WATER VAPOR ISOTHERMS AND HEAT OF IMMERSION OF Na/Ca-MONTMORILLONITE SYSTEMS—II: MIXED SYSTEMS[1]

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Abstract—Adsorption isotherms for water vapor, c-spacing and heat of immersion in water of mixed Na/Ca-montmoril-lonite were measured at 25°C at various RH. There was good agreement between the calorimetric data, the heat calculated from the isotherms by use of BET equation, and the calculations from the ion-dipole model. It was concluded that the electrostatic forces between the adsorbed cations and the water molecules are the dominant forces in the hydration of the clay. Thus, at low moisture content, only the adsorbed Ca-ions are hydrated. The heat released when Na-platelets condense to form Ca-packets was measured, and it was suggested that this energy term is the driving force for the demixing phenomena.

Key Words—Adsorption, Calcium, Electrostatic, Hydration, Isotherm, Montmorillonite, Sodium.

INTRODUCTION

The adsorption isotherms for water vapor, c-spacing, and heat of immersion in water of homoionic Na- and Ca-montmorillonite were measured at 25°C at various relative humidities (Keren and Shainberg, 1975). Reasonable agreement was found between the heat of immersion data, the heat calculated from the isotherms by use of the BET equation, and the calculation based on the ion-dipole model. This agreement indicates that at low moisture content, the hydration of the interlayer cations (vs. the hydration of the exposed clay surfaces) is the main interaction between the dry clay and the water molecules. If the hydration of the cations is the main mechanism for water adsorption on dry clay then, in mixed Na/Ca-montmorillonite, the adsorption isotherm for water vapor and the heat of immersion should be the sum of the contributions of the individual cations. This paper constitutes a report on the results of such measurements and proposes a model for Na/Ca-montmorillonite–water interaction.

MATERIALS AND METHODS

The method of preparation of the two homoionic montmorillonite clays was described in detail in the first paper of this series (Keren and Shainberg, 1975). Basically, it consists of separating the coarse fraction of Wyoming bentonite by sedimentation, saturating the exchange complex with Na- or Ca-ions by repeated washing (4 times) with a 1.0 N solution of the appropriate ion, and then washing the $<2 \mu$ clay with distilled water and high-speed centrifuge until free of Cl^- as tested with $AgNo_3$ solution. The salt-free gels were freeze-dried and stored in desiccators.

The bi-ionic mixtures were prepared by two methods, which may be called, for convenience, a "physi-cal" and "chemical" mixture. The physical mixture was obtained by mixing the two dried homoionic clays in the appropriate amounts. The mixed sample was then immersed in water to determine its heat of immersion. The "chemical" mixture was obtained by suspending the physical mixture of the two homoionic clays in water (3.5% suspension). The suspensions were then stirred for about 2 hr until redistribution of the cations in the exchange complex was complete (Shainberg and Caiserman, 1969). Then the suspensions were centrifuged and the gels were freeze-dried and stored in a desiccator. The main difference between the two methods of preparation is that upon immersion in water of the physical mixture, two processes take place simultaneously: redistribution of the adsorbed ions and hydration of the clay systems. With the second method, the redistribution of the adsorbed ions is already complete, and upon immersion in distilled water only hydration of the exchangeable ions and the clay takes place.

The methods of obtaining the adsorption isotherms, the X-ray spacing, and the heat of immersion of the clay were described in detail in the first paper of the series (Keren and Shainberg, 1975).

RESULTS AND DISCUSSION

The adsorption isotherms

The adsorption and desorption isotherms for the sorption of water molecules on montmorillonite surfaces saturated with a mixture of Na-and Ca-ions were obtained. It was observed that the two branches of the sorption isotherms do not overlap and that hysteresis takes place. The water retained by the clay at each of the relative humidities (RH) studied, was higher in the desorption than in the adsorption curve. The hysteresis phenomenon for the homoionic clays was discussed in detail in our previous paper. Since it was suggested that the adsorption isotherms are less affected by capillary
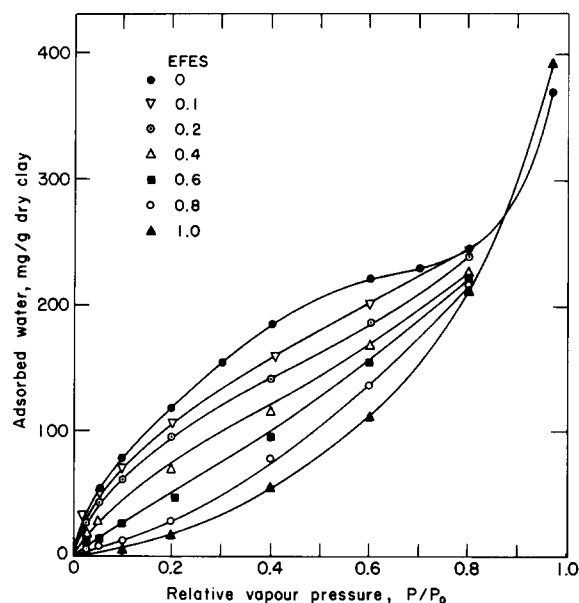

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Figure 1.   Adsorption isotherms on Na-Ca-montmorillonite mixtures at various equivalent fractions of exchangeable Na (EFES) at 25°C.

condensation of water and are more directly related to the interaction between adsorbed water and the exchangeable ions and the surfaces of the clay, only these curves are presented in Figure 1. It is evident that at RH up to 0.8, the amount of water adsorbed on Ca-clay is the highest, and the amount of water adsorbed decreases, with increase in the Na fraction in the exchange complex. At a RH of 0.85, the adsorption isotherms of Na- and Ca-clay crosses and at higher RH the amount of water adsorbed on Na-montmorillonite exceeds that on Ca-clays. At the high range of RH the water molecules may condense on external surfaces, and thus the content of water adsorbed on Na-clay exceeds that on Ca-tactoids. At this moisture content, water condensation and osmotic swelling are the dominant mechanisms for retaining water molecules. This moisture range has been studied by Shainberg et al. (1971).

Since the adsorption of water molecules on the clay usually involves the formation of many molecular layers of water molecules on the surface, the adsorption isotherm is best analyzed according to the BET theory. The BET equation may be written as follows:

$$\frac{P}{X(P_0 - P)} = \frac{1}{X_m C} + \frac{C - 1}{X_m C} \cdot \frac{P}{P_0} \qquad (1)$$

where X is the amount of vapor adsorbed at pressure P, P_0 is the saturation vapor pressure, X_m is the quantity of adsorbate forming a monolayer, and C is a constant from which the average heat of adsorption for the monolayer is obtained, according to the equation
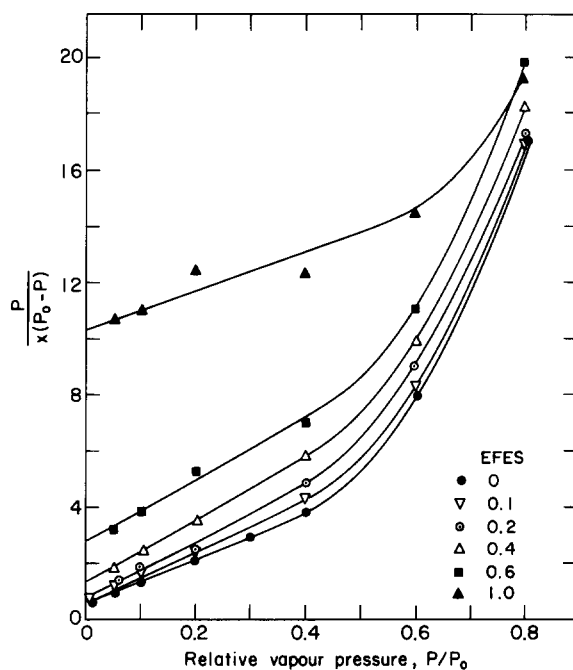
$$C = \exp[(E_1 - E_L)/RT] \qquad (2)$$

Figure 2.   BET curves of the adsorption isotherms.

where E_1 is the heat of adsorption of the first monolayer, E_L is the heat of liquification of the gas ($-10,480$ cal/mole for water at 25°C), R is the molar gas constant, and T is the absolute temperature.

According to equation (1), a plot of $P/X(p_0 - P)$ vs. P/P_0 should give a straight line if the BET theory can be applied to our systems. It is evident from Figure 2 that straight lines are obtained over the RH range up to 0.4. From the slopes and intercepts of these lines the amount of water forming a monolayer (X_m) and the heat of adsorption of the first monolayer were calculated and are tabulated in Table 1.

It is evident that the $E_1 - E_L$ values for Ca-clay, and for Ca systems with 10 and 20% Na in the exchange complex, are all the same. Thus, it seems that most of the adsorbed water in these ionic mixtures forms monolayers around the Ca-ions. Furthermore, by considering the amount of water forming monolayers, X_m, it

Table 1.   The BET parameters and heat of adsorption of water molecules adsorbed on Na-Ca-montmorillonite.

EFES	X_m (mg H$_2$O/g clay)	X_m^{Ca} [1] (mg H$_2$O/g clay)	Molecules H$_2$O per negative charge	$E_1 - E_L$ (kcal/mole H$_2$O)
0	114	114	7.0	1.58
0.1	104	103	6.4	1.58
0.2	93	92	5.7	1.58
0.4	80	69	5.0	1.30
0.6	74	46	4.5	0.96
1.0	58	—	3.6	0.34

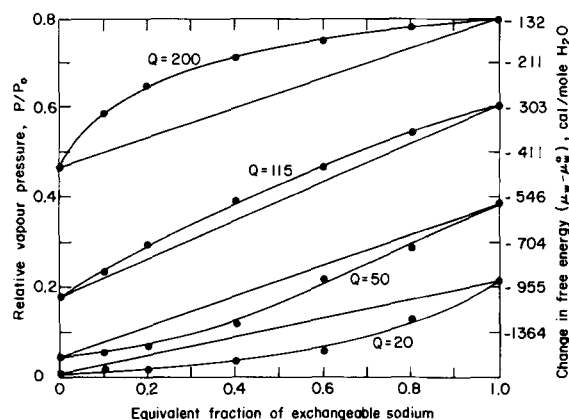[1] $X_m^{Ca} = 114(1.0 - EFES)$, is the amount of water adsorbed on the adsorbed Ca only.

Figure 3. The changes in vapor pressure (linear scale) and free energy (logarithmic scale) of the adsorbed water with EFES for constant amounts of adsorbed water, Q, in mg/g of clay.

seems that the adsorbed water is located only around the Ca-ions (column 3, Table 1). This point is discussed further in the next section.

The chemical potential of adsorbed water

The chemical potential of the vapor, μ_w, at pressure P, is related to the chemical potential of pure bulk water (μ_w^0) at the same temperature by the equation

$$\Delta\mu = \mu_w - \mu_w^0 = RT \ln P_w/P_w^0 \qquad (3)$$

By applying this equation to the adsorption isotherms (Figure 1) it is possible to plot the change in chemical potential (and free energy) of adsorbed water as a function of the Equivalent Fraction of Exchangeable Sodium (EFES) (Figure 3). It should be noted that in Figure 1 three variables are presented (amount of adsorbed water, P/P_0, and EFES). Thus, in order to compare the effect of the exchangeable Na on P/P_0 one has to maintain the moisture content constant. The reasons for choosing the moisture contents of 20, 50, 115, and 200 mg/g of clay are as follows:

1) The weight of water adsorbed in the first BET monolayer on Na-clay is 58 mg/g. A similar value was obtained when considering the Na calorimetric data (Keren and Shainberg, 1975); the heat of adsorption for the first 54 mg of water per gram of clay is constant at a value of 1.8 kcal/mole of water. Similarly, for Ca-clay, 57 mg water/g clay was needed to open the c-spacing to 15 Å, and the heat evolved per one mole of adsorbed water as calculated from the calorimetric measurement was 2.5 kcal/mole H_2O (and above). Thus, a water content of 50 mg/g clay was our first choice.

2) The value of interlayer water in the complete one layer hydrate is 0.114 ml/g clay. In Na-montmorillonite the amount of water adsorbed increases continuously with increasing RH up to 114 mg/g without any change in the c-spacing (being constant at 12.6 Å). Thus, a value of 115 mg H_2O/g clay was chosen.

3) The amount of water adsorbed on Ca-montmorillonite increases continuously with increasing RH up to 200 mg water/g clay. At about this point an inflection point in the curve exists, with a reduction in the rate of increase in the sorbed water with an increase in the RH. This moisture content corresponds also to two monolayers of water molecules and the c-spacing is maintained at 15.0 Å. Thus, it seems that because there is no room for more water molecules, less water is being adsorbed. This is the reason for choosing a value of 200 mg H_2O/g clay as one of the moisture content values.

4) At the lowest moisture content (20 mg H_2O/g clay) the hydration of both ions is not complete, and the c-spacing of both homoionic clays corresponds to opening layers. It is of interest to note the free energy of adsorbed water at this moisture content.

It is evident from Figure 3 that at each of the moisture contents, the more sodium there is in the exchange complex, the closer is the free energy of the adsorbed water to that of free water. Similarly, it is clear that adsorbed calcium reduces the free energy of adsorbed water.

However, the relative effect (compared with the straight lines connecting the two homoionic clays: these lines represent the ideal situation in which the effect of Na- and Ca-montmorillonite is additive) of increasing the fraction of exchangeable sodium on the free energy of adsorbed water depends on the moisture content of the system. At water contents of 20 and 50 mg H_2O/g clay, increasing the EFES affects only slightly the free energy of the water up to EFES = 0.4. At this EFES, the free energy of adsorbed water is determined mainly by the adsorbed Ca. This is another indication that at the low EFES range, the water molecules are adsorbed mainly on the Ca-ions. At higher values of EFES, the free energy changes more markedly with an increase in fraction of exchangeable Na. As a result, the free energy curve at this moisture content is concave downward.

At the high moisture contents (115 and 200 mg H_2O/g clay), most of the change in the free energy of adsorbed water took place at the low values of EFES. This resulted in a curve concaving upward (the upper two curves in Figure 3). These observations may be explained by considering the following numerical examples:

a) The free energy of adsorbed water in Na-montmorillonite retaining 20 mg of water per gram of clay is −912 cal/mole (equivalent to a RH of 0.215, as obtained from Figure 1). The free energy of the adsorbed water on Ca-montmorillonite with the same moisture content is −3030 cal/mole. By mixing these two systems together, it is expected that water molecules will flow from the Na-sites where their free energy is high, to the Ca-ions, where their free energy is low. This flow of water decreases the free energy of the water remaining
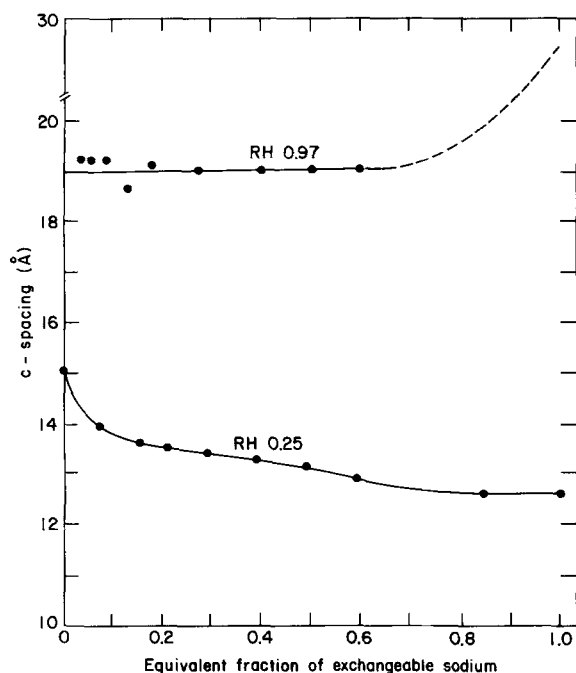
Figure 4. C-spacing of Na/Ca-montmorillonite mixtures equilibrated with water molecules in the gas phase at RH of 0.25 and 0.97.

on the Na^+ ions, and increases the free energy of the water clustered around the Ca-ions. When 0.5 g of Na-montmorillonite is mixed with 0.5 g of Ca-montmorillonite (each saturated with 20 mg H_2O/g clay), equilibrium is maintained when the free energy of the water in the system is -1840 cal/mole or the RH is ~0.045.

b) At a water content of 200 mg/g clay, the free energies of the adsorbed water are -136 and -450 cal/mole for Na- and Ca-montmorillonite, respectively. There is again the tendency for the water molecules to diffuse from the Na-sites, where their chemical potential is high, to the Ca-sites where their chemical potential is low. Theoretically, we might therefore expect a curve similar to the one obtained in the low moisture range. However, this time, there is no space for the water molecule to diffuse to. The c-spacing of the Ca-clay is 15.0 Å, and this space can accommodate only two molecular layers of water, or a maximum of 220 mg water/g Ca-clay. As a result only some water molecules will move to the Ca-region where pressure will be built up to enhance its free energy and compensate for the decrement in free energy due to the Ca-ions and most of the water associated with the Na-sites will remain there and the average free energy of the water will deviate positively from the ideal line.

These findings explain the observation by Mering and Glaeser (1954) on the X-ray patterns of Na/Ca-montmorillonites at low RH, in which Ca-montmorillonite had two monolayers of water molecules and Na-montmorillonite had only one monolayer of water molecules

between the platelets. They suggested that at this low RH demixing of the two ionic species took place, namely, that Ca-ions concentrated on some interlayers, while the Na-ions were adsorbed on other interlayers. It seems, from our results, that the energy of hydration of the adsorbed ions might be the driving force for the demixing phenomenon. Our results suggest that at low RH, and at EFES below 0.4, only the Ca-ions are hydrated and the Na-ions are not. Thus, the interplatelet space close to an adsorbed Ca-ion is enough to accommodate two layers of water molecules. Unhydrated adsorbed Na-ions will not fit, energetically, into this spacing and are excluded into interlayers where Ca-ions are not present. This leads to the "demixing" phenomenon observed by Mering and Glaeser (1954).

C-spacing

The c-spacing of Na/Ca-montmorillonite mixtures was measured at two RH (0.25 and 0.97), and is presented in Figure 4. At RH of 0.25, the c-spacing of Ca-clay is 15.0 Å, which corresponded to two molecular layers of water molecules between the sheets and decreased rapidly as the equivalent fraction of exchangeable sodium (EFES) values increased to 0.6. Thereafter, the c-spacing is constant at 12.6 Å, which is the c-spacing of Na-montmorillonite and corresponds to one layer of water molecules between the surfaces, between 0.6 and 1.0. McAtee (1956) found a similar decrease in the c-spacing with the increase in EFES values at RH = 0.52.

The decrease of c-spacing by increasing the EFES values indicates that some of the surfaces are adsorbed mainly with Na with a c-spacing of 12.6 Å and other surfaces are saturated mainly with Ca-ions. The overall c-spacing measured represents a statistical distribution of the two spacings occurring at random. These results supplement our interpretation of the data in Figure 3. It is evident that at EFES of 0.1, there are already Na-dominated surfaces which determine the experimental c-spacing (14.0). The Ca-ions at these surfaces cannot exercise their potential in attracting the water molecules, as is evident from Figure 3.

At RH = 0.97 (Figure 4), the c-spacing of Ca-montmorillonite (=19.0 Å) remains constant up to EFES of 0.6. Thereafter a diffuse peak, indicating a lack of particle orientation in the mixture, is obtained. The results indicate that up to EFES of 0.6 the tactoids with internal surfaces dominated by Ca-ions still exist, and the tendency of the Na-surfaces to expand is not so strong. When the EFES increases beyond 0.6, the Na surfaces start to dominate and a diffuse c-spacing is obtained.

Calorimetric measurements

The heat of immersion of Na/Ca-montmorillonite in water depends on the composition of the exchangeable phase and on the method of preparation of the Na/Ca mixtures (Figure 5). The heat evolved per gram of clay
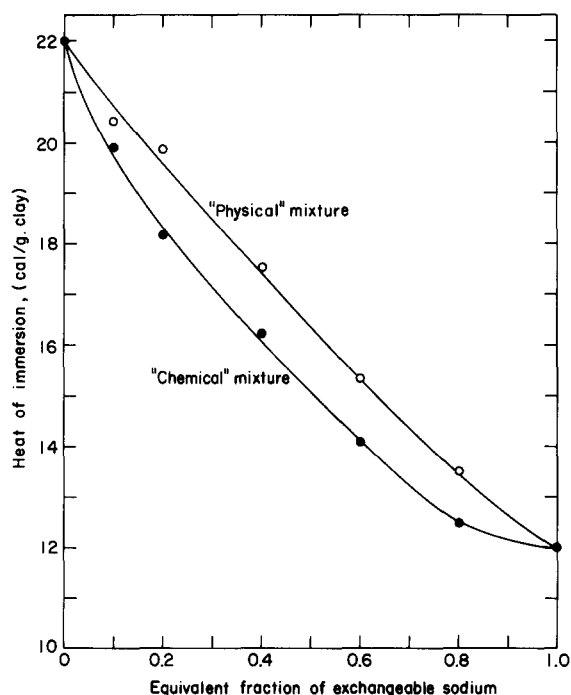
Figure 5. Heat of immersion of dry Na/Ca-montmorillonite in water ("physical" and "chemical" mixtures).

Figure 6. Heat of immersion of Na/Ca-montmorillonite in water at various amounts of adsorbed water.

when dry Ca-montmorillonite is immersed in distilled water (22 cal/g) is about twice as much as the corresponding value for Na-clay (12 cal/g). As expected, the amount of heat evolved decreases the increase in the fraction of exchangeable Na in the exchange complex. It is also evident from Figure 5 that the heat evolved when a "physical" mixture of the two homoionic clays is immersed in water is higher than that for the "chemical" mixture. This difference may be explained as follows: the heat of immersion of Na/Ca-montmorillonite in water may consist of two terms: 1) the heat of hydration of the adsorbed ions and the clay surfaces and

Table 2. Heat released for 3 mmole H_2O adsorbed on Na/Ca-montmorillonite at various EFES values (experimental and calculated values at 25°C).

	Experimental values[1] $-\Delta E$ (kcal/mole H_2O)			Calculated values[2] $-\Delta E$ (kcal/mole H_2O)
EFES	1st	2nd	3rd	
0	3.3	3.3	2.5	3.2
0.1	3.2	3.2	3.1	3.0
0.2	3.1	3.1	2.2	2.8
0.4	2.7	2.7	1.6	2.4
0.6	2.0	2.0	1.4	2.0
1.0	1.8	1.8	1.8	1.2

[1] Values correspond to the first three mmole H_2O adsorbed per gram of clay.
[2] Based on the ion-dipole model discussed in Keren and Shainberg, 1975. The values for the Na/Ca mixtures are based on the weighted contribution of the homoionic clays.
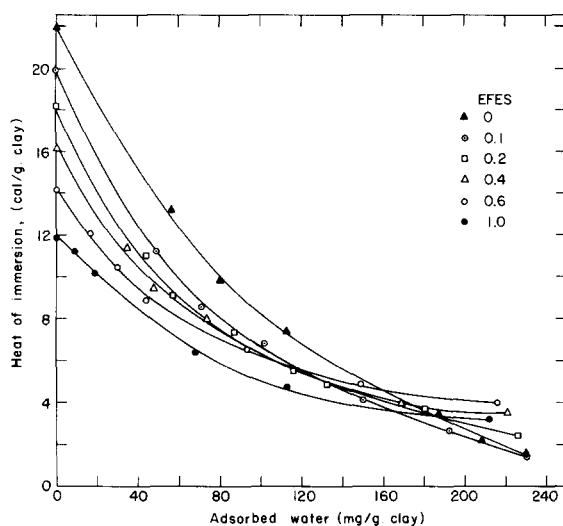
2) the heat of mixing of the ions and the possibility of packet formation. The heat evolved when the "physical" mixture is immersed in water is equal to the sum of the heat of mixing and the heat of hydration. Conversely, the heat evolved when the "chemical" mixture is immersed in water is equal to the heat of hydration of the clay and the ions only. Thus, the difference between the two heats (1.25 cal/g clay or 1.4 kcal/eq) gives the heat of mixing of Na and Ca on the montmorillonite surfaces, with the energy of the mixed Na/Ca-clay being lower than that of the two homoionic clays. Since no exchange or adsorption reaction takes place when two adsorbed ions are mixed, (because both ions are already in the exchange phase) the heat evolved upon mixing is due mainly to the condensation of the single Na-platelets into the Ca-packets. It seems that this heat release is the driving force for the "demixing" of the adsorbed ions because formation of the packets and concentrating the adsorbed Ca-ions inside the packets is energetically favorable.

Heat of immersion of wet Na/Ca-montmorillonite

The heats of immersion of Na/Ca-montmorillonite ("chemical" mixture) equilibrated with different amounts of water in the adsorbed phase are presented in Figure 6. It is evident that the heat evolved upon wetting decreases as the initial water adsorbed on the clay increases. The data also show that the heat evolved depends on the ionic composition of the clay. However, it should be noted that in the dry state, the heat of immersion decreased with the rise in EFES values, whereas in the wet range the opposite is true, and for clay mixtures with water contents above 200 mg/g, the heat evolved increases with an increase in EFES. This phenomenon for homoionic clays was discussed by us previously (Keren and Shainberg, 1975).

The heat of adsorption (per mole of water) on Na/Ca-montmorillonite has been calculated from Figure 6 and equation (5) and is presented in Table 2.

$$E = \frac{U_{N_2} - U_{N_1}}{N} \qquad (5)$$

where U_{N_1} and U_{N_2} are the heat of immersion of clays adsorbed with N_1 and N_2 moles of water, respectively, and N is equal to $(N_2 - N_1)$.

The data in Table 2 show that the heat evolved per mole of adsorbed water decreases with increasing the adsorbed Na-ions on the clay and increasing the amount of adsorbed water. It is evident that the values of the heat of hydration of the mixed systems range between the values obtained for the homoionic Na- and Ca-montmorillonite systems (Keren and Shainberg, 1975). These values are also in reasonable agreement with those calculated from the ion-dipole model (Table 2). It seems, therefore, that the energy of hydration of Na/Ca-montmorillonite may be calculated from two energy terms: (1) the coulombic interaction between the cations and the dipoles of the water molecules, and (2) the electrostatic interaction between the cations and the negative charge on the clay surface.

SUMMARY AND CONCLUSIONS

Results presented thus far show the following:

A) The amount of water forming a monolayer decreases with an increase in the Na fraction in the exchange complex. This suggests that the "monolayer" of water molecules is more closely associated with the adsorbed cations than with the exposed surfaces.

B) In the low range of moisture contents, the Ca-ions are hydrated and the Na-ions are not.

C) The heat of mixing of Na- and Ca-montmorillonite in water was calculated to be about 1.4 kcal per equivalent of exchangeable ions.

D) The electrostatic forces between the ions and the water molecules and between the ions and the negative charge on the clay surfaces are the dominant forces in the hydration reaction and may be used to calculate the heat of immersion of Na/Ca-clay in water.

E) In montmorillonite systems saturated with a mixture of Na- and Ca-ions, demixing of the adsorbed ions takes place, which means that Ca-ions are concentrated on some interlayers while Na-ions are adsorbed on other interlayers. The demixing phenomenon is energetically favorable and amounts to 1.4 kcal per equivalent of exchangeable ions.

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Резюме—Изотермы адсорбции для водяного пара, с-промежутки и теплота иммерсии в воде смешанного Na/Ca монтмориллонита были замерены при 25°C и различных относительных влажностях. Существует хорошее соответствие между калориметрическими данными, теплотой, вычисленной по данным изотерм с использованием уравнения Брунауера, Эмметта, и Теллера, и вычислениями по данным ионной дипольной модели. Было сделано заключение, что электростатические силы между адсорбированными катионами и молекулами воды являются доминирующими силами при гидратации глины. Таким образом, при низком содержании влаги, гидратируются только адсорбированные ионы Ca. Была замерена теплота, выделяющаяся при сокращении пластинок Na и формровании, вследствии этого, пакетов Ca, и сделано предположение, что эта энергия является ведущей силой для явлений расслаивания.

Resümee—Wasserdampfadsorptionsisothermen, c-Abstand und Immersionshitze in Wasser von gemischten Na/Ca Montmorilloniten wurden bei 25°C und verschiedenen RH gemessen. Die kalorimetrischen Daten, die Hitze, welche von den Isothermen mit der BET-Gleichung errechnet wurde und Berechnungen von den Ionendipolmodellen stimmten gut überein. Es wurde beschlossen, daß die elektrostatischen Kräfte zwischen den adsorbierten Kationen und den Wassermolekülen die Hauptkräfte in der Hydration der Tonerden sind. Daher sind bei niedrigem Wassergehalt nur die adsorbierten Ca-Ionen hydratisiert. Die Hitze, die freigelassen wird, wenn Natriumtäfelchen zusammenkommen, um Ca-Päckchen zu formen, wurde gemessen, und es wurde vorgeschlagen, daß dieser Energieausdruck die treibende Kraft für die Entmischungsphänomen ist.

Résumé—Les isothermes d'adsorption de montmorillonite composée d'un mélange Na/Ca pour la vapeur d'eau, l'espacement-c, et la chaleur d'immersion dans l'eau ont été mesurés à 25°C et à des humidités relatives (RH) variées. Il y avait un bon accord entre les données calorimétriques, la chaleur calculée des isothermes par l'emploi de l'équation BET, et les calculs du modèle de l'ion dipôle. Il a été conclu que les forces électrostatiques entre les cations adsorbés et les molécules d'eau sont les forces dominantes dans l'hydratation de l'argile. C'est ainsi qu'à des humidités basses, seuls les ions de Ca adsorbés sont hydratés. La chaleur produite par la condensation de plaquettes de Na pour former des paquets de Ca a été mesurée, et il a été suggéré que ce terme d'énergie est la force responsable pour le phénomène de séparation.