ADSORPTION OF n-ALIPHATIC ALCOHOLS FROM DILUTE AQUEOUS SOLUTIONS ON RNH3-MONTMORILLONITES. III. INTERLAMELLAR AGGREGATION OF THE ADSORBATE

MICHAEL S. STUL AND JOZEF DE BOCK
Laboratorium voor Oppervlaktescheikunde, Katholieke Universiteit Leuven
Kardinaal Mercierlaan 92, B-3030 Leuven (Heverlee), Belgium

Abstract—The large amount of water in the interlamellar space of alkylammonium montmorillonites in aqueous solutions is not fixed by intercalated hexanol or octanol. The hydration of the NH3+-group and the filling of the empty spaces between the carbon chains are responsible for this phenomenon. Hydrogen bonds between the alcohols and the ammonium groups reduce the enthalpy of solution of hexanol and octanol in the interlamellar region at infinite dilution to +17.6 and +12.7 kJ/mole, respectively. Self-association of the alcohols further diminishes the enthalpy of solution at higher alcohol concentration. The interlamellar fixation of the RNH3 cations prevents a micellization as has been obtained in bulk solutions. At a given alcohol concentration smectic type aggregates, i.e., double layers of alcohol molecules, appear as an increase of the basal spacing of the organo-clay complexes. The aggregate formation is favored by a longer chain length of both the cation and the alcohol.

Key Words—Adsorption, Alcohol, Alkylammonium cations, Intercalation, Micellization, Montmorillonite.

Sammenvatting—Het hoge watergehalte van de interlamellaire fase van alkylammonium-montmorillonieten in waterige oplossing is niet gefixeerd door de binnenkomende hexanol of oktanol. De hydratatie van de NH3+-groep en het opvullen van de ruimtes tussen de koolwaterstofketens zijn er verantwoordelijk voor. Bij oneindige verdunning reduceren waterstofbruggen tussen alkoholen en ammoniumgroepen de oplossings-enthalpie van respectievelijk hexanol en oktanol in de interlamellaire fase tot +17,6 en 12,7 kJ/mol. Bij hogere alkoholkonzentratie vermindert deze oplossings-enthalpie verder door associatie van de alkoholen. De interlamellaire fixatie van RNH3 kationen verhindert het micellisatiefenomeen zoals het zich in bulk oplossingen voordoet. Bij een bepaalde alkoholkonzentratie duidt een verhoging van de basisafstand van de organo-kleikompleksen het optreden aan van aggregaten van het smektiet type, d.i. een dubbellaag van alcohol moleculen. Deze aggregaat vorming wordt bevorderd door een langere keten van zowel het kation als van de alcohol.

INTRODUCTION

The adsorption behavior of n-hexanol and n-octanol on alkylammonium (RNH3) clay minerals is the sum of several phenomena. (1) In the interlamellar space adsorption can take place (a) between flat-lying organic cations, (b) between flat-lying organic cations eventually accompanied by a reorientation of these cations as demonstrated by the expansion of the clay layers, or (c) by a uniform packing of the alcohols in the expanded interlayer space which may also be characterized by a further increase of the basal spacing. (2) On the basal surface and the edges the adsorption may occur in mono- or multimolecular layers. (3) The adsorption may also occur in capillaries created by stacking of clay particles.

Mechanism (1a) is predominant at infinite dilution (Stul et al., 1978). Comparing the interlayer cations with the action of an organic solvent, adsorbed alkylammonium acts as an even stronger solvent than CCl4. Hydrogen bonds are probably formed between the OH group of the alcohol and the NH3+ group. The replacement of water by alcohol on the interlamellar ammonium ion is the major factor in the transfer process of alcohol from water into the interlamellar phase, and the interlamellar adsorption for adsorption mechanisms 1a, 1b, and 1c is further characterized by an association of the alcohol molecules (Stul et al., 1979). The alcohols can associate with alcohol monomers fixed on the NH3+ group and on free moving monomers. The ratio of immobilized to free alcohol monomers is about 10/1. Mechanisms (1b) and (1c) can be detected by an increase of the basal spacing of the clay. The expansion of the clay is caused by the development of an aggregate structure similar to phenomena in ternary bulk systems for which variations of Bragg spacings are indicative of different aggregate types (Ekwall et al., 1971). The low concentration of interlamellar alcohol at which this phenomenon started demanded that some of the cations were surrounded by sufficient alcohol molecules to form aggregate patches acting as pillars.

It is the purpose of the present paper to follow the equilibrium distribution of an alcohol between an interlamellar solvent and the bulk solution in order to study the interlamellar phase. The interlamellar phase was first treated as a binary system: alcohol-organic
solvent, alcohol-water, or water-surfactant systems. This treatment was extended to a ternary system, water-surfactant-alcohol. In such a ternary system alcohol molecules were incorporated in a mesophase aggregate which forms lamellar micelles composed by double layers of amphiphile molecules, whose lyophilic groups face outwards towards the surrounding solvent, while its lyophobic groups are oriented inwards and form the core of the aggregate.

EXPERIMENTAL

Adsorption isotherms

The procedure for the preparation of the RNH₃⁺-Camp Berteau montmorillonite has been described elsewhere (Stul et al., 1979). The chemical composition of the RNH₃⁺-clay was calculated from micro-Kjeldahl analyses and the weight loss upon calcination at 800°C and expressed per gram of cation-free silicate framework (g.s.f.). Adsorption isotherms were measured by the equilibrium dialysis method as follows.

Two-hundred milligram samples of RNH₃⁺-clay and 5 ml of distilled water were placed in a dialysis bag. The bags were placed in 20 ml of aqueous alcohol solutions of concentrations varying from 5 to 90% of their solubility limit. Equilibrium was obtained after 5 days of end-over-end shaking at a given temperature. The amount adsorbed was calculated from the differences between initial and the equilibrium concentrations. Hexanol adsorption on octyl- and decylammonium clays at 25°C was measured by a colorimetric method (Moroff, 1959; Stul et al., 1978). Hexanol and octanol adsorption on decylammonium montmorillonite at 5°, 25°, and 45°C were determined by radiotracer methods using ¹⁴C-labeled alcohols (ICN Tracerlab, Waltham, Massachusetts). Radiometric assays were made of 5 ml aliquots of the initial and equilibrium solutions using a 2425 Packard liquid scintillation spectrometer. Adsorption on tubes and bags was negligible (less than 1% of the amount adsorbed by the clay).

X-ray powder diffraction (XRD)

The samples together with their equilibrium solutions were placed into Lindemann glass capillaries which were sealed using a very small torch and mounted into a Debye-Scherrer camera (diameter 114.6 mm). A Philips X-ray diffractometer with CuKα radiation was used. The accuracy of the d(001) values is ~0.04 Å. Decisions on the existence of an integral series of basal reflections were based on the 001, 002 and 003 reflections.

RESULTS

Adsorption isotherms of hexanol and octanol on alkylammonium montmorillonite are shown in Figures 1a and 1b. The amount of alcohol in the interlamellar zone was calculated by assuming that all the additional alcohol entered these spaces. The interlamellar space amounted to 89.3% of the total surface. Multilayer adsorption was expressed for each point along the isotherm in the following formula:

\[
V_F = V_I - V_C - V_A
\]

where \(V_F\) = free interlamellar volume; \(V_I\) = interlamellar volume; \(V_C\) = mmol alcohol adsorbed x volume/mmole; and \(V_A\) = volume of the interlamellar alcohol = 0.893 x mmole alcohol adsorbed x volume/mmole; and interlamellar concentration (CA) = mmole interlamellar alcohol/Vf. The volume of the molecules, calculated from their length as measured on catalin models and a cross section of 20 Å² (Barrer et al., 1967), were intermediate between those of the corresponding n-amines and n-alcohols, as derived from molecular weights and liquid densities. The interlamellar composition was calculated assuming a homogeneous distribution of the alcohols over the whole interlamellar phase and was used as such in most of the following considerations. It was also altered to compositions in unexpanded and expanded spaces. The interlamellar composition of the expanded spaces was then obtained by adopting a constant composition for the unexpanded regions corresponding to the alcohol concentration just before expansion started. In this way, an apparent spacing as was demonstrated by Stul and Mortier (1974). With hexanol the expansion of RNH₃⁺-clay started at a threshold equilibrium concentration of 21.8, 16.7, and 3 mmole/liter for RNH₃ with a chain length n~ = 8, 10, and 12, respectively. With octanol the expansion of dodecylammonium clay started at 0.75 mmole/liter. The interlamellar alkylammonium content was taken to be 0.85 x 10⁻³ mole/g of dry silicate framework, assuming a clay surface of 700 m²/g and a mean charge density of 0.34 cations per 46.5 Å², the available surface per formula unit (Al₂Si₄O₁₀(ΟΗ)₂) (Stul and Mortier, 1974). Double layer complexes of alcohol were thus obtained for RNH₃+-montmorillonite saturated with pure n-alcohol (Stul et al., 1979; Lagaly and Weiss, 1969a, 1971).

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The foregoing is a simplification of the real situation which was expressed for each point along the isotherm in the following formula:
Figure 1. Adsorption isotherms at 25°C of interlamellar hexanol (a) on RNH₃⁺-montmorillonite from Camp Berteau. Arabic numbers represent the length of the alkyl chain of the alkylammonium cation. ‖ and ‖‖ indicate the start and the end of the successive expansion. Adsorption isotherms of interlamellar hexanol (a) and octanol (b) on dodecylammonium clay at 5°C (x), 25°C (O), and 45°C (D). Basal spacings of hexanol complexes (c) and octanol complexes (d) at different equilibrium concentrations. Open symbols point to a nonintegral series of 001 reflections; solid symbols to an integral one.

\[
\text{mmole alcohol} = \sum_{n=a}^{n=b} X_{1, n} \cdot V_1 \cdot \text{conc}_{1, n} + \sum_{n=c}^{n=d} X_{2, n} \cdot V_2 \cdot \text{conc}_{2, n},
\]

where \( n \) = cation density class, inasmuch as the interlayer cation density in montmorillonites, as determined by the alkylammonium method (Stul and Mortier, 1974; Lagaly and Weiss, 1976), extends over several classes; 1 and 2 = unexpanded and expanded space; \( X_{1, n} \) = percentage of unexpa-
ed spaces with a cation density \( n \) at an alcohol equilibrium concentration \( j \); \( \text{conc}_{\text{r},n,j} \) = interlamellar concentration in the unexpanded space at a cation density \( n \) and an equilibrium concentration \( j \); and \( V_i \) = unit of interlamellar volume of the unexpanded space.

**DISCUSSION**

*Fixation of water by alcohols in the interlamellar solvent*

The distribution of alcohol between water and an organic solvent is characterized by an autoassociation of the alcohols in the organic phase which is accompanied by fixation of \( H_2O \) through these alcohols in the organic solvent (Huyskens et al., 1980). This picture, however, did not adequately explain the high water content in the interlamellar clay phases (see Figure 2).

At low alcohol concentration the high water content originated from a matrix effect of the mineral surface exchanged with \( \text{RNH}_3^+ \)-cations; i.e., the hydration of the \( \text{NH}_3^+ \)-group and the filling of the empty spaces between the flat lying carbon chains (Stul et al., 1978).

At higher alcohol concentration the additional water uptake was caused by a reorganization of the interlamellar phase (see Figure 1c and 1d).

*Enthalpy of solution in the interlamellar phase*

The enthalpy of solution of alcohol \( \Delta H \) in the interlamellar phase \( \beta \) was obtained by considering the preference of an alcohol vs. water by the following equilibrium:

\[
\text{nH}_2\text{O} + \text{ROH} \rightleftharpoons \overline{\text{ROH}} + \text{nH}_2\text{O},
\]

which is characterized by

\[
K = \frac{x_{\beta}^{\beta} \cdot (x_{w})^{\alpha}}{(x_{\beta}^{\alpha})^{\beta} \cdot x_{w}^{\alpha}},
\]

where \( n = 7 \) and \( 9 \) for hexanol and octanol, as derived from volume calculations, respectively. The molar fractions are:

\[
x_{\beta}^{\beta} = \frac{\text{ROH}}{\text{ROH} + \text{H}_2\text{O}} \quad \text{and} \quad x_{w}^{\alpha} = \frac{\text{ROH}}{\text{ROH} + \text{H}_2\text{O}},
\]

where ROH and \( \text{H}_2\text{O} \) and ROH and \( \text{H}_2\text{O} \) are the mole numbers of alcohol and water in the clay phase (\( \beta \)) and the aqueous phase (\( \alpha \)), respectively. The mole numbers in the clay phase are expressed per gram of cation-free silicate framework.

The enthalpy of transfer, \( \Delta \beta H \), was determined from the temperature dependency of the equilibrium, assuming that the basal distance at 5° and 45°C equals that at 25°C. This assumption was justified by the adsorption behavior of octanol on dodecylammonium clay (Figure 1b). The adsorption rate changed at the same alcohol loading (0.335 mmole/g.s.f.) along the isotherm at different temperatures. By raising the temperature to 57°C, no conformational changes took place in the alkyl chains of alcohol-alkylammonium clay complexes because of temperature changes (Lagaly and Weiss, 1972).

From \( \Delta H = \Delta \beta H - \Delta \alpha H \), in which \( \Delta \beta H \) and \( \Delta \alpha H \), stand for the heat of solution in the interlamellar phase and water, respectively, and using the \( \Delta \alpha H \) data of Aveyard and Mitchell (1968), \( \Delta H \) at different loadings of the interlamellar phase was calculated and is presented in Figure 3a. \( \Delta H \) was taken equal to \( \Delta \alpha H = -5.77 \) and \(-3.44 \) kJ/mole for hexanol and octanol, respectively, in the concentration range under consideration. The latter value was obtained by extrapolating the data of Aveyard and Mitchell (1968) to octanol. The interlamellar \( \text{RNH}_3^+ \)-cations acted as an organic phase as illustrated by the association of alcohols in \( \text{RNH}_3^+ \)-clay on transfer from the bulk solution (Stul et al., 1979). At extreme dilution the enthalpy of solution of the alcohol \( \Delta \alpha H \) was 17.6 and 12.7 kJ/mole for hexanol and octanol, respectively (Figure 3a). In alkane, Aveyard and Mitchell (1969) found a constant \( \Delta \alpha H \) of 22.4 kJ/mole independent of the alcohol-alkane combination, and Kertes et al. (1980) measured 21.3 kJ/mole for the system octanol-octane. At infinite dilution the interaction of the hydroxyl group with the \( \text{NH}_3 \)-group compensated partially for the high endothermicity of breaking the hydrogen bonds in pure alcohol. This phenomenon was also demonstrated for octanol in octanoic acid (\( \Delta \alpha H = 5.57 \) kJ/mole; Kertes et al., 1980). n-Alcohols have even an exothermic heat of mixing with pure n-butylamine (Ratkovics and László, 1973).

A concentration dependence of \( \Delta H \) due to the self-association of the alcohols (Stul et al., 1979) was dem-

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**Table 1. Interlamellar octylammonium clay composition for the adsorption of hexanol.**

<table>
<thead>
<tr>
<th>Equilibrium concentration (mmole/liter)</th>
<th>Interlamellar alcohol (mmole/g)</th>
<th>Interlayer distances (Å)</th>
<th>( V_i ) (10^{23} Å³)</th>
<th>( V_j ) (10^{23} Å³)</th>
<th>( c^* ) (10^{-4} mmole/liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.1340</td>
<td>8.7</td>
<td>3.05</td>
<td>0.176</td>
<td>1.496</td>
</tr>
<tr>
<td>21.8</td>
<td>0.476</td>
<td>9.0</td>
<td>3.15</td>
<td>0.691</td>
<td>1.086</td>
</tr>
<tr>
<td>23</td>
<td>0.6251</td>
<td>17% of 18</td>
<td>2.61</td>
<td>(1.07)</td>
<td>(0.246)</td>
</tr>
<tr>
<td>29.2</td>
<td>1.286</td>
<td>55% of 18</td>
<td>1.42</td>
<td>(3.47)</td>
<td>(1.337)</td>
</tr>
</tbody>
</table>

Parentheses = data of the expanded interlamellar spaces; other data = unexpanded spaces.

1 All data are expressed per gram of cation-free silicate framework.
Figure 2. Solubility $F_\text{w}$ of water at various concentrations $F_\text{w}$ of alcohols in different organic phases (β) at 25°C. Hexanol in CCl₄ (©) in the interlamellar phase of RNH₃⁺-clays with $n_\text{c} = 8$ (Δ), 10 (V), 12 (©) and octanol in dodecylammonium clay (©). A homogeneous distribution of the alcohols over the whole interlamellar phase is indicated by a full line; a different composition of the expanded and unexpanded zones is given by a dotted one.

Demonstrated for both alcohols (see Figure 3a). The octanol adsorption with expansion of the clay layers resulted in a constant $\Delta F$. Further experimental work is necessary to elucidate this phenomenon. From the sorption of the two alcohols, the van der Waals interaction was obtained and is presented in Figure 3b. At a loading of 1 mmole ROH/g.s.f., which means 60% of expanded interlamellar spaces with hexanol and 40% with octanol sorption, the van der Waals interaction amounted to 2 kJ/mole CH₂ which approaches the interaction between the alkyl chains of n-alcohol in dry dodecylammonium montmorillonite (Lagaly and Weiss, 1969b).

Swarm building of nearly hexagonally packed alcohols around the cation and separation of these by 0.5 Å from the next pillar caused a reduction of the interaction with respect to pure liquid alcohol with a van der Waals interaction of 5.85 kJ/mole CH₂ (Lagaly and Weiss, 1970).

In the systems H₂O-nRNH₃Cl two different isotropic micellar solutions appear at different molar concentrations as shown in Table 2 of Nery et al., 1980. In the ternary systems H₂O-ionic surfactant-n-alcohol the critical micelle concentration (CMC) of the system H₂O-surfactant decreases by addition of n-alcohol as shown by hexanol for the system H₂O-C₁₂H₂₅NH₃Cl (Herzfeld et al., 1950), by butanol for C₁₂H₂₅N(CH₃)₃Br-H₂O (Guyeli et al., 1979), and by n-alcohols in aqueous sodium dodecyl sulfate solution (SDS) (Hayase and Hayano, 1978). The last authors showed a linear decrease of the logarithm of CMC of SDS (mole fraction) as a function of the mole fraction of 1-alcohol in the aqueous phase. The In CMC depends linearly on the number of carbon atoms in the alkyl chain indicating

Table 2. Concentrations (mole/liter) at which different types of aggregates of RNH₃Cl (with different chain length) appear in bulk solution at 25°C.¹

<table>
<thead>
<tr>
<th>Number of carbon atoms of RNH₃</th>
<th>8</th>
<th>10</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Globular (L₁)</td>
<td>0.25</td>
<td>0.055</td>
<td>0.013</td>
</tr>
<tr>
<td>Rod-shaped (E)</td>
<td>—</td>
<td>0.75</td>
<td>0.27</td>
</tr>
<tr>
<td>$V_{\text{uexp}}$</td>
<td>2.70</td>
<td>2.82</td>
<td>2.38</td>
</tr>
<tr>
<td>$V_{\text{exp}}$</td>
<td>1.34</td>
<td>1.30</td>
<td></td>
</tr>
</tbody>
</table>

¹ Data taken from Nery et al. (1980), supplemented with concentrations of the RNH₃⁺ cations in the unexpanded and expanded interlamellar clay volumes (V). Mesomorphic phase E = hexagonally packed hydrophilic rods. Mesomorphic phase D = double layers of amphiphile molecules.
a constant energy variation corresponding to the transfer of a CH$_2$-group from the aqueous phase to the micellar phase. The transition from the micellar solution of lower concentration to a mesophase can be produced by solubilization of alcohol as shown in the system cetyltrimethylammonium bromide (CTAB)-hexanol-water (Ekwall et al., 1971). In the CTAB-water system with low hexanol content a mesomorphic phase E with hexagonally packed hydrophilic rods is present in addition to the isotropic globular micelle phase (L$_1$, see Danielsson, 1976 for the alphabetical notation). With higher alcohol concentration a mesophase D of the smectic type appeared, formed by the parallel arrangement of indefinitely lamellar “sandwich” micelles consisting of double layers of amphiphile molecules. At still higher concentration an isotropic solution of inverted globular micelles is present in hexanol (L$_2$) as shown by XRD and viscosity data.

Quantitative evidence of the occurrence of lateral interaction between adsorbed alkyl surfactants into two-dimensional patches at the solid-liquid interface has been obtained from determinations of the effect of the chain length on the electrokinetic potential of silica in aqueous solutions of alkylammonium acetates (So-masundaran et al., 1964). The patches of associated ions were termed “hemimicelles.” Dodecylammonium chloride also exhibits this phenomenon at the hydroxyapatite surface (Mishra et al., 1980). Structuring effects at the solid/liquid interface has also been shown by the phase transitions of 1-octanol/heptane mixtures on a graphitized carbon black (Brown et al., 1975).

In the unexpanded state of the interlamellar clay phase and below 2.4 mole RNH$_3^+$/liter, no aggregate formation was observed, only cation-alcohol associates. Different types of surfactant aggregates were present in bulk solution in this concentration range as shown in Table 2. The lack of aggregate formation in clay was probably caused by an anchoring of the cations at a silicate platelet. Raising the alcohol concentration induced an expansion of the clay platelets caused by the formation of an aggregate of the smectic type with a double layer of amphiphile molecules as indicated by the XRD data (Stul et al., 1979), in which the clay platelets behaved as a rigid anionic solvent. At high alcohol concentrations the composition of the interlamellar micelle merged to an [(ROH)$_x$RNH$_3$]$_m$(H$_2$O)$_n$ phase. The CMC was defined as the molar fraction of the cations in V$_1$, the unexpanded interlamellar volume of the clay at the alcohol concentration in the aqueous phase just before expansion started, i.e.: 

$$x_{RNH3}^m = 0.85/0.85 + ROH + H_2O.$$  

The ln CMC of the interlamellar RNH$_3^+$-cations as a function of the molar fraction of 1-alcohol in the aqueous phase is given in Figure 4, analogous to the treatment of Hayase and Hayano (1978). In comparison with their system water-SDS-alcohol a higher cation concentration was needed but a lower alcohol concentration for the aggregate formation. In the interlamellar clay phase, aggregate formation was favored by a longer alkyl chain of both the cation and the alcohol which was also observed in bulk solutions. This type of consideration, as presented in Figure 4, allows, by exchanging another clay mineral with a different charge density and consequently with a different interlamellar cation concentration and by observing the CMC for a given alcohol-cation combination, a prediction to be made of what type of clay mineral should be chosen to obtain a surface-induced micellization, even at very dilute alcohol concentration.

ACKNOWLEDGMENTS

The authors thank Prof. G. Lagaly (University of Kiel, F.R.G.) and Prof. S. Friberg (University of Missouri, Rolla, Missouri) for valuable advice.

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(Received 16 March 1984; accepted 14 January 1985; Ms. 1345)