 for C_6 to 27.07 mJ/m² for C_{15} (Jasper, 1972). LW forces originating from

Table 5. Values of the surface tension components and parameters for Laponite RD after exchange by different organic cations as described in Table 3. All values are in mJ/m².

	Amm	C = 8	C = 10	C = 12	TMA	HDTMA
γ^{LW}	42.5	42.1	41.4	41.5	44.4	43.0
$\gamma^{\oplus}$	1.5	1.0	0.8	0.9	1.5	0.6
$\gamma^{\ominus}$	30.7	24.2	24.3	24.5	31.2	24.7
γ^{AB}	13.6	10.0	8.8	9.3	13.7	8.0

an appreciable thickness of a solid material make their presence felt to a longer distance than do the AB forces; the latter only begin to exert their influence from the layer of molecules situated at the solid/liquid interface. Hence, partially covering the surface of the clay, which has an inherent $\gamma^{LW} \simeq 40$ mJ/m², with a thin layer (3–5 Å) of organic material would tend to reduce the γ^{LW} of the pristine clay surface by a small amount in relation to the extent of surface coverage by the amine tail. This should produce a slowly decreasing γ^{LW} as n changes from 6 to 15, as observed, although the statistical significance of the trend is difficult to evaluate.

In short, the change in surface properties of a smectite resulting from organic matter on the surfaces of the clay are not due to changes in the Lifshitz-van der Waals interactions. In fact, replacing the inorganic cations with other mono- and divalent cations has a greater influence on the value of γ^{LW} of SWy-1 than is observed here (Costanzo *et al.*, 1991a).

As is typical of oxides in general and smectites in particular (Giese *et al.*, 1989), the values of $\gamma^{\oplus}$ are small for the organo-montmorillonites of this study (Figure 1). For comparison, alkanes are apolar with $\gamma^{\oplus} = \gamma^{\ominus} = 0$. The values for the primary amine treated montmorillonite are 1.0 mJ/m² or less. In the case of the quaternary amine-treated montmorillonite, the values of the electron acceptor (Lewis acid) parameter exceed this range for all the amines except HDTMA. It is
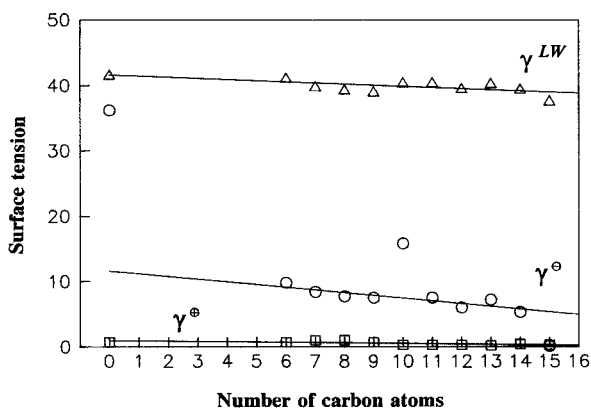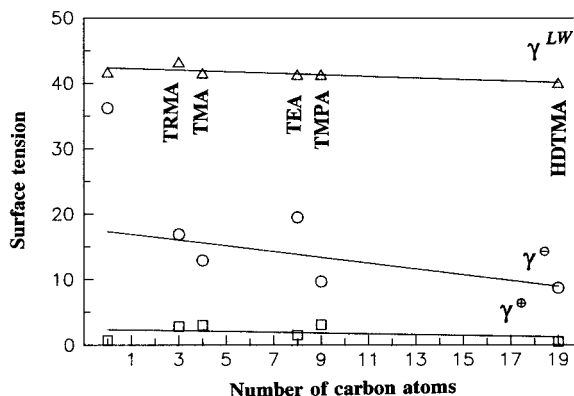

Figure 2. The same plot as in Figure 1 but for the quaternary ammonium cations of Table 1.

noteworthy that the $\gamma^{\oplus}$ values for TMA and TMPA (3.0 and 3.1 mJ/m², respectively) are among the largest observed to date for any solid or liquid material with the exception of water, the most polar of materials. The value of 3 mJ/m² is equalled only by ethylene glycol and slightly surpassed by glycerol (3.92 mJ/m²). Chloroform is an exception with a value of 3.8 mJ/m² (as reviewed by van Oss *et al.*, 1989) but this value should be regarded as uncertain, being based on a single measurement of the interfacial tension, γ_{12}, between chloroform and water (Girifalco and Good, 1957).

Although γ^{LW} is constant and $\gamma^{\oplus}$ varies little among the 16 samples in Table 4, the values of $\gamma^{\ominus}$ change from sample to sample. Here it is simple to distinguish between an organo-clay ($0 < \gamma^{\ominus} < 17$ mJ/m²) and the parent ammonium montmorillonite ($\gamma^{\ominus} = 36.2$ mJ/m²). Thus, in terms of altering the surface thermodynamic properties of the montmorillonite, the major factor is the variability of the Lewis basicity. Plotting the value of $\gamma^{\ominus}$ versus the number of carbon atoms in the primary amines shows a linear trend with a decreasing Lewis basicity as the number of carbon atoms increases (Figure 1). There are two amines which do not fall on the line; the C_{10} and the C_{15} amines. The relatively high value of $\gamma^{\ominus}$ for the C_{10} amine directly reflects the water contact angle (Table 2) which is substantially smaller than for the neighboring amines. The origin of the C_{10} anomaly is not known. On the other hand, the very small values of $\gamma^{\oplus}$ and $\gamma^{\ominus}$ for the C_{15} sample may reflect a complete coverage of the external surface of the clay, i.e., the maximum possible hydrophobicity. Similarly, a plot of $\gamma^{\ominus}$ versus the number of carbons for the quaternary amines shows an inverse linear trend but with more scatter (Figure 2).

Laponite

Examination of the contact angles for the five test liquids on Laponite saturated with ammonium or surface-treated with a few organic ammonium cations (Table 3) shows that the contact angles for the apolar

Figure 1. The variation of γ^{LW}, $\gamma^{\oplus}$, and $\gamma^{\ominus}$ in mJ/m², versus the number of carbon atoms in the n-alkylammonium cations covering the surface of the SWy-1 montmorillonite. The straight line was fitted without the data point for C_{10}.

liquids on the organo-Laponite samples and on ammonium Laponite are roughly the same. For these samples, γ^{LW} also decreases slightly as the number of carbon atoms in the amines increases. The values of $\gamma^{\oplus}$ are small and the values of $\gamma^{\ominus}$ show the most variation. In the case of Laponite, the Lewis basicity of the organic treated samples tends to be greater than for the organo-montmorillonite samples of this study, and there is an inverse relation between $\gamma^{\ominus}$ and the number of carbon atoms in the amine.

CONCLUSIONS

The measurements of both Wyoming montmorillonite and Laponite RD of this study indicate that the Lifshitz-van der Waals interactions of smectites are not influenced perceptibly by the adsorption of a variety of organic molecules on the surface of the clay particles. Neither is the Lewis acid activity of the clay substantially changed by an external organic coating. The site of the Lewis acidity has been assigned to the broken edges of the clay particles (Giese *et al.,* 1991) and it seems likely that the organic material principally covers the 001 surfaces leaving the edges largely unmodified. The greatest change in the surface thermodynamic properties of the clays brought on by conversion to an organo-clay is the reduction in the strength of the Lewis basicity. The Lewis base sites are assigned to the 001 oxygens and their lone pair electrons. In the context of an organo-clay, the decrease in the Lewis base strength is seen to occur as the extent of 001 surface coverage increases, thus, decreasing the number of available Lewis base sites at the surface of the clay. For the quaternary ammonium cations, differences in the values of $\gamma^{\oplus}$ and $\gamma^{\ominus}$ may explain the difference in adsorption of a given organic molecule from a solvent, as seen in the greater adsorption of phenol onto HDTMA-montmorillonite compared to TMPA-montmorillonite (Mortland *et al.,* 1986). At present, because there are no measurements of the surface tension components for phenol nor for halogenated phenols, this preference cannot be examined in terms of the free energy of adsorption (Costanzo *et al.,* 1991b).

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