

THE EXCHANGE OF ALKYLAMMONIUM IONS ON Na-LAPONITE

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Abstract—The exchange of various alkylammonium cations from aqueous solution by sodium laponite has been studied. The affinity of the clay for these organic cations was linearly related to the molecular weight, molecular size or chain length of the alkylammonium ions. The affinity for the clay increases regularly with increasing chain length of the primary amines. A comparison of primary, secondary, and tertiary amines, containing the same alkyl groups shows that the affinity increases in the order $R_1NH_3^+ < R_2NH_2^+ < R_3NH^+$. These affinity sequences were attributed to important van der Waals contributions and changes in ion hydration states. The thermodynamic excess function, ΔG_m^E , was calculated and indicated that with respect to the pure homoionic forms the heterogeneous Na^+ -alkylammonium surface phases were more stable than they would be if the mixing were ideal.

Key Words—Alkylammonium, Exchange, Equilibrium, Isotherms, Laponite.

INTRODUCTION

A number of field and laboratory experiments have shown that exchanged alkylammonium cations could considerably modify the hydration and swelling properties of soils and clays (Clare, 1947; Jordan, 1949; Emmerston, 1960). The exchange process of various alkylammonium ions on Na-montmorillonite has been studied intensively by a number of workers (Theng et al., 1967; Vansant and Uytterhoeven, 1972; Cowan and White, 1958). Typical for all these observations was a) a regular increase in the change in free energy or adsorption strength of the adsorbed alkylammonium ions with molecular weight or number of carbon atoms in the aliphatic chain and b) the presence of a single layer of alkylammonium ions adsorbed between the clay sheets. The affinity enhancement was interpreted in terms of an increasing contribution of van der Waals forces and variations in the hydration state of the clay.

In order to clarify further the influence of the type of clay mineral on the exchange behavior, the exchange reactions of mono-, di- and trialkylammonium ions on synthetic Na-Laponite were studied.

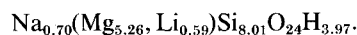
EXPERIMENTAL

Material

The synthetic clay used in this work was Na-Laponite CP, supplied as powder by Laporte Ind. Ltd. (England), with a C.E.C. of 0.89 meq/g. To ensure complete saturation with sodium, the Na-Laponite was brought into dialysis bags and washed several times with 1 N NaCl solutions, before dialyzing against distilled water until free of chloride. After drying at 40°C and grinding, the powder was stored in a desiccator over saturated NH_4Cl .

Exchange method

Standard chemical methods were used to obtain the composition of the synthetic Na-Laponite CP. The structure formula was



The rheological and optical properties of this synthetic swelling clay have been studied in detail by Newmann and Sansom (1970 a,b).

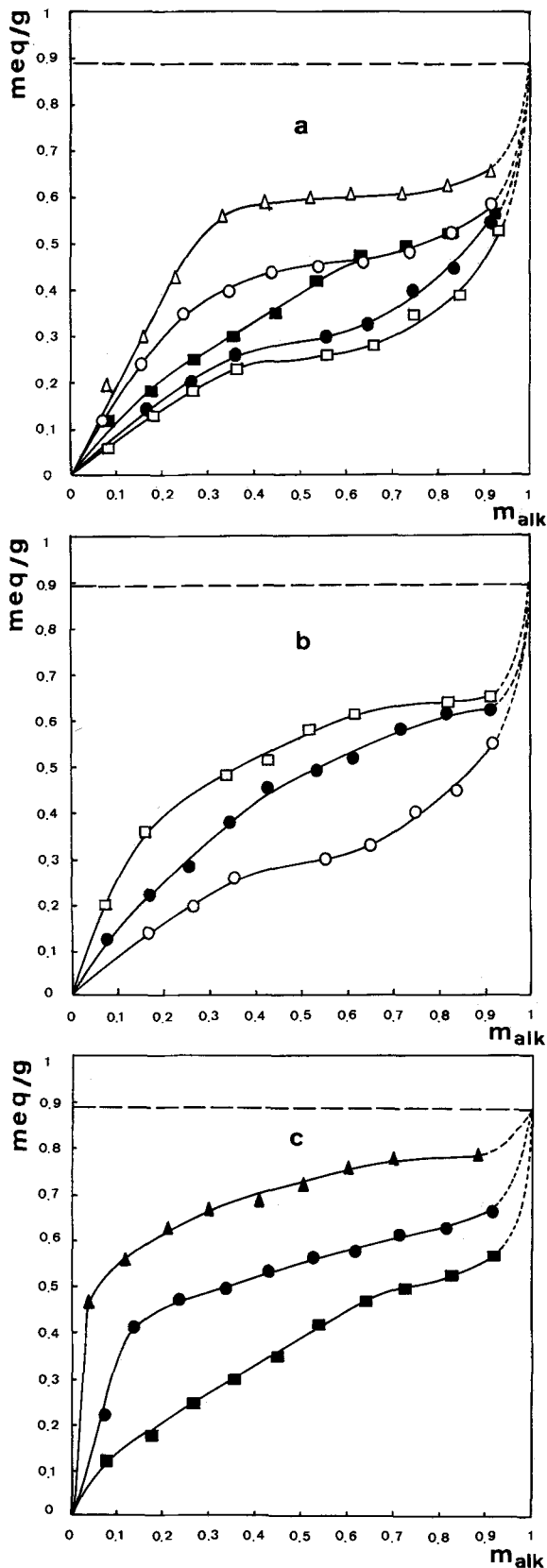
The exchange between sodium and the different alkylammonium cations on the Na-Laponite was studied using the dialysis technique in order to establish exchange isotherms. Ten milliliters of a 2% Na-Laponite suspension of an exactly known dry weight was pipetted into dry dialysis bags. These were closed, leaving air enclosed to facilitate stirring. The bags were transferred to polyethylene bottles containing 40 ml of alkylammonium-sodium solutions of known composition and at a 0.03 N total normality. After shaking 72 hr at room temperature (25°C) no further increase in the amount adsorbed alkylammonium ions was observed.

The alkylammonium ions in solution were estimated by a steam distillation of small portions with excess 40% NaOH. The ammonia or amine liberated was collected in a 2% boric acid solution and titrated with a standard H_2SO_4 solution using a mixed bromocresol green-methyl red indicator. The amount adsorbed was found by the difference in concentration between the solution initially added to and that after equilibration.

RESULTS

Exchange isotherms

The isotherms for the ion pairs $Na^+NH_4^+$, Na^+Me_1 , Na^+Et_1 , Na^+Pr_1 , Na^+Bu_1 , Na^+Me_2 , Na^+Et_2 , Na^+Me_3 , and Na^+Et_3 are shown in Figure 1. The symbols Me, Et, Pr, and Bu refer to methyl-, ethyl-, n-propyl-, and n-butylammonium, respectively. The subscripts 1, 2, and 3 denote the mono-, di- and tri-derivatives. On the abscissae in Figure 1 is set out the equivalent fraction (m) of ammonium or alkylammonium ions in solution and on the ordinates the corresponding amount (meq g^{-1}) on the Laponite clay.



Estimation of the equilibrium constant

The exchange reaction between the alkylammonium ions (Alk⁺) in solution and the sodium ions on the clay may be represented by:



The overall equilibrium constant K_a can be estimated using the simplified form of the equation developed by Gaines and Thomas (1953):

$$\ln K_a = \int_0^1 \ln K' \, dN_{\text{Alk}} \quad (2)$$

where N_{Alk} is the equivalent fraction of the alkylammonium ions on the clay and K' the "corrected" rational selectivity coefficient defined as:

$$K' = K_{\text{Na}}^{\text{Alk}} \cdot \gamma_{\text{Na}} / \gamma_{\text{Alk}} \quad (3)$$

with

$$K_{\text{Na}}^{\text{Alk}} = \frac{N_{\text{Alk}} \cdot m_{\text{Na}}}{N_{\text{Na}} \cdot m_{\text{Alk}}}$$

(N and m are the equivalent fractions of the ions on the clay and in the liquid phase, respectively).

The ratio of the activity coefficients of Na^+ and Alk^+ in solution, $\gamma_{\text{Na}} / \gamma_{\text{Alk}}$ at a total concentration of 0.03 N, does not deviate significantly from unity (Robinson and Stokes, 1959). Therefore, $K_{\text{Na}}^{\text{Alk}}$ instead of K' has been used in Equation 2.

As desorption experiments were not carried out, the extent of reversibility was not known. By applying the general theory of Gaines and Thomas (1953) (Eq. 2) to the adsorption and desorption data, Neumann and Sansom, (1970a,b) have suggested that the ion-exchange on Laponite CP of large cations tends to be irreversible. It is observed that a hysteresis effect is present in the present Na-alkylammonium Laponite systems or, the same equilibrium conditions could not be obtained by approach from either direction. However, as there was equilibrium at each point of the isotherm, microscopic reversibility was probably obtained. Because of the limitations regarding reversibility the ordinate of Figure 3 is given as $-RT \ln K_a$ (or ΔG_a), a nonstandard free energy of exchange. Comparison with earlier data (Theng et al., 1967; Vansant and Uytterhoeven, 1972; Cowan and White, 1958) should therefore be made with appropriate caution.



Fig. 1. Exchange isotherms of different alkylammonium ions on Na-Laponite at 25°C. Abscissae: the equivalent fraction m of the alkylammonium ions in solution; ordinate: the amount exchanged in meq g^{-1} on the Na-Laponite (dotted lines: maximum exchange capacity). (a) \square : NH_4^+ ; \bullet : Me_1 ; \blacksquare : Et_1 ; \circ : Pr_1 ; \triangle : Bu_1 . (b) \circ : Me_1 ; \bullet : Me_2 ; \square : Me_3 . (c) \blacksquare : Et_1 ; \bullet : Et_2 ; \blacktriangle : Et_3 .

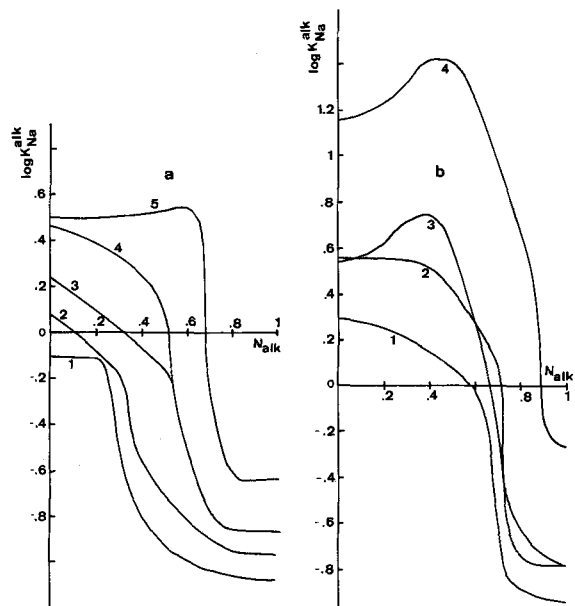


Fig. 2. The variation of $\log K_{Na}^{Alk}$ vs. N_{Alk} for the different alkylammonium exchange reactions. (a) 1: NH_4^+ ; 2: Me_1 ; 3: Et_1 ; 4: Pr_1 ; 5: Bu_1 . (b) 1: Me_2 ; 2: Me_3 ; 3: Et_2 ; 4: Et_3 .

The variations of $\ln K_{Na}^{Alk}$ vs. N_{Alk} for all the alkylammonium exchange reactions are shown in Figure 2. The corresponding values of ΔG_a (summarized in Table 1) versus molecular weight, molecular size or chain length of the ingoing alkylammonium ions are plotted in Figure 3.

The thermodynamic excess functions

The excess functions express the deviation from ideality of the heteroionic exchanger with respect to the pure homoionic forms. The excess free energy change of mixing (ΔG_m^E) is defined as:

$$\Delta G_m^E = \Delta G_m - \Delta G_m^{id} \tag{4}$$

The free energy change of mixing (ΔG_m) is the difference between the observed value of the thermodynamic function and the sum of the free energies of the pure constituents or

$$\Delta G_m = RT[N_{Alk} \ln N_{Alk} \cdot f_{Alk} + (1 - N_{Alk}) \ln(1 - N_{Alk}) \cdot f_{Na}] \tag{5}$$

where $f_{Alk/Na}$ is the activity coefficient of the adsorbed cations. ΔG_m^{id} is the free energy change of mixing in a solid solution or at the surface phase which obeys Raoult's law or

$$\Delta G_m^{id} = RT[N_{Alk} \ln N_{Alk} + (1 - N_{Alk}) \ln(1 - N_{Alk})] \tag{6}$$

The excess free energy change of mixing at 25°C for

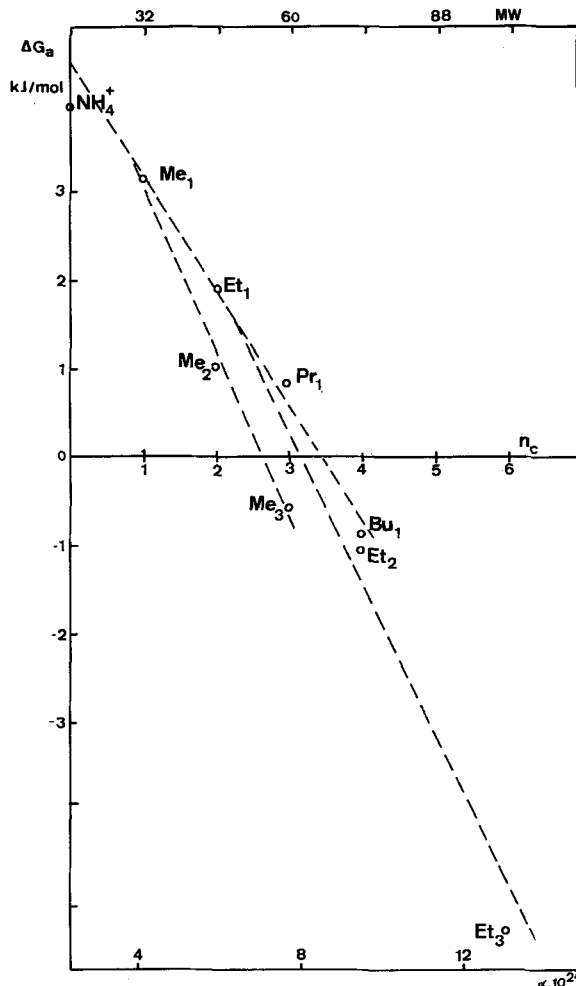


Fig. 3. Variations in ΔG_a ($kJ\ mole^{-1}$) with molecular weight, polarisability and number of carbon atoms in the aliphatic chain of the different alkylammonium ions.

the different alkylammonium ions as a function of the extent of exchange (N_{Alk}) is shown in Figure 4.

DISCUSSION

Since Na-Laponite CP shows considerable interlamellar swelling in an aqueous medium, steric and space factors do not influence the extent of exchange. As shown in Figure 1, all of the alkylammonium ions could therefore effect a complete replacement of the sodium ions initially present. X-ray analysis shows that the interlamellar space, when alkylammonium ions were adsorbed, was 1–1.5 Å and indicate a single layer of organic ions in the interlamellar space. Furthermore, the alkylammonium ions are adsorbed with their shorter axis perpendicular to the clay surface.

The observed isotherms, together with the ΔG_a values, reveal a regular increase in the affinity of the alkylammonium ions for Laponite with increasing molecular weight, molecular size or chain length of the

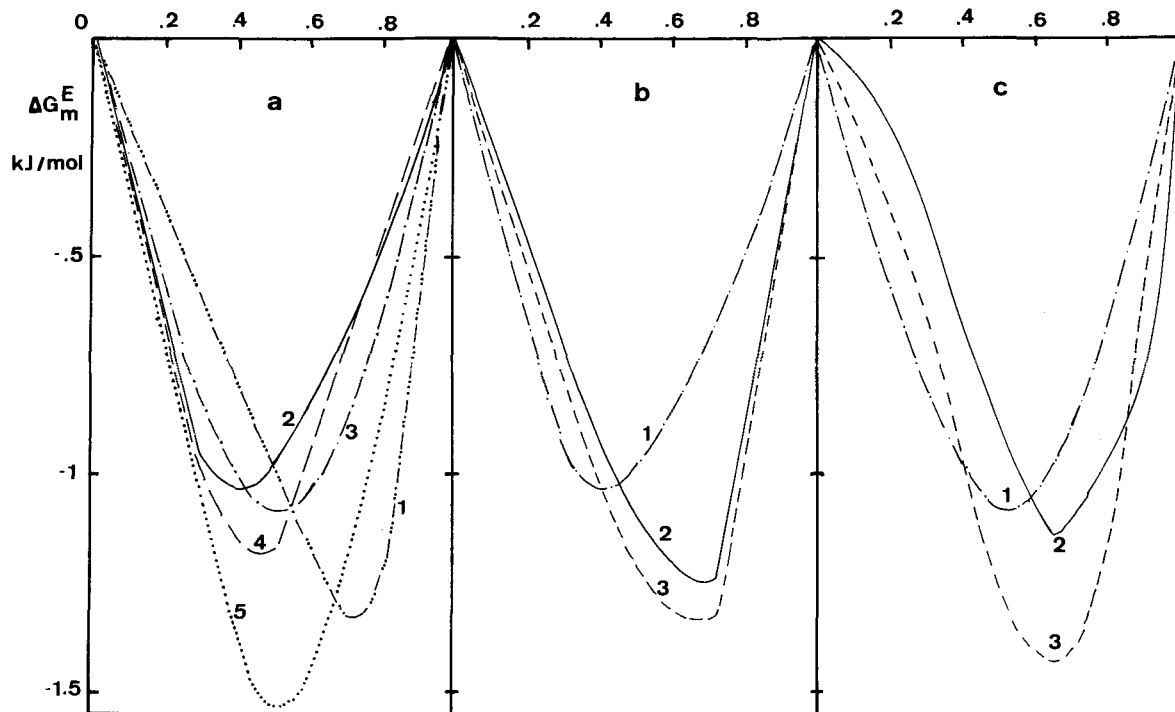


Fig. 4. The excess free energy change of mixing, ΔG_m^E , against the equivalent fraction N_{Aik} of alkylammonium ions on the Laponite at 25°C. (a) 1: NH_4^+ ; 2: Me_1 ; 3: Et_1 ; 4: Pr_1 ; 5: Bu_1 . (b) 1: Me_1 ; 2: Me_2 ; 3: Me_3 . (c) 1: Et_1 ; 2: Et_2 ; 3: Et_3 .

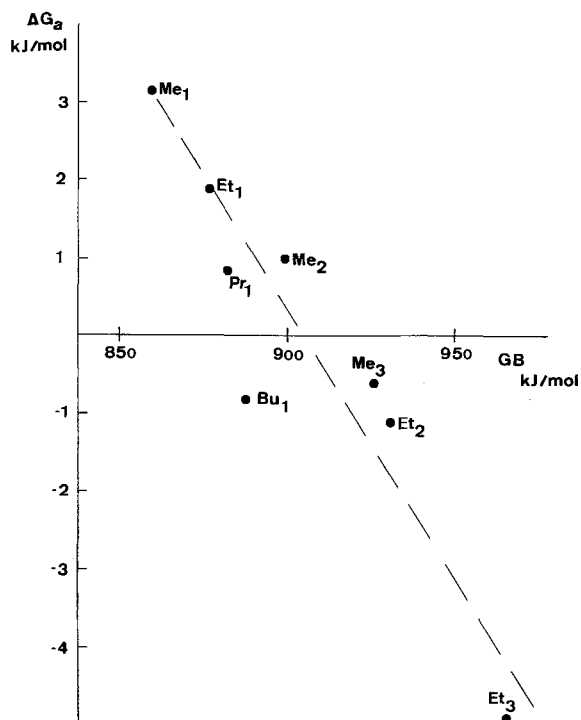


Fig. 5. Correlation between the observed ΔG_a values of the exchange of sodium for alkylammonium ions in Laponite and the amine gas phase basicities.

cations. This relationship is illustrated in Figure 3. For the primary amine cations the affinity towards the Laponite clay increases regularly with increasing chain length. A comparison of primary, secondary, and tertiary amines containing the same alkyl groups shows that the affinity of the alkylammonium ions for the clay decreases in the order $R_3\text{NH}^+ > R_2\text{NH}_2^+ > R_1\text{NH}_3^+$. The average increment of ΔG_a per CH_2 for the straight-chain monoalkylammonium ions was $1.35 \text{ kJ mole}^{-1}$. The increments per CH_3 and C_2H_5 going from monomethyl- to trimethylammonium and from monoethyl- to triethylammonium, respectively, were $1.86 \text{ kJ mole}^{-1}$ and $3.69 \text{ kJ mole}^{-1}$.

This is of general applicability to the adsorption of organic compounds by layer silicates (Theng et al., 1967; Vansant and Uytterhoeven, 1972; Cowan and White, 1958; Maes et al., 1977), and has been attributed to the increased contribution of van der Waals forces to the adsorption energy. This would be expected for a flat orientation, as van der Waals forces are additive and hence increase as the size of the adsorbed cation becomes larger.

A comparison in exchange behavior of the monoalkylammonium ions for the montmorillonite and Laponite clay minerals reveal that a) the affinity of the organic cations for the Na-montmorillonite is larger compared to the Na-Laponite; b) the increment per CH_2 in ΔG_a is larger in the Laponite system. These observations

Table 1. The nonstandard free energy of exchange, ΔG_a for the Na^+ -alkylammonium Laponite systems at 25°C.

Ion	ΔG_a (kJ mole^{-1})
NH_4^+	3.97
Me_1	3.13
Me_2	1.01
Me_3	-0.58
Et_1	1.88
Et_2	-1.04
Et_3	-5.39
Pr_1	0.83
Bu_1	-0.87

may be explained in terms of differences in charge density and in magnitude of the van der Waals contributions. Indeed, Maes and Cremers (1977) investigated the effect of charge density on the ion exchange equilibria and concluded that the free energy of exchange decreases linearly with the logarithm of the charge density. Therefore, the significantly higher affinity of the alkylammonium ions for the montmorillonite can be attributed to the higher surface charge density, compared to the Laponite clay. Moreover, recently, Maes et al. (1977) and Maes and Cremers (1977) discussed the thermodynamic stability of alkylammonium ions in the clay interlayer space in terms of hydration changes and van der Waals forces. The stability sequence of the alkylammonium ions in aqueous solutions exhibits the well-known "amine anomaly" i.e., the screening of the solvent molecules for the inductive effects of the carbon chain. The correlation between the change in free energy for the Na-alkylammonium Laponite systems versus the amine gas phase basicities, relating to the gas phase reaction (Aue et al., 1972) (Figure 5), reveals that the stability difference between methyl- and butylammonium is about 4 kJ mole^{-1} in the Laponite clay (1 kJ for the montmorillonite) and 18 kJ mole^{-1} in the gas phase (it is zero in the bulk solution). This difference illustrates that the extent of ion hydration is lowered upon adsorption in the Laponite clay interlayer and that the hydration change is more pronounced in

the Laponite compared to the montmorillonite clay. Therefore, the solvent screening effect is less important in the Laponite clay, so that a higher contribution of van der Waals forces, caused by the interaction of the aliphatic chain of the alkylammonium ions with the clay surface, can be expected.

Considering the excess free energy change of mixing (ΔG_m^E) for the different organic ions as a function of the extent of exchange (Figure 4) indicates negative values for all the Na-alkylammonium Laponite systems. This means that, with respect to the pure homoionic forms, the heterogeneous surface phases (Na^+ -alkylammonium ions) are more stable than they would be if the mixing were ideal. The deviation from the ideal occurs in the sense of a more stable mixture. This stabilization effect increases in the order $\text{Me}_1 < \text{Et}_1 < \text{Pr}_1 < \text{Bu}_1$ and $\text{R}_1\text{NH}_3^+ < \text{R}_2\text{NH}_2^+ < \text{R}_3\text{NH}^+$. Under the experimental conditions described here, the opposite behavior was observed for the Na^+ -monoalkylammonium montmorillonite systems (Vansant and Uytterhoeven, 1972). However, this opposite sequence in ΔG_m^E can be the result of the lower ion hydration state and the more pronounced van der Waals contributions in the Laponite compared to the montmorillonite systems. Indeed, both effects intensify the stability of the heterogeneous Na-alkylammonium mixtures with respect to the homoionic forms.

In conclusion, the exchange behavior of the alkylammonium-Laponite systems demonstrates that the affinity of the Laponite clay for the alkylammonium ions is related to the molecular weight. Furthermore, the affinity is the greatest for the tertiary amine and the least for the primary. These affinity sequences can be attributed to important van der Waals contributions and changes in the hydration state. Comparison of the exchange behavior between the Laponite and montmorillonite clay minerals shows that the affinity of the alkylammonium ions towards the montmorillonite is significantly higher compared to the Laponite clay. Moreover, the thermodynamic excess function, ΔG_m^E , indicates that with respect to the pure homoionic forms the heterogeneous Na-alkylammonium surface phases are more stable than they would be if the mixing was ideal.

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Резюме- Изучался обмен различными катионами между водным раствором алкил-аммония и натриевым лапонитом. Сродство глины к этим органическим катионам линейно связано с молекулярным весом, молекулярным размером или длиной цепи ионов алкиламмония. Сродство к глине увеличивается закономерно с увеличением длины цепи первичных аминов. Сравнение первичных, вторичных и третичных аминов, содержащих одинаковые алкильные группы, показывает что сродство увеличивается в последовательности $R_1NH_3^+ < R_2NH_2^+ < R_3NH^+$. Эта последовательность сродства относится за счет важного вклада сил Ван-Дер-Ваалса и изменений в ионных гидратационных состояниях. Была вычислена термодинамическая избыточная функция, ΔG_m^E , которая показала, что по отношению к чистым гомоионным формам гетерогенные Na^+ -алкиламмониевые поверхностные фазы были более стойкими, чем они были бы, если бы смешивание было идеальным.

Kurzreferat- Der Austausch von verschiedenen Alkylammoniumkationen in wäßrigen Lösungen durch Natriumlaponit wurde examiniert. Die Affinität der Tonerden für diese organischen Kationen war in linearischer Verwandtschaft mit Molekulargewicht, Molekülgröße oder Kettenlänge der Alkylammoniumionen. Die Affinität für den Ton steigt an mit zunehmender Kettenlänge der primären Amine. Ein Vergleich primärer, sekundärer und tertiärer Amine, welche dieselben Alkylgruppen enthalten, zeigt, daß die Affinität in der folgenden Reihenfolge zunimmt: $R_1NH_3^+ < R_2NH_2^+ < R_3NH^+$. Diese Affinitätsreihenfolge wurde wichtigen Van der Waalsschen Kräften und Änderungen im Ionenhydratzustand zugeschrieben. Die thermodynamische Überschuffunktion, Δ_m^E , wurde berechnet und deutet an, daß mit Hinsicht auf die reinen, homoionischen Formen, die heterogenen Natrium-Alkylammonium Oberflächenphasen waren stabiler als unter Umständen, in denen das Mischen ideal war.

Résumé- L'échange par la laponite de sodium de cations variés d'alkylammonium d'une solution aqueuse a été étudié. L'affinité de l'argile pour ces cations organiques était apparentée de manière linéaire au poids moléculaire, à la taille moléculaire ou à la longueur de la chaîne des ions alkylammonium. L'affinité de l'argile croît régulièrement avec la longueur croissante de la chaîne des amines primaires. Une comparaison d'amines primaires, secondaires, et tertiaires, contenant le même groupe alkyl montre que l'affinité croît dans l'ordre $R_1NH_3^+ < R_2NH_2^+ < R_3NH^+$. Ces suites d'affinités étaient attribuées à d'importantes contributions Van der Waals et à des changements dans les états d'ions hydratés. La fonction d'excès thermodynamique, ΔG_m^E , a été calculée et a indiqué que relativement aux pures formes homoioniques, les phases de surface hétérogènes Na^+ -alkylammonium étaient plus stables qu'elles ne le seraient si le mélange était idéal.