

THE ADSORPTION OF N-ALIPHATIC ALCOHOLS FROM DILUTE AQUEOUS SOLUTIONS ON RNH₃-MONTMORILLONITES. PART I. DISTRIBUTION AT INFINITE DILUTION

MICHEL S. STUL, ANDRÉ MAES, AND JAN B. UYTTERHOEVEN

Centrum voor Oppervlaktischeikunde en Colloïdale Scheikunde
Katholieke Universiteit Leuven, De Croyleaan 42, B-3030 Heverlee, Belgium.

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Abstract—The adsorption of butanol, hexanol, and octanol on alkylammonium clays of different chain length is studied. The adsorption at infinite dilution compares to the distribution of alcohol between alkane and water in bulk solution. The interlamellar phase of the montmorillonite acts as a solvent even more reactive than carbon tetrachloride. Hydrogen bonds probably occur between the OH group of the alcohol and the NH₃⁺ group. The exchange of water by alcohol on the interlamellar alkylammonium ion is the major factor in the transfer process.

Key Words—Adsorption, Alkylammonium, Butanol, Hexanol, Interlayer, Octanol.

INTRODUCTION

Adsorption studies of n-aliphatic alcohols from dilute aqueous solutions on montmorillonites saturated with inorganic ions are scarce. Alcohol adsorption in Ca-bentonite increases with the chain length of the alcohol (German and Harding, 1969). Up to pentanol no adsorption is observed (Hoffmann and Brindley, 1960). Swelling of the clay occurs up to a certain alcohol concentration (Brindley et al., 1969). The change in the interlamellar composition is however not determined.

The adsorption of alcohols from toluene mixtures was followed in gelation studies of organo-bentonites (Jordan, 1949; Granquist and McAtee, 1963; McAtee and Cheng, 1967) and laponites (Neumann and Sansom, 1970). A more quantitative study was made for the selective adsorption of n-alkylalcohol-bromide mixtures by montmorillonite (Heydemann and Brindley, 1968): the alcohol is more strongly adsorbed than the bromide indicative of a different adsorption mechanism.

For the alcohol applied as a pure sorbate a number of papers describe the interlamellar structure of montmorillonite with inorganic cations (Barshad, 1952; Mac Ewan, 1955; Brindley and Ray, 1964; Bissada et al., 1967), with organic cations (Lagaly and Weiss, 1969) and of uncharged lamellae such as tetracalcium-aluminumhydrates (Dosch, 1967) and oxidized graphite (Aragón and Castro Castro, 1969).

The interlamellar organic cations change the hydrophilic character of the silicate surface. Weiss (1966) distinguishes three classes of RNH₃-clays depending on their affinity for water which was determined by shaking samples in a mixture of water and toluene. The clays are classified as hydrophilic, neutral, or hydrophobic according to their tendency to concentrate in the aqueous phase, the interphase, and the toluene phase, respectively. An alternative approach will be given below by a more quantitative study of the adsorption of

alcohols from dilute aqueous solutions on RNH₃-clays as a function of the chain length of the cation and the alcohol and of the charge density of the mineral. As in general adsorption isotherms can be considered as distribution diagrams (Kipling, 1965; Giles, 1970), we will consider the interlamellar clay phase as an organic phase and will compare the adsorption of n-alcohols from aqueous solutions on the clays with a distribution over the system water-alkane.

MATERIALS AND METHODS

Preparation of the alkylammonium clays

The fraction smaller than 0.5 μm of a Camp Berteau montmorillonite (Morocco) is separated using standard methods of centrifugation and is successively washed with acidified (pH = 3.5) and neutral normal NaNO₃ solutions for the removal of hydroxy-aluminum compounds. It is stored at 5°C in the dark as a 2% suspension. From this stock suspension 100 ml portions are transferred to dialysis bags and dialyzed to 10⁻² N NaNO₃ before exchange with 10⁻² N alkylammonium chloride solutions at room temperature. The alkylammonium (further on indicated by RHN₃⁺) solutions are renewed 4 times. Four pure methanol washes are carried out to remove the excess ions and the physically bonded amines. For ions in which the number of carbon atoms n_c is ≥ 14 the exchange temperature is 50°C while methanol-water mixtures (2 to 1 ratio) are used as the solvent. Then the clays are dried at room temperature and 10⁻³ torr and passed through a 0.1 mm sieve. The methanol is completely removed by a 24-hr vacuum treatment (10⁻⁵ torr) and the clay is stored in a 80% relative humidity atmosphere for 1 week. Llano vermiculite (U.S.A.) is ground and exchanged with octylammonium for 1 week and subsequently treated analogously to the montmorillonite samples.

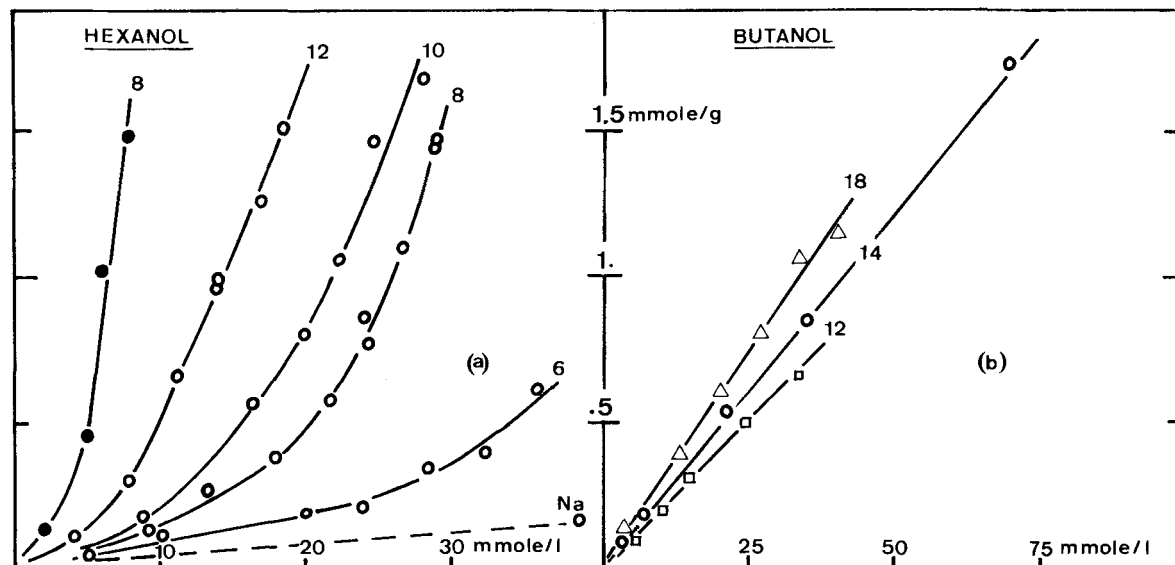


Fig. 1. Adsorption isotherms at 25°C of (a) hexanol on RNH_3 -montmorillonites (○) and on octylammonium vermiculite (●); (b) butanol on RNH_3 -montmorillonites. The arabic figures represent the number of carbon atoms in the cation.

Colorimetric determination of alcohols

A colorimetric method for the quantitative determination of alcohols in solution is used. Higher alcohols can be dehydrated in the presence of cyclic aldehydes to form a colored compound (Komarowsky, 1910). The method can be made quantitative by a suitable choice of concentrations. It has been applied for the quantitative determination of fusel oil in distilled beverages (Boruff, 1959). Two-milliliter samples are pipetted into 15-ml test tubes. These are closed and cooled in an ice bath. One milliliter of a 1% p-dimethylaminobenzaldehyde solution in 5% H_2SO_4 is added, and cooled again for another 3 min. With the tubes still in the ice bath 10 ml of concentrated H_2SO_4 is added and allowed to cool for 3 min. The tubes are then transferred to a water bath at 100°C for 20 min for color development, cooled again in the ice bath and brought to room temperature. The percent transmittance is determined on a Shimadzu QV-50 spectrophotometer at 504 nm. The accuracy is $\pm 1\%$.

Adsorption isotherms

Adsorption isotherms are obtained by the equilibrium dialysis method. Two hundred milligrams of RNH_3 -clay is weighed into a dialysis bag and 5 ml of distilled water is added. These bags are placed in 20 ml of aqueous alcohol solutions in polyethylene tubes. The applied concentrations varied from 5 to 90% of the solubility limit. Equilibrium is obtained after 5 days end-over-end shaking at 25°C. The amount adsorbed is derived from the differences between the initial and the equilibrium concentration. Hexanol adsorption at 25°C is measured by the colorimetric method. Butanol ad-

sorption on RNH_3 -montmorillonites at 25°C, hexanol and octanol adsorption on dodecylammonium montmorillonite at 5°, 25°, and 45°C are determined by radiotracer methods using C^{14} labeled alcohols (ICN Tracerlab, Waltham, Mass.). Radiometric assays are taken on 5-ml aliquots of the initial and equilibrium solutions using a 2425 Packard liquid scintillation spectrometer. Adsorption on tubes and bags is negligible (less than 1% of the amount adsorbed by the clay).

X-ray powder diffraction

X-ray powder diffraction experiments are carried out in order to determine the basal separation $d(001)$ of RNH_3 -montmorillonites in water. The suspension is brought into Lindemann glass capillaries which are sealed using a very small torch, and are mounted into a Debye-Scherrer camera (diameter 114.6 mm). A Philips X-ray diffraction instrument with CuK_α radiation is used. The accuracy of the $d(001)$ values is of the order 0.04 Å.

Alcohol distribution between water and n-alkanes

The partition of butanol, hexanol, and octanol between water and two alkanes (hexane and octane) is investigated at 5°, 25°, and 45°C. Ten milliliters 0.002 M C^{14} tagged aqueous alcoholic solutions are shaken with 10 ml alkane for at least 1 hr. After equilibrium and phase separation 1-ml portions of both phases are assayed. Precautions are taken to obtain equal counting efficiencies in both phases in order to calculate the distribution ratios.

The alkylamines, alkanes, and alcohols are pur-

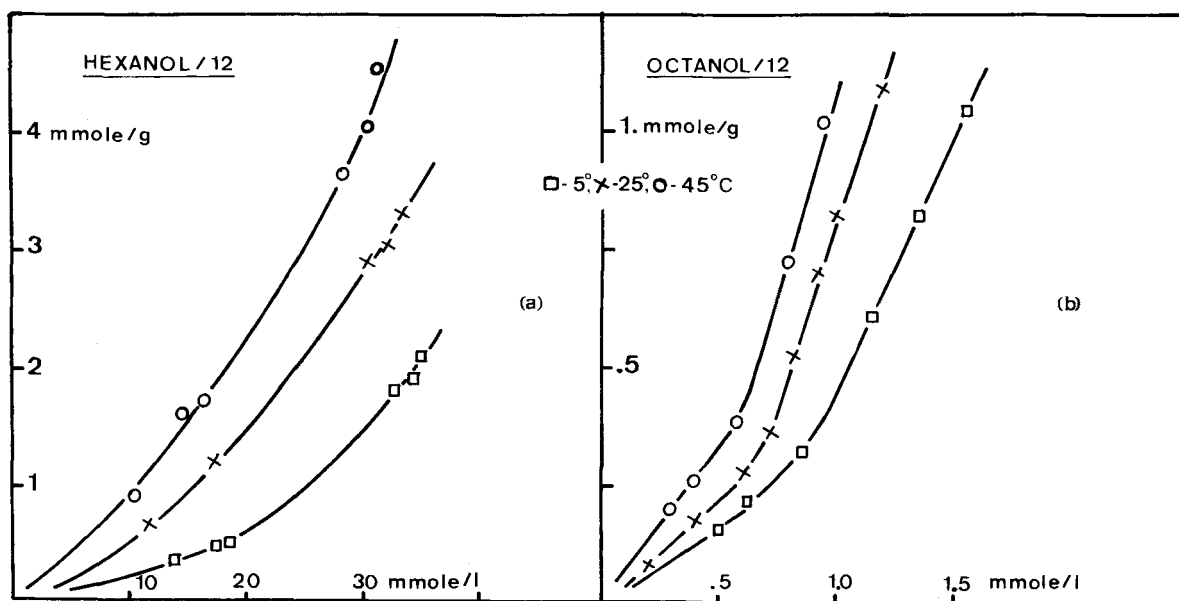


Fig. 2. Adsorption isotherms of hexanol (a) and octanol (b) on dodecylammonium clay at 5°C (□), 25°C (×) and 45°C (○).

chased from Fluka in the purest available grade and are not further purified. Alkylammonium forms are obtained by titration with HCl.

RESULTS

The composition of the RNH_3 -montmorillonites at 80% relative humidity is given in Table 1 in weight percentages of framework, exchangeable cations, and water. The structural formula $(\text{R}-\text{NH}_3)_{0.41}(\text{Si}_4^{4+})^{1V}(\text{Al}_{1.45}^{3+}\text{Mg}_{0.34}^{2+}\text{Fe}_{0.22}^{3+})^{VI}\text{O}_{10.035}(\text{OH})_2 \cdot \chi\text{H}_2\text{O}$ is the one as given by Cremers (1968) corrected for isomorphous substitution as calculated by Stul and Mortier (1974) and adapted to satisfy the electrical neutrality condition. The amount of RNH_3 is determined by calcination at 800°C and chemical analysis of the RNH_3 -content. The vermiculite has a charge density of 0.7 $\text{é}/(\text{Si},\text{Al})_4\text{O}_{10}$ (Lagaly and Weiss, 1970).

The $d(001)$ spacings and the interlamellar water content of the different RNH_3 -clays in water are shown in Table 3. The volume of the interlamellar water is calculated by subtracting the volume of the interlamellar RNH_3^+ -ions from the total interlamellar volume. A clay surface of 700 m^2/g with a mean charge density of 0.34 cations per 46.5 Å^2 or 0.85 10^{-3} mole RNH_3^+ -ions is

used in the calculations. The volumes of the RNH_3^+ -ions (Table 3) are found from their length measured on catalin models and a cross section of 20 Å^2 (Barrer et al., 1967). Generally an increase in $d(001)$ spacing and interlamellar water content is observed in going from hexylammonium to dodecylammonium clay. Octyl- and decylammonium clay have the same basal spacing of 18.6 Å . On account of the higher volume of decylammonium its interlamellar water content is lower than the one for octylammonium clay.

The adsorption isotherms of hexanol on Na- and RNH_3 -montmorillonites and on octylammonium vermiculite are shown in Figure 1a. Figure 1b shows the data of butanol on C_{12} , C_{14} , and C_{18} . The amount of alcohol adsorbed is calculated per gram dry silicate framework. The adsorption is seen to increase with the chain length of the RNH_3 -ions and with the number of these ions per unit cell as is deduced from the higher adsorption data on octylammonium vermiculite compared to octylammonium montmorillonite. The effect of temperature on the adsorption process is studied for hexanol and octanol on dodecylammonium montmorillonite (Figures 2a and b). The adsorption is endothermic.

The influence of the alcohol chain length on the adsorption can be seen by comparing the isotherms for butanol (Figure 1b), hexanol (Figure 2a), and octanol (Figure 2b) on dodecylammonium montmorillonite. Increasing the alcohol chain length by four CH_2 -groups results in an adsorption rise by a factor of 10 at 5 mmole/liter. A comparable increase in RNH_3 chain length increases the adsorbed hexanol by a factor 3 to 4 at the same equilibrium concentration. Alcohol adsorption is

Table 1. Chemical composition of the samples, derived from thermogravimetric data and alkylammonium determination (weight %), x is the number of water molecules per formula unit.

n_c	4	6	8	10	12	14	18
% framework	82.1	81.8	80.5	77.7	75.2	74.63	72.6
% cations	6.7	9.5	11.8	13.8	15.7	17.91	22.0
% water	11.2	8.8	7.7	8.5	9.1	7.46	5.4
x	2.78	2.18	1.95	2.23	2.47	2.03	1.51

Table 2. Standard free energies ($\Delta_{\alpha}^{\beta}G^{\circ}$) at 25°C in kJ/mole, enthalpies ($\Delta_{\alpha}^{\beta}H^{\circ}$) in kJ/mole and entropies ($\Delta_{\alpha}^{\beta}S^{\circ}$) in J/mole, deg. of alcohol transfer at infinite dilution from the water phase to the alkane- and interlamellar R—NH₃ phase. The standard thermodynamic data of solutions of alcohols in water ($\Delta^{\circ}G^{\circ}$, $\Delta^{\circ}H^{\circ}$), alkane ($\Delta^{\circ}G^{\circ}$, $\Delta^{\circ}H^{\circ}$) and R—NH₃⁺ clays ($\Delta^{\circ}G^{\circ}$) are also given. n_c indicates the number of carbon atoms in the alkane and alkylammonium chain. Data marked with an asterisk are taken from Aveyard and Mitchell (1969).

Alcohol	Water			Alkane					Interlamellar RNH ₃		
	$\Delta^{\circ}G^{\circ}$	$\Delta^{\circ}H^{\circ}$	n_c	$\Delta_{\alpha}^{\beta}G^{\circ}$	$\Delta_{\alpha}^{\beta}H^{\circ}$	$\Delta_{\alpha}^{\beta}S^{\circ}$	$\Delta^{\circ}G^{\circ}$	$\Delta^{\circ}H^{\circ}$	$\Delta_{\alpha}^{\beta}G^{\circ}$	$\Delta_{\alpha}^{\beta}H^{\circ}$	$\Delta^{\circ}G^{\circ}$
			6								
C ₄ H ₉ OH	9.00*	-8.99*		-1.03	32.85	113.70	7.97	23.9			
C ₆ H ₁₃ OH	16.35*	-5.77*		-7.71	25.33	110.90	8.64	19.6	-14.55		+1.80
C ₈ H ₁₇ OH	23.50*	-3.34*		-12.75	10.66	78.60	10.75	7.3			
			8								
C ₄ H ₉ OH				-1.26	35.28	122.60	7.74	26.3			
				-0.80*	31.40*	110*	8.20*	22.7*			
C ₆ H ₁₃ OH				-7.90	24.66	109.30	8.45	18.9	-15.54		+0.81
				-6.89*	28.10*	120*	9.40*				
C ₈ H ₁₇ OH				-13.18	12.41	85.90	10.30	9.1			
			10								
C ₆ H ₁₃ OH									-16.03		-0.32
			12								
C ₄ H ₉ OH				-0.80*	31.40*	110*		22.5*	-17.26		-8.26
C ₆ H ₁₃ OH				-7.39*	28.10*	121*			-18.00	23.98	-1.65
C ₈ H ₁₇ OH									-23.81	16.68	-0.31

thus more sensitive to the alcohol chain length than to the R—NH₃ chain length.

The distribution of alcohols between water and alkanes is usually expressed in terms of mole fraction ratios (Aveyard and Mitchell, 1969). The corresponding standard free energy of transfer is given in Table 2 together with the standard enthalpy and entropy. The chemical potentials of the solute in both the aqueous (α) and alkane phase (β) are defined on the molar fraction scale by

$$\mu_A^{\alpha} = \mu_A^{\circ,\alpha} + RT \ln \gamma_A^{\alpha} x_A^{\alpha} \quad (1)$$

and

$$\mu_A^{\beta} = \mu_A^{\circ,\beta} + RT \ln \gamma_A^{\beta} x_A^{\beta} \quad (2)$$

in which the standard state is the hypothetical unit mole fraction, while $\gamma_A \rightarrow 1$ as $x_A \rightarrow 0$. The standard free energy of transfer of a monomeric solute molecule from the aqueous phase to the organic phase is obtained by

$$\mu_A^{\circ,\beta} - \mu_A^{\circ,\alpha} = \Delta_{\alpha}^{\beta}G^{\circ} = -RT \ln P_x \quad (3)$$

P_x is the distribution ratio obtained at high dilution, where it is implicitly understood that only monomeric alcohol molecules are present. The free energy of transfer is mainly determined by the alcohol chain length (Table 2). An average increment in $\Delta_{\alpha}^{\beta}G^{\circ}$ of -2.9 kJ/mole per CH₂-group in the alkyl chain of the alcohol is observed which is comparable to literature data (Kinoshita et al., 1958; Shinoda et al., 1963; Somasundaran et al., 1964; Hanssens et al., 1968; Aveyard and Mitchell, 1969). The effect of the chain length of the alkane is small (0.1 kJ/mole, CH₂). The thermodynamic data relating to the distribution at high dilution are obtained

at only one concentration of the alcohol but are a mean of three independent determinations. (The error is smaller than 1%.) This procedure is justified since at low alcohol concentration (0.002 mole/liter) the distribution coefficients are constant and equal to their value at infinite dilution (Aveyard and Mitchell, 1969).

DISCUSSION

Distribution of alcohol between water and alkane

The free energy of transfer is a composite of the free energy of solution of alcohol in the aqueous ($\Delta^{\circ}G^{\circ}$) and alkane ($\Delta^{\circ}G^{\circ}$) phase according to:

$$\Delta_{\alpha}^{\beta}G^{\circ} = \Delta^{\circ}G^{\circ} - \Delta^{\circ}G^{\circ}$$

Using $\Delta^{\circ}G^{\circ}$ values calculated from the data of Aveyard and Mitchell (1969) and extrapolated to octanol $\Delta^{\circ}G^{\circ}$ values are found and shown in Table 2. A slight increase in the absolute value of the free energy of solution in

Table 3. Comparison of $\ln P_x$ and $\ln K_{sp}$ for the adsorption of butanol, hexanol, and octanol on alkylammonium montmorillonites of different chain length n_c . The d(001) spacings of the pure alkylammonium clays in water and the volume of the interlamellar water are also given.

	n_c	Volume alkyl-ammonium (Å ³)	$\ln P_x$	$\ln K_{sp}$	d(001) Å	Volume of interlayer water (10 ²³ Å ³)
Butanol	12	369.2	7.0	4.6	20.0	1.75
Hexanol	6	218	5.9	5.2	13.6	0.28
	8	268.4	6.3	3.8	18.6	1.78
	10	318.8	6.5	4.2	18.6	1.52
	12	369.2	7.3	4.8	20.0	1.75
Octanol	12	369.2	9.7	7.4	20.0	1.75

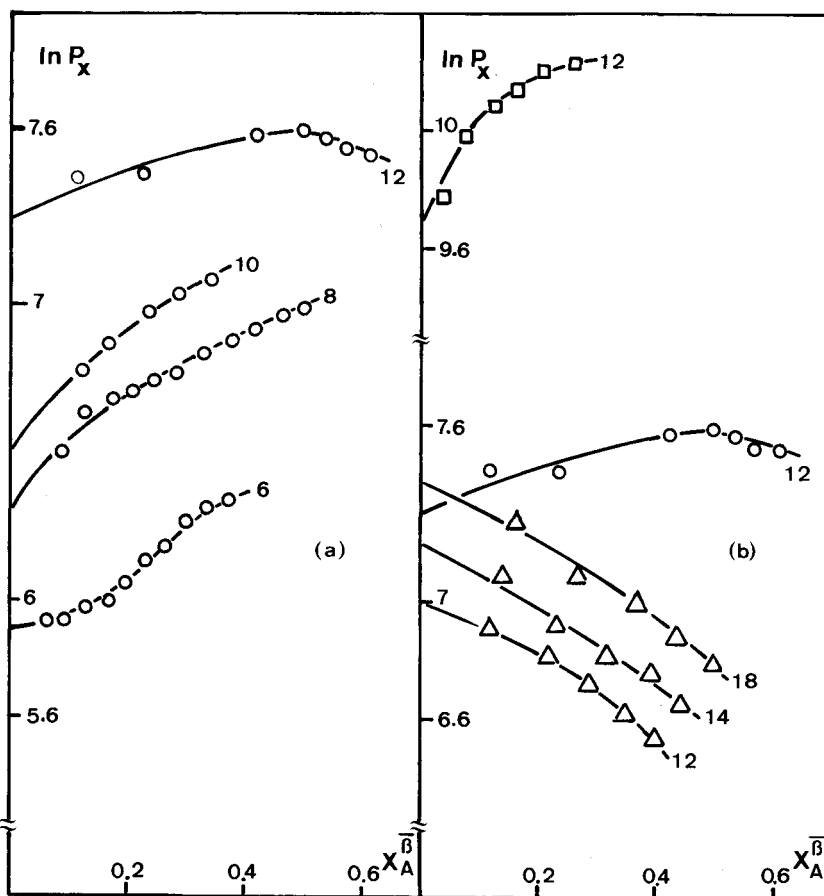


Fig. 3. $\ln P_x$ as a function of the mole fraction in the interlamellar phase for (a) hexanol, (b) butanol (Δ), hexanol (\circ), and octanol (\square) on different RNH_3^+ clays. The arabic figures represent the number of carbon atoms in the alkyl chain.

alkane is observed on increasing the alcohol chain length. The $\Delta^\beta G^\circ$ is independent of the alkane used. Comparing $\Delta^\alpha G^\circ$ and $\Delta^\beta G^\circ$ for the different alcohols it follows that the higher alcohol preferably solvates in the alkane phase. This phenomenon can be ascribed to the difference in energy involved in the creation of a hole in water or in an organic solvent to locate a CH_2 -group. To a first approximation the interaction between a CH_2 -group and an organic solvent (inert or active) equals the interaction between a CH_2 -group and water (Hanssens et al., 1968).

The transfer of alcohol from water into alkane is an endothermic process (Table 2) which is believed (Aveyard and Mitchell, 1969) to be mainly due to the dehydration of the hydroxyl group upon the transfer. A decrease in the enthalpy of transfer from about 33 kJ/mole for butanol to ≈ 12 kJ/mole for octanol is observed (Table 2). $\Delta_\alpha^\beta H$ for butanol and hexanol compare relatively well to the data of Aveyard and Mitchell (1969) especially in view of the uncertainty in the determination of $\Delta_\alpha^\beta H$ from the temperature dependency of the equilibrium. Our $\Delta_\alpha^\beta H$ value for octanol (≈ 12 kJ/mole) is however much lower than the 26 kJ/

mole extrapolated from the data of Aveyard and Mitchell (1969). From

$$\Delta_\alpha^\beta H^\circ = \Delta^\beta H^\circ - \Delta^\alpha H^\circ \quad (4)^*$$

in which $\Delta^\beta H^\circ$ and $\Delta^\alpha H^\circ$ stand for the heat of solution of alcohol in alkane and water respectively and using $\Delta^\alpha H^\circ$ data of Aveyard and Mitchell (1968), $\Delta^\beta H^\circ$ is calculated and shown in Table 2. A decrease is observed from about 25 (butanol) to ≈ 19 (hexanol) and ≈ 8 kJ/mole (octanol) on both alkanes studied. The latter value is found by using a $\Delta^\alpha H^\circ$ value of 3.34 kJ/mole obtained by extrapolating the data of Aveyard and Mitchell (1968) to octanol. They find a constant $\Delta^\beta H^\circ$ of 22.4 kJ/mole, independent of the alcohol-alkane combination a result which is intermediate between our butanol and hexanol data.

Alcohol distribution between water and the interlamellar alkylammonium phase

All the adsorption data with the exception of butanol follow an S-type isotherm, which is characteristic in the

* In the U.S. (4) would be: $\Delta_\alpha^\beta H_0 = \Delta^\beta H_0 - \Delta^\alpha H_0$.

adsorption of solutes which (a) are monofunctional, (b) have a strong tendency to associate and (c) strongly compete with the solvent for substrate sites. However, diagnosis of adsorption mechanisms based only on the shape of the isotherm must be treated with caution. The final result of the adsorption of alcohols on clay minerals results from the superposition of several phenomena. The adsorption can occur: (1) in the interlamellar space; (2) on the basal surface in mono- or multimolecular layers; (3) on the edges; (4) in capillaries created by stacking of clay particles.

The following discussion will be restricted to the phenomenon at high dilution of the alcohol, while it will be supposed that mainly adsorption in the interlamellar space occurs. The amount of alcohol present in the interlamellar zone is approximated by assuming that alcohol adsorption occurs proportionally to the available surface. The interlamellar surface, the edges, and basal surfaces correspond, respectively, to 89.3, 6.46, and 7.24% of the total surface. The interlamellar alkylammonium content is taken to be $0.85 \cdot 10^{-3}$ mole/g as previously mentioned.

To compare the distribution data of alcohols between an organic phase and water with the adsorption of alcohols on RNH_3 -clays the interlamellar phase is treated as an organic solvent. Interlamellar water will be neglected or assumed only to perturb the quantitative treatment. Accordingly distribution constants $P_x = x_A^{\bar{\beta}}/x_A^{\alpha}$ are calculated and plotted as a function of $x_A^{\bar{\beta}}$ in Figure 3a and b. Calculations are made on interpolated values of smooth drawn adsorption isotherms. The chemical potentials of the species are defined analogous to equations (1) and (2) in which now $\bar{\beta}$ stands for the adsorbed phase.

$$\mu_A^{\alpha} = \mu_A^{\ominus, \alpha} + RT \ln x_A^{\alpha}$$

$$\mu_A^{\bar{\beta}} = \mu_A^{\ominus, \bar{\beta}} + RT \ln x_A^{\bar{\beta}}$$

with

$$x_A^{\bar{\beta}} = \frac{\overline{\text{ROH}}}{\overline{\text{ROH}} + \overline{\text{RNH}_3^+}}$$

and

$$x_A^{\alpha} = \frac{\text{ROH}}{\text{ROH} + \text{H}_2\text{O}}$$

in which $\overline{\text{ROH}}$ and $\overline{\text{RNH}_3^+}$ are respectively the mole numbers of alcohol and alkylammonium in the clay phase (expressed per gram backbone clay); ROH and H_2O stand for the mole numbers of alcohol and water in the equilibrium solution. Since only the data extrapolated to infinite dilution are used, ideal behavior is assumed as is reflected in the neglect of the activity coefficients. From the value of $\ln P_x$ at infinite dilution the

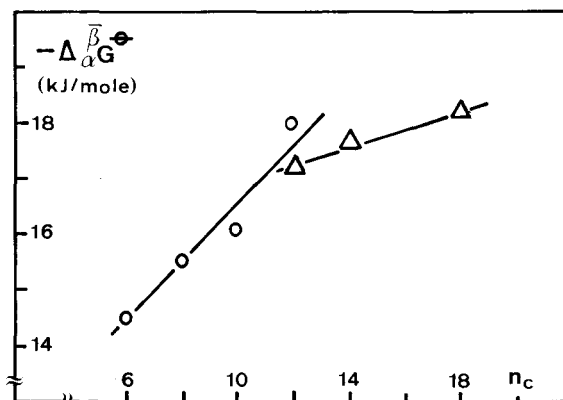


Fig. 4. $\Delta_{\alpha}^{\bar{\beta}}G^{\ominus}$ for butanol (Δ) and hexanol (\circ) on RNH_3 -montmorillonites as a function of the cation chain length.

free energy of transfer of a monomeric alcohol from the water to the R-NH_3^+ phase is obtained and plotted in Figure 4 as a function of the RNH_3^+ chain length. A linear relation is obtained. The mean increment per CH_2 -group of the RNH_3^+ is -0.68 kJ/mole for the adsorption of hexanol in the RNH_3^+ series C_6 to C_{12} , and -0.17 kJ/mole in the case of butanol between C_{12} and C_{18} RNH_3^+ chains. $\ln P_x$ increases with the hexanol and octanol occupancies, while for butanol the reverse behavior is observed.

If the distribution are calculated by taking all the adsorbed alcohol and alkylammonium into account, $\ln P_x$ values are obtained which are 3 to 5% lower than the present data.

Comparing the $\Delta_{\alpha}^{\bar{\beta}}G^{\ominus}$ of butanol, hexanol and octanol on dodecylammonium clay, in Table 2, an increase of -0.37 kJ/mole CH_2 is observed between butanol and hexanol, while -2.9 kJ/mole is found between hexanol and octanol. This result is comparable with the one of Aveyard and Mitchell (1969) in the range butanol to heptanol (-3.3 kJ/mole) where it is found to be independent of the chain length of the alkane ($n_c = 8, 10, 16$). The differences in $\Delta_{\alpha}^{\bar{\beta}}G^{\ominus}$ observed on increasing the alcohol chain length may thus be explained analogously to the distributions of several alcohols between water and alkane as being primarily due to interactions of alcohols in the aqueous phase.

The absolute values of $\Delta_{\alpha}^{\bar{\beta}}G^{\ominus}$ exceed the ones of $\Delta_{\alpha}^{\beta}G^{\ominus}$ by a factor of at least 2 for all the combinations of alcohol and alkylammonium studied (see Table 2). By comparing the $\Delta_{\alpha}^{\bar{\beta}}G^{\ominus}$ of hexanol e.g., with $\Delta_{\alpha}^{\beta}G^{\ominus}$ of hexanol in different solvents of increasing affinity (cyclohexane -6.87 , Hanssens et al., 1968, hexane -7.7 , this work, CCl_4 -9.48 kJ/mole, Hanssens et al., 1968), it is deduced that the adsorbed alkylammonium acts as an even stronger solvent than CCl_4 . In the interlamellar phase specific bonds are formed, most probably between the OH groups of the alcohol and the $-\text{NH}_3^+$

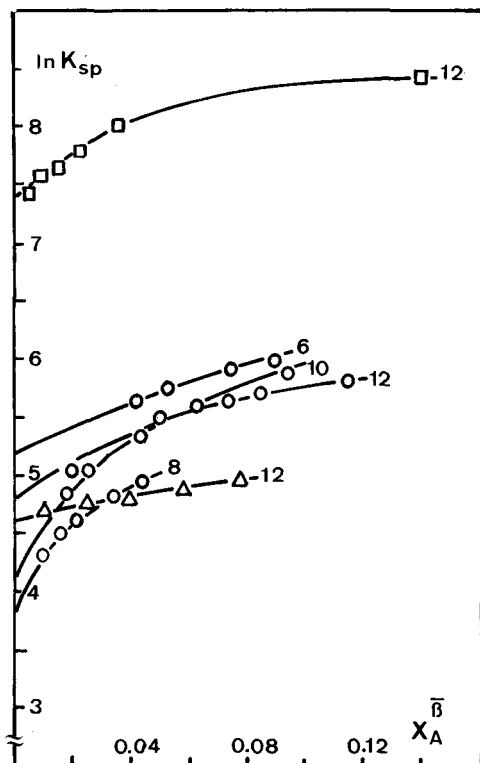


Fig. 5. $\ln K_{sp}$, as a function of the mole fraction in the interlamellar phase for butanol (Δ), hexanol (\circ), and octanol (\square) on RNH_3^+ -clays of different chain length as indicated by the arabic figures.

groups of the alkylammonium ions. Since the adsorption of hexanol on Na-clay is almost negligible, the interaction between alcohol and the clay framework oxygens is considered as less important (Laby and Theng, 1964). The interaction of alcohols with the alkyl chain of the RNH_3^+ is considered as nonspecific and comparable to their interaction with alkanes.

Since $\Delta_{\alpha}^{\beta}G^{\circ} = \Delta^{\beta}G^{\circ} - \Delta^{\alpha}G^{\circ}$ using $\Delta^{\alpha}G^{\circ}$ values given in Table 2, $\Delta^{\beta}G^{\circ}$ is calculated. The absolute values of $\Delta^{\beta}G^{\circ}$ compared to $\Delta^{\alpha}G^{\circ}$ indicate the preferential solvation of the interlamellar (alkylammonium) phase by the alcohols. Dodecylammonium montmorillonite dissolves better in butanol than in hexanol and octanol as seen by the $\Delta^{\beta}G^{\circ}$ data which respectively vary from -8.26 to -1.65 and -0.31 kJ/mole. This result is qualitatively comparable to the decreasing dissolving power of the alcohols on increasing their chain length (see $\Delta^{\beta}G^{\circ}$ in Table 2).

In the case of hexanol the variation of $\Delta_{\alpha}^{\beta}G^{\circ}$ with the number of carbon atoms in the alkyl chain definitely exceeds the change of $\Delta_{\alpha}^{\alpha}G^{\circ}$ as exemplified in Figure 4. The corresponding $\Delta^{\beta}G^{\circ}$ values (Table 2) for hexanol range from $+1.80$ ($n_c = 6$) to -1.65 ($n_c = 12$) kJ/mole. The variation of $\Delta^{\beta}G^{\circ}$ for hexanol with the RNH_3^+ chain length is 0.58 kJ/mole and per CH_2 while the

variation of $\Delta^{\beta}G^{\circ}$ is to 0.1 kJ/mole nearly independent of the alkane chain length (see Table 2).

Summarizing, one can say that for hexanol the change of $\Delta_{\alpha}^{\beta}G^{\circ}$ and $\Delta^{\beta}G^{\circ}$ with the number of carbon atoms in the alkylammonium chain exceeds the corresponding changes in $\Delta_{\alpha}^{\alpha}G^{\circ}$ and $\Delta^{\alpha}G^{\circ}$. On the other hand $\Delta_{\alpha}^{\alpha}G^{\circ}$ and $\Delta^{\alpha}G^{\circ}$ are constant for an alcohol in different alkanes. The differences observed on the surface on adding a CH_2 -group to the alkylammonium chain originates from the fact that the alkylammonium is adsorbed onto a surface. Other factors than those acting in solution could be invoked, such as the adsorbed water, which we neglected and/or the spatial restrictions in the interlamellar phase.

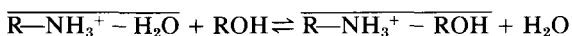
As the free space, which is correlated with the $d(001)$ spacing of pure water RNH_3 -clays rises towards dodecylammonium the increase of $\Delta_{\alpha}^{\beta}G^{\circ}$ in the case of hexanol seems to be correlated with the smaller interlamellar restrictions imposed. However as the volume of the interlamellar water (see Table 3) rises from hexylammonium clay to dodecylammonium clay with the exception of octylammonium, hexanol will encounter more difficulties in solubilizing in the interlamellar solution since $\Delta^{\alpha}G^{\circ}$ is more endergonic than $\Delta^{\beta}G^{\circ}$. Nevertheless, the reverse behavior is observed.

$\Delta^{\beta}G^{\circ}$ is constant, or in any case increases only slightly (≈ 0.1 kJ/mole), between octane and dodecane (Aveyard and Mitchell, 1969). Assuming that the interlamellar water is present as hydration water of the alkylammonium ion and as free water, the unfavorable barrier created by the presence of the free water should be surmounted to explain the observed data. The lower solubility of the longer alkylammonium ion can explain the observed effect either by the weaker water-alkane interaction (or eventually a smaller water- NH_3^+ interaction).

The smaller increment per CH_2 group observed in the adsorption of butanol in the range of RNH_3 chain lengths of C_{12} to C_{18} is probably due to the smaller solubility dependency on the RNH_3^+ chain length between C_{12} to C_{18} compared to the short chain RNH_3^+ -ions.

The foregoing points to the conclusion, that apart from possible influences of the interlamellar water the R-NH_3^+ acts analogously to an alkane phase but is a better solvent for the alcohols. It is believed that the total effect is a composite of specific interactions of the alcohol with the $-\text{NH}_3^+$ -group and a nonspecific interaction on the alkyl chain analogous to the distribution of alcohols between water and alkane.

The relative preference of an alcohol versus a water molecule for the solvation of an alkylammonium ion in the interlamellar space can be obtained by considering the following equilibrium:



Defining the chemical potentials of the alcohol as

$$\mu_A^{\bar{\beta}} = \mu_A^{\theta, \bar{\beta}} + RT \ln x_A^{*\bar{\beta}} \gamma_A$$

and

$$\mu_A^{\alpha} = \mu_A^{\theta, \alpha} + RT \ln x_A^{*\alpha} \gamma_A \quad (7)$$

together with two analogous equations for water: $\mu_w^{\bar{\beta}}$ and μ_w^{α} in which

$$x_A^{*\bar{\beta}} = \frac{\overline{\text{ROH}}}{\overline{\text{ROH}} + \overline{\text{H}_2\text{O}}}$$

$\overline{\text{ROH}}$, $\overline{\text{H}_2\text{O}}$ and ROH , H_2O are the mole numbers of alcohol and water in the clay phase and the aqueous phase, respectively. The amount of interlamellar water is calculated from the $d(001)$ spacings in an analogous way as for the pure R-NH_3^+ -clays, taking due account of the adsorbed alcohol and alkylammonium ion. Only the data at low alcohol concentrations where the $d(001)$ spacing remains the same as the one of the pure water-alkylammonium clay complex are considered. The standard state for μ_A^{α} and $\mu_A^{\bar{\beta}}$ is the hypothetical ideal unit mole fraction, while γ tends to unity as x_A^* tends to zero. In the case of μ_w^{α} and $\mu_w^{\bar{\beta}}$ the pure solvent is taken as standard while its activity coefficient approaches unity as $x_w^* \rightarrow 1$. At infinite dilution the activity coefficients are unity and $\Delta_w^{\text{AG}^{\theta}}$ refers to the replacement of water by alcohol on the R-NH_3^+ clay through.

$$K_{\text{sp.}} = \frac{x_A^{*\bar{\beta}} \cdot x_w^{*\alpha}}{x_w^{*\bar{\beta}} \cdot x_A^{*\alpha}} \quad (8)$$

Plots of $\ln K_{\text{sp.}}$ as a function of the interlamellar mole fraction of alcohol ($x_A^{\bar{\beta}}$) are then obtained and shown in Figure 5. The values of $\ln K_{\text{sp.}}$ extrapolated to infinite dilution are compared with $\ln P_x$ in Table 3. The alcohol water distribution is in favor of the alcohol. On dodecylammonium clay $\ln K_{\text{sp.}}$ increases from 4.6 (butanol) to 4.8 (hexanol) and 7.4 (octanol). The same trend was also observed for $\ln P_x$. Hexanol adsorption on different RNH_3^+ clays is correlated to the chain length of the RNH_3^+ -ion, as was the case for $\ln P_x$, if hexylammonium clay is not considered.

The replacement of water by hexanol on R-NH_3^+ clays varies from -9.4 (octylammonium) to -11.8 (dodecylammonium) and -12.8 kJ/mole (hexylammonium) which are reasonable values for the difference in solvation of an amine by water and alcohol. Since the $K_{\text{sp.}}$ is calculated by taking all the interlamellar water into account, it also suffers from the presence of the variable amount of free water (not bound to the R-NH_3^+) in the interlamellar solution. In this respect the higher value observed on hexylammonium clay correlates with the low interlamellar volume of water. The comparison of $\ln K_{\text{sp.}}$ with $\ln P_x$ in any case reveals that most of the effect of transfer is due to the alcohol-amine interaction.

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Резюме— Изучалась адсорбция бутанола, гексанола и октанола алкиламмониевыми глинами с различной длиной цепи. Адсорбция при бесконечном растворении сравнивается с распределением алкоголя между алкиленом и водой в объемном растворе. Межпластинчатая фаза монтмориллонита действует как растворитель, даже более химически активный, чем четыреххлористый углерод. Водородные связи, возможно, появляются между алкогольной группой OH и группой NH_3^+ . Замена воды алкоголем в межпластинчатом алкиламмониевом ионе является главным фактором в процессе переноса.

Kurzreferat— Die Adsorption von Butanol, Hexanol und Oktanol auf Alkylammoniumtonerden mit verschiedenen Kettenlängen wurde untersucht. Die Adsorption bei endloser Verdünnung ist mit der Verteilung von Alkohol zwischen Alkan und Wasser in Massenslösungen vergleichbar. Die interlamellare Phase des Montmorilloniten benimmt sich wie ein Lösungsmittel, welches noch reaktiver als Tetrachlorkohlenstoff ist. Wasserstoffbrücken kommen wahrscheinlich zwischen den OH-Gruppen des Alkohols und der NH_3^+ Gruppen vor. Der Austausch von Wasser durch Alkohol auf den interlamellaren Alkylammoniumionen ist der Hauptfaktor in diesem Übergangsprozess.

Résumé— L'adsorption de butanol, d'hexanol et d'octanol sur des argiles alkylammonium de longueur de chaînes différente est étudiée. L'adsorption à dilution infinie peut être comparée à la distribution d'alcool entre l'alkane et l'eau dans la solution totale. La phase interlamellaire de la montmorillonite se comporte comme un solvant plus réactif encore que le tétrachlorure de carbone. Les liaisons d'hydrogène surviennent sans doute entre le groupe OH de l'alcool et le groupe NH_3^+ . L'échange d'eau par l'alcool sur l'ion interlamellaire alkylammonium³ est le facteur majeur dans le processus de transfert.