THERMODYNAMICS OF THE EXCHANGE OF *n*-ALKYLAMMONIUM IONS ON Na–MONTMORILLONITE

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Abstract — A thermodynamic study has been made of the ion exchange equilibria of the *n*-alkylammonium ions in sodium montmorillonite. Exchange isotherms of ammonium, methylammonium, ethylammonium, propylammonium and butylammonium with sodium montmorillonite were determined at 4°, 25° and 55°C. From these data the changes in free energy, enthalpy and entropy for the exchange reactions were calculated. In the temperature region used in this work, no enthalpy change was observed. Thus the exchange was only controlled by entropy effects. The thermodynamic excess functions were calculated from the surface activity coefficients. The affinity of the organic ions for the clay increases with chain length. It is shown that this increase can not be ascribed to van der Waals forces, but must be due to the combined effect of variations in electrostatic interactions with the clay lattice and of the hydration state.

INTRODUCTION

THE ADSORPTION of various alkylammonium salts from aqueous solutions by sodium montmorillonite has been studied by a number of workers.

Cowan and White (1958) made a study of the adsorption of straight-chain monoalkylammonium salts by sodium bentonite. A linear relationship between the change in free energy and the number of carbon atoms in the aliphatic chain was found. The increment of free energy per CH_2 group was about 105 cal for the low molecular weight alkylammonium ions (C_2–C_4). For the long chain amines (C_5–C_9) a value of 400 cal per CH_2 was found. The increment in the free energy was ascribed to van der Waals interactions. Therefore, a mechanism of the exchange process was proposed, in which the length of the hydrocarbon chain was considered to play the most important role.

Theng, Greenland and Quirk (1967) investigated the adsorption of primary, secondary, tertiary and quaternary ammonium ions on sodium and calcium montmorillonite. The length of the aliphatic chains was between C_1 and C_4. With the exception of the quaternary cations, the same relationship as observed by Cowan and White (1958) between the affinity and the molecular weight of the organic cations was found. The affinity sequence of primary, secondary and tertiary amines with the same alkyl groups showed that the affinity of the clay decreased with increasing number of aliphatic groups on the nitrogen atom. For the primary ions, the increment per CH_2 was about 53 cal per CH_2 going from methyl- to propylammonium. Between propyl- and butylammonium an increment of 150 cal was found. Besides the adsorption study, X-ray diffraction experiments indicated the presence of a single layer of alkylammonium ions adsorbed between the clay sheets.

Slabaugh (1954) examined on a thermodynamic basis the exchange of various high molecular weight alkylammonium ions on sodium bentonite. He found that the exothermicity of the exchange reaction increased with increasing molecular weight of the alkylammonium ions. A firm conclusion on the adsorption mechanism could not be formulated because, with the long-chain ammonium derivatives, some organic material was adsorbed on the clay in excess of the cation exchange capacity.

In this note, a thermodynamic study of the adsorption of short-chain *n*-alkylammonium ions on sodium montmorillonite is made. The possible contribution of the van der Waals-forces to the interaction clay-organic cations will be discussed.

EXPERIMENTAL

The clay used in this work was a sodium montmorillonite from Camp Berteau with a C.E.C. of 0·94 meq.g^{-1} and an average particle diameter of 0·6 μ. The clay fraction of 0·6 μ was separated from the crude clay by centrifuging a 2% aqueous Na$^+$ clay suspension during 10 min at 1800 rev/min. Excess electrolyte was removed by a dialysis process. The dialysed material was dried at 60°C, hand ground and passed through a 60 mesh sieve.

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The exchange isotherms were determined by shaking overnight 0·3 g samples of the Na–clay with 40 cm³ solutions containing different proportions of the alkylammonium chloride and NaCl. The temperature was maintained at 4°, 25° and 55°C and the total ionic concentration was kept constant at 0·025N. After equilibration, the suspensions were centrifuged and the supernatants were analyzed. The alkylammonium ions in solution were estimated by 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 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 with the clay crystals. Reversibility was checked by carrying out backward reactions using the appropriate end-members of the series.

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

$$Na - Z + A^+ \rightleftharpoons A - Z + Na^+.$$
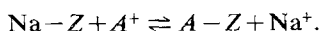
The thermodynamic equilibrium constant K is defined as

$$K = \frac{N_A m_{Na}}{N_{Na} m_A} \times \frac{f_A \gamma_{Na}}{f_{Na} \gamma_A} = K_c \times \frac{f_A \gamma_{Na}}{f_{Na} \gamma_A} = K_c' \times \frac{f_A}{f_{Na}}$$

where K_c is the rational selectivity coefficient, N and m the equivalent fractions of the ions on the solid and in the liquid phase, f the activity coefficient of the ions in the solid phase and γ the activity coefficient of the ions in the liquid phase. The ratio of the activity coefficients in the liquid phase at a total concentration of 0·025N, does not deviate significantly from unity (Robinson and Stokes, 1959). The notation is simplified by introducing $K_c' = K_c \times (\gamma_{Na}/\gamma_A)$, where K_c' is the corrected rational selectivity coefficient.

According to Gaines and Thomas (1953) the activity coefficients on the solid and the thermodynamic equilibrium constant can be expressed as:

$$\ln f_A = -(1 - N_A) \ln K_c' + \int_{z_A}^{1} \ln K_c' \, dN_A$$

$$\ln f_{Na} = N_A \ln K_c' - \int_{0}^{z_A} \ln K_c' \, dN_A$$

and

$$\ln K = \int_{0}^{1} \ln K_c' \, dN_A.$$

The change in standard free energy is calculated using the relation

$$\Delta G_0 = -RT \ln K.$$

The changes of the standard enthalpy (ΔH_0) and of the standard entropy (ΔS_0) are obtained using the equations:

$$\frac{d \ln K}{dT} = \frac{\Delta H_0}{RT^2} \quad \text{and} \quad \Delta S_0 = \frac{\Delta H_0 - \Delta G_0}{T}.$$

Replicate experiments indicated that the overall accuracy was of ±0·8% for the change in standard free energy.

RESULTS AND DISCUSSION

The exchange isotherms are presented in Fig. 1 in the usual manner, by plotting the equivalent fraction of the alkylammonium ions in solution (m) on the ordinate against the corresponding fraction on the solid (N). The exchange isotherms
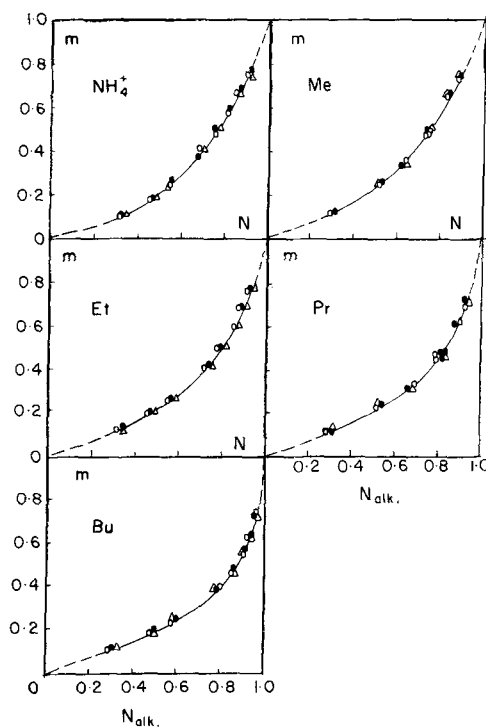

Fig. 1. Exchange isotherms of different alkylammonium ions on Na–montmorillonite, at different temperatures. Abscissae: equivalent fraction N of alkylammonium ions on the montmorillonite; ordinate: equivalent fraction m of alkylammonium ions in solution. $\triangle = 4°C$; $\bullet = 25°C$; $\bigcirc = 55°C$.

of the ammonium (NH_4^+), methylammonium (Me), ethylammonium (Et), propylammonium (Pr) and butylammonium (Bu) ions were determined at 4°, 25° and 55°C. The values of ΔG_0, ΔH_0 and ΔS_0 derived from these isotherms are collected in Table 1. The isotherms are independent of the temperature, indicating that there are no enthalpy effects.

The possible contribution of van der Waals forces

Since montmorillonite in aqueous media has interlamellar swelling properties, steric and space factors do not influence the extent of the exchange. All the alkylammonium ions used could effect a complete replacement of the sodium ions initially present and the isotherms extrapolated to $N = 1$ for $m = 1$. Figure 1 shows that the isotherms are of the L or Langmuir type, indicating a flat orientation of the adsorbed cations at the surface (Giles *et al.*, 1960). This is consistent with the X-ray data (Theng, Greenland and Quirk, 1967). The temperature has no influence on the extent of the exchange nor on the shape of the isotherms. The ΔG_0 data in Table 1 and in Fig. 2 show that, with the exception of NH_4^+, the affinity for the alkylammonium ions increases with increasing molecular weight. A linear relationship between ΔG_0 and the molecular weight was observed for the ions Et, Pr and Bu, but NH_4^+ and Me did not quite fit the same linear relation. This behaviour is not affected by the temperature.

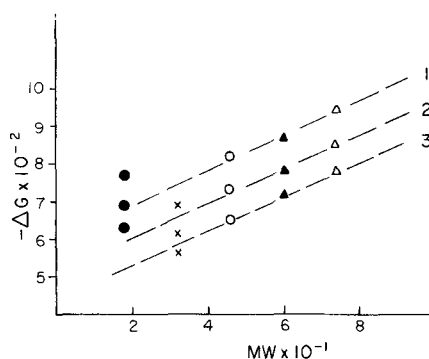In the earlier literature (Cowan and White, 1958; Greenland, 1970; Theng, Greenland and

Fig. 2. Variations in ΔG_0 (cal.mole^{-1}.10^{-2}) with molecular weight (g. 10^{-1}) for the adsorption of alkylammonium cations by montmorillonite, at different temperatures. ●–NH_4^+; x–Me; ○–Et; ▲–Pr; △–Bu. 1 = 328°K; 2 = 298°K; 3 = 277°K.

Quirk, 1967) the variation of ΔG_0 with increasing molecular weight was attributed to an increasing contribution of van der Waals forces. The literature data are summarized in Table 2. From these data it appears that the increment of ΔG_0 per CH_2 must not be considered as constant. The data of different authors are obtained on different minerals (montmorillonite and bentonite) and differ from each other by a factor of 2 or 3. In this work the increment of ΔG_0 was of the same order of magnitude; it was constant only within a factor of two, and was influenced by the temperature.

Table 1. Thermodynamic values of the exchange Na$^+$–n–alkyl-ammonium ions on montmorillonite

Ion	Temp. (°K)	ΔG_0 (cal/mole)	ΔH_0 (cal/mole)	ΔS_0 (cal/°K mole)
NH_4^+	277	−732	0	2·6
	298	−788	0	2·6
	328	−867	0	2·6
Me	277	−664	0	2·4
	298	−715	0	2·4
	328	−787	0	2·4
Et	277	−755	0	2·8
	298	−834	0	2·8
	328	−918	0	2·8
Pr	277	−815	0	2·9
	298	−877	0	2·9
	328	−965	0	2·9
Bu	277	−881	0	3·2
	298	−948	0	3·2
	328	−1·043	0	3·2

Table 2. Literature data on ΔG_0 per CH_2 as a function of the chain
length of the n-alkylammonium ions

	Cowan and White (1958) (20°C)	Theng et al. (1967) (25°C)	This work		
			4°C	25°C	55°C
C_1–C_2		58	91	119	132
C_2–C_3	105*	50	60	43	47
C_3–C_4	105*	150	66	71	78
C_4–C_5	105*				
C_5–C_9	400				

*Mean values calculated from the slope of the relation between ΔG_0
and the number of carbon atoms for the short chain alkylammoniums.

If these increments were due only to the van der Waals forces, one would expect to find a more or less constant value, less dependent on the experimental conditions than the absolute values of ΔG_0 itself. The comparison of the data in Table 2 suggests to us that the increment of ΔG_0, like any other property of the exchange reaction, must be considered to result from the combined variation of all the possible factors at the surface of the clay, and cannot be ascribed exclusively to van der Waals interactions.

The isotherms in Fig. 1, together with the results in Table 1, indicate that there is no change in enthalpy. According to

$$\frac{d \ln K}{dT} = \frac{\Delta H_0}{RT^2} = \frac{(H^{os}_{Alk} - H^s_{Alk}) - (H^{os}_{Na} - H^s_{Na})}{RT^2}$$

the difference between the relative partial molar enthalpies of the ions $(H^{os}_{Alk} - H^s_{Alk})$ and $(H^{os}_{Na} - H^s_{Na})$ are independent of the composition of the surface phase. This implies that the eventual interionic interactions and van der Waals forces are absent or negligibly small. Instead, as ΔH_0 is zero, the Na^+–short-chain alkylammonium exchange reactions are ruled only by entropy effects. The effect of the chain length is only reflected in the ΔS_0 values, and a distinction is seen between NH_4^+, Me and the other organic ions.

The activity coefficients of the ions at the surface, calculated from the Gaines and Thomas relation, are shown in Fig. 3. These coefficients are smaller than 1 for NH_4^+ and Me, and larger than 1 for the other ions. A regular increase of activity coefficient with increasing size of the organic ions is obvious. This is another objection towards taking the van der Waals forces as an important factor in the exchange properties of the organic ions. Important deviations of the activity coefficients from unity can be considered as an indication of an important heterogeneity at the surface. Van der Waals forces
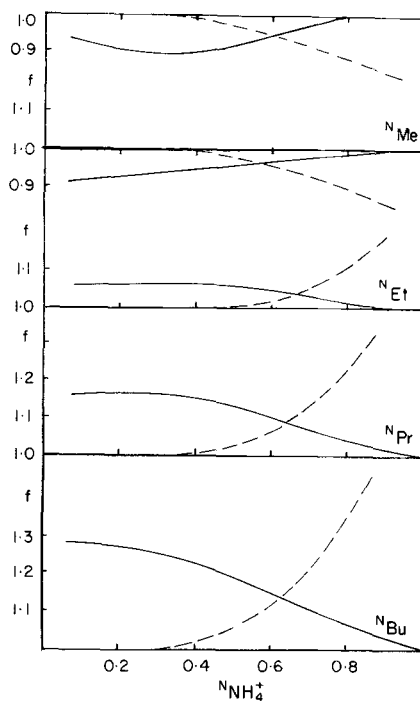

Fig. 3. The surface activity coefficients for different Na^+–alkylammonium compositions at the clay surface.

would probably effect a more uniform distribution of the ions and not cause such an important change in activity coefficient when the chain length increases.

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 functions for the ions in the surface phase can be interpreted in terms of probability or stability of this phase. The

excess thermodynamic functions for the formation of a heteroionic Na–alkylammonium exchanger are estimated from the activity coefficients of the adsorbed ions and the relative partial molar enthalpies.

The excess free energy change of mixing is defined as:

$$\Delta G_m^E = \Delta G_m - \Delta G_m^{id} \qquad (1)$$

where ΔG_m, the free energy change of mixing, is the difference between the observed value of the thermodynamic function and the sum of the free energies of the pure constituents. When N_{alk} is the equivalent fraction of alkylammonium ions at the surface and f the corresponding activity coefficient of the ions at the surface we write:

$$\Delta G_m = RT \{ N_{alk} \ln N_{alk}.f_{alk}$$
$$+ (1 - N_{alk}) \ln (1 - N_{alk}) f_{Na} \}. \qquad (1')$$

ΔG_m^{id} is the free energy change of mixing in a solid solution or at the surface phase which obeys Raoult's law. For an equivalent fraction N_{alk}, ΔG_m^{id} can be expressed as

$$\Delta G_m^{id} = RT \{ N_{alk} \ln N_{alk} + (1 - N_{alk}) \ln (1 - N_{alk}) \}. \qquad (1'')$$

ΔG_m^E can also be calculated following a method proposed by Scatchard (1931):

$$\Delta G_m^E = a v_{Na} \frac{N_{Na} \times N_{alk}}{\rho N_{Na} + N_{alk}} \qquad (2)$$

where a is a constant, v the equivalent volume of the ions, N the equivalent fraction of the ions at the surface of the clay,

$$\rho = \frac{v_{Na}}{v_{alk}} = \left[\frac{N_{alk}}{N_{Na}} \right]^2$$

and

$$a v_{Na} = \Delta G_m^E (\text{max. exp}) \times \frac{\sqrt{\rho} + 1}{N_{Na}^{\max}}.$$

The excess free energy change of mixing for the different ions as a function of the extent of exchange (N_{alk}) is given in Fig. 4. In this figure only the excess free energy change of mixing at 25°C for different alkylammonium ions is shown. Similar tendencies were found for the other exchange temperatures. The solid lines are obtained from the application of (1), the dotted lines, obtained by the method of scatchard (equation (2)), give almost identical results.

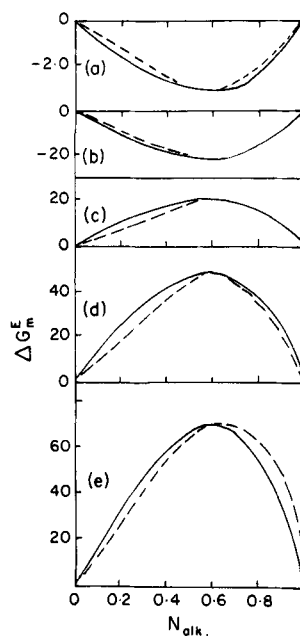Considering the ΔG_m^E values, the following general conclusions can be drawn. There is in fact

Fig. 4. The excess free energy change of mixing. ΔG_m^E (cal.mole^{-1}) against the equivalent fraction N of alkylammonium ions on the montmorillonite, at 298°K. a– NH$_4^+$; b–Me; c–Et; d–Pr; e–Bu.

an increase in the excess functions from NH$_4^+$ towards Bu. The excess function is negative for the systems NH$_4^+$ and Me. This means that, with respect to the pure homoionic forms, the heterogeneous surface phases (NH$_4^+$ or Me–Na$^+$) are more stable than they would be if the mixing were ideal. The deviation from ideality occurs in the sense of a more stable mixture. The ΔG_m^E functions are positive from Et to Bu, and the absolute values increase in that order. A positive excess function implies a deviation from ideality in the sense of a less stable mixture of Na$^+$ and alkylammonium ions with respect to the ideal mixture. To understand this behaviour, it must be emphasized that the variation in any thermodynamic entity results from the combined effect of all the variations occurring at the clay surface. The interactions between clay surface and ions and between ions and solvent must be considered together. It is understandable that these interactions in a mixed NH$_4^+$–Na$^+$ surface population can be different from the interactions in a pure Na$^+$ and in a pure NH$_4^+$ system. The organic part of the alkylammonium ions can be considered to be hydrophobic. This may affect the hydration properties of the residual Na$^+$ ions, and the increase of the ΔG_m^E with increasing chain length could probably be due to the variation of the hydration state of the ions at the surface.

Barrer and Brummer (1963), studied the progression of the (001) spacings with increasing proportions of mono- and tetramethylammonium ions on Na^+ montmorillonite. They concluded that a partially exchanged methylammonium – or tetramethylammonium montmorillonite must be considered to have a random interstratification of sodium-rich and alkylammonium-rich layers. Under the experimental conditions described here, the opposite behaviour was observed for the methylammonium montmorillonite. Indeed, the ΔG_m^E for the systems $Na^+-NH_4^+$ or Na^+-Me indicates that a homogeneous mixture of sodium and alkyl ammonium ions on the clay surface is more stable than the pure homoionic forms. We are inclined to interpret our thermodynamic data in terms of homogeneous mixtures of organic ions and sodium at the level of each individual clay particle even for the systems Et, Pr and Bu. This need not be in contradiction with Barrer's data (1963). Indeed, the positive ΔG_m^E values for these systems indicate that the homoionic forms are more stable than the ideal Na–alkylammonium mixtures. Therefore we believe it is possible that a segregation into sodium-rich and alkylammonium-rich layers occurs upon drying of the samples for the XR determinations.

The enthalpy and entropy terms of ΔG_m^E can be considered separately. In this case the enthalpy of mixing is zero. The relation between the partial molar enthalpy and the activity coefficient is expressed by

$$\frac{d \ln f_{alk/Na}}{d\, 1/T} = \frac{\bar{H}_{alk/Na}^s - \bar{H}_{alk/Na}^{os}}{R}$$

where $\bar{H}_{alk/Na}^s$ is the partial molar enthalpy of the alkylammonium or of the sodium ions at the surface phase at a given exchange, and $\bar{H}_{alk/Na}^{os}$ is the partial molar enthalpy of the alkylammonium or sodium ions in the standard state. In the standard state the solvent activity and the equivalent fraction of the alkylammonium- or sodium ions at the surface are equal to 1.

Therefore the enthalpy of mixing ΔH_m,

$$\Delta H_m = \bar{H}_{alk}^s + \bar{H}_{Na}^s - \bar{H}_{alk}^{os} - \bar{H}_{Na}^{os} \qquad (3)$$

is equal to zero, since the activity coefficients of the cations at the clay surface are independent of the temperature.

According to Prigogine (1957) the enthalpy of mixing can be understood as a combination of two terms, one being related to the potential energy of the system, the other to an excess volume term. In our case $\Delta H_m = 0$, also $\Delta H_m^{id} = 0$ but the system

has not an ideal behaviour because $\Delta G_m^E \neq 0$. This means that the two terms responsible for the enthalpy effect cancel each other. The volume excess term, $V_m - V_m^{id}$ is positive in any case because the ideal system has no interaction with the solvent, whereas the ion–solvent interaction in the real system involves an increased volume. Therefore, the potential energy of the system decreases with respect to the ideal behaviour. This can be understood if it is assumed that in the mixed system one of the ionic species is closer to the surface than in the unmixed state. This behaviour is in agreement with the large deviations of f_{Na} and f_{alk} from unity (Fig. 3).

Since the enthalpy of mixing is zero, ΔG_m^E can only result from an entropy effect. Therefore the excess entropy change of mixing can be obtained as

$$\Delta S_m^E = -\Delta G_m^E/T$$

and its sign is opposite to that of the excess free energy change of mixing. Therefore, considering the Fig. 4, ΔS_m^E is positive for the system $NH_4^+-Na^+$ and $Me-Na^+$. For the systems containing Et, Pr and Bu ions mixed with sodium ΔS_m^E is negative. ΔS_m^E can be considered as a measure of the randomness of the distribution of the cations at the clay surface in comparison with the pure forms. On theoretical grounds one would expect ΔS_m^E of the mixtures to be negative, because $\Delta S_m^E = \Delta S_m - \Delta S_m^{id}$. ΔS_m^{id} is positive in any case, as the complete randomness (highest entropy) is considered as the ideal state of the mixture. Deviations from ideal behaviour, responsible for ΔS_m^E, produce a state for which $\Delta S_m < \Delta S_m^E$ so that ΔS_m^E is negative. The observed ΔS_m^E values for the mixed systems containing Et, Pr and Bu agree with these theoretical reflections.

For the systems $NH_4^+-Na^+$ and $Me-Na^+$ positive ΔS_m^E values are observed. Van Bladel (1966) observed a similar behaviour for montmorillonite saturated with a mixture of NH_4^+ ions and alkaline earth ions. Positive ΔS_m^E values can not be explained on the basis of the adopted assumptions. A probable reason for this observation is in the fact that we did not take into account the influence of the solvent at the surface face. The NH_4^+ (or Me) and the Na^+ ions have different hydration numbers at homoionic surfaces. The realization of a more or less homogeneous hydration number in the mixture would result in an increase of the entropy with respect to the homoionic forms. In this way we can understand the positive excess entropy, because the calculation of ΔS_m^{id} did not take into account possible changes in the hydration of the cations. Although there is a difference in the

sign of ΔS_m^E for the ions NH_4^+ and Me on one hand, and the ions Et, Pr and Bu on the other hand, there is a clear and general decrease of ΔS_m^E with increasing chain-length going from NH_4^+ to Bu. This indicates an increasing heterogeneity at the surface with increasing importance of the organic character of the ingoing ion. We believe that this heterogeneity includes the initial inorganic ions, the ingoing organic ions and the solvent molecules as well.

CONCLUSIONS

In the exchange reaction with NH_4^+ and short-chain alkylammonium ions on Na–montmorillonite, a selectivity in favour of the organic ions was observed. ΔG_0 was negative in all cases, and an average increment of the free energy of -53 cal. mole^{-1} per CH_2 was observed for the ions Et, Pr and Bu. For the ions NH_4^+ and Me the increment per CH_2 was higher.

The exchange is independent of temperature. Therefore the change in standard enthalpy of exchange is zero, and the exchange is ruled only by entropy effects. A thermodynamic treatment, based on the excess functions of mixing, indicates that there is a regular decrease in stability of the mixed system Na–alkylammonium going from NH_4 to Bu. For the systems with NH_4^+ and Me a deviation from ideality in the sense of a more stable mixture was observed. For the other ions the mixtures with Na$^+$ were less stable than the pure homoionic forms.

The behaviour of the Na–NH_4^+ and Na–Me systems suggests a complete randomness of the ions and of the solvent molecules along the clay surface. The regular decrease of the stability with increasing molecular weight of the organic ions probably reflects the variation of the hydration properties. With increasing hydrophobic character of the ions the surface must become very heterogeneous, which is indeed reflected by the important entropy term.

An accurate thermodynamic treatment cannot be made because of the complexity of the system. However, the variation in any thermodynamic property will result from the combined effect of all the possible interactions. In the earlier literature the increase of ΔG_0 with the chain length of the alkylammonium ion was attributed to the only effect of increasing van der Waals forces. This was probably an oversimplification. The zero enthalpy effect suggests that the van der Waals interactions are negligible. The variations of the hydration properties and the coulombic interaction between the cation and the clay are more important than the van der Waals forces. The importance of the entropy effect substantiates this conclusion.

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Résumé – On a effectué une étude thermodynamique des équilibres d'échange ionique des ions *n*-alkylammonium dans la montmorillonite sodique. Les isothermes d'échange des ions ammonium, méthylammonium, éthylammonium, propylammonium et butylammonium avec la montmorillonite sodique ont été déterminés à 4°, 25° et 55°C. En partant de ces données on a calculé les variations d'énergie libre, d'enthalpie et d'entropie pour les réactions d'échange. Dans le domaine de température exploré dans ce travail, aucune variation d'enthalpie n'a été observée. L'échange est donc contrôle seulement par des effets d'entropie. Les fonctions thermodynamiques d'excès ont été calculées à partir des coefficients d'activité de surface. L'affinité des ions organiques pour l'argile augmente avec la longueur de la chaîne. On montre que cette augmentation ne peut pas être attribuée à

des forces de Van der Waals, mais qu'elle doit être due à l'effet combiné de variations dans les inter-actions électrostatiques avec le réseau de l'argile et de l'état d'hydratation.

Kurzreferat – Es wurde eine thermodynamische Untersuchung der Ionenaustauschgleichgewichte der *n*-Alkylammonium-Ionen in Natrium-Montmorillonit durchgeführt. Austauschisothermen von Ammonium, Methylammonium, Ethylammonium, Propylammonium und Butylammonium mit Nat-rium-Montmorillonit wurden bei 4°, 25° und 55°C bestimmt. Aus diesen Daten wurden die Verän-derungen der freien Energie, der Enthalpie und der Entropie für die Austauschreaktionen berechnet. In dem bei dieser Arbeit verwendeten Temperaturbereich konnte keine Veränderung der Enthalpie fest-gestellt werden. Der Austausch wurde daher einzig durch Entropieeffekte gesteuert. Die thermo-dynamischen Überschussfunktionen wurden aus den Oberflächenaktivitätskoeffizienten berechnet. Die Affinität der organischen Ionen für den Ton nimmt mit der Kettenlänge zu. Es wird dargelegt, dass diese Zunahme nicht van der Waalsschen Kräften zugeschrieben werden kann, sondern eine Folge der kombinierten Wirkung von Änderungen elektrostatischer Wechselwirkungen mit dem Tongitter und des Hydratationszustandes sein muss.

Резюме — Проведено термодинамическое изучение равновесия обмена ионов п-алкил-аммония в натриевом монтмориллоните. Изотермы обмена аммония, метиламмония, этиламмония, пропиламмония и бутиламмония в натриевом монтмориллоните были определены при тем-пературах 4, 25 и 55°C. По полученным данным были вычислены изменения свободной энергии, энтальпии и энтропии для обменных реакций. В температурном интервале, использо-ванном в этой работе, никаких изменений энтальпии не наблюдалось. Таким образом, обмен контролировался только энтропийными эффектами. Избыточные термодинамические функции были получены из коэффициентов поверхностной активности. Сродство органических ионов к глине увеличивается с возрастанием длины цепи. Показано, что это увеличение не вызывается действием вандерваальсовских сил, но может быть обусловлено совместным влиянием изменений в электростатических взаимодействиях с решеткой глины и степенью ее гидратации.