

WATER VAPOR ISOTHERMS AND HEAT OF IMMERSION OF Na- AND Ca-MONTMORILLONITE SYSTEMS. III. THERMODYNAMICS¹

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Abstract—The integral thermodynamic quantities of adsorbed water on Na- and Ca-montmorillonite have been calculated from water adsorption isotherms on Na- and Ca-montmorillonite at 298° and 313°K and from one adsorption isotherm and calorimetric measurements at 298°K. The integral entropy values decrease and then increase as the amount of adsorbed water approaches zero. In both systems, the curves approach the entropy value of free liquid water at the high content water. The thermodynamics of adsorbate on a non-inert adsorbent is discussed in some detail. The two-isotherm method gives the energy change of the water phase only, whereas the calorimetric method gives the energy change of the whole system (clay, exchangeable cations, and the adsorbed water). Only when the energy changes in the solid phase are negligible (=inert surface) should the two methods give similar results. An hypothesis was developed to explain the entropy-change data of water adsorbed on clay surfaces, in which the clay surface behaves as a non-inert adsorbent.

Key Words—Adsorption, Heat of immersion, Montmorillonite, Thermodynamics, Water.

INTRODUCTION

The adsorption of water molecules on montmorillonite under controlled vapor pressures and heat of immersion in water have been studied by a number of investigators (Brooks, 1960; Fripiat *et al.*, 1965; Kijne, 1969; Keren and Shainberg, 1975, 1979). Keren and Shainberg (1975) proposed a model which described quantitatively the interactions among the clay surfaces, the ions, and the water molecules. The experimental data of this investigation can also be used to calculate thermodynamic quantities which may in turn be used as an indication of the physical properties of the adsorbed water.

When n moles of water are adsorbed on the surface of montmorillonite, there is a change in the entropy, energy, and free energy per mole of the adsorbed water molecules. However, since the adsorption takes place in the vapor phase, it is impossible to measure the change of temperature accompanying the slow adsorption of water molecules. Thus, it is necessary to calculate the heat changes and the derived functions. These functions can be calculated by either of two methods: (1) By determining adsorption isotherms at more than one temperature, as suggested by Hill (1950) and as applied to clay systems by several investigators (Kohl *et al.*, 1964; Cary *et al.*, 1964; Sharma *et al.*, 1969); and (2) By combining calorimetric heat of immersion data with one adsorption isotherm at the same temperature, as suggested by Jura and Hill (1952) and as applied to clay systems by Kohl *et al.* (1964), Kinje

(1969), and many others. From these two methods, the integral thermodynamic quantities can be obtained.

In general, all thermodynamic functions represent the net change of the system. This means that the net change in a thermodynamic property includes the changes that might take place in all the components in the same system. Literature values of thermodynamic quantities vary widely. Kohl *et al.* (1964), Van Olphen (1965), and Kijne (1969) found a negative change of entropy (relative to bulk water) for adsorbed water on Li-kaolinite or Na-vermiculite and on Na- and Ca-montmorillonite. They obtained their data from the adsorption isotherms and calorimetric measurements. Conversely, Martin (1960) reported positive values of integral entropy change when water adsorbed on Na- and Li-kaolinite between 0 and 50% relative humidity, and Sharma *et al.* (1969) and Cary *et al.* (1964) found positive values for adsorption of water on soils by using two adsorption isotherms at two temperatures. The objectives of the present study are (1) to compare the thermodynamic quantities on the same system by the two methods described, and (2) to measure the effect of the adsorbed ion (Na/Ca) on the thermodynamic quantity.

THEORY

To calculate integral quantities from the two methods mentioned above, an evaluation of the spreading pressure, ϕ , is required. This quantity is given by Bangham (1937), Bangham and Mosallam (1938), and Bangham and Razouk (1937):

$$\phi = \gamma^0 - \gamma^n = RT \int_{P=0}^P \Gamma d \ln P \quad (1)$$

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where γ^0 and γ^n are the free energies required to produce 1 cm² of new surface of solid in a vacuum when the surface is adsorbed with n moles of water per cm² and equilibrated with the water molecules in the gas phase at pressure P , respectively, and Γ is the concentration of water at the surface, in moles/cm², as given by

$$\Gamma = \theta/MA \quad (2)$$

where θ is the grams adsorbed per gram of clay, A is the specific surface area (cm²/g), and M is the molecular weight of the vapor.

By substituting Eq. (1) into Eq. (2),

$$\phi = RT/MA \int_{P=0}^P \theta d \ln P \quad (3)$$

The expression on the right-hand side of Eq. (3) is evaluated from the experimental adsorption isotherm. If the equation of the isotherm, i.e., the relationship between θ and P , is known over the whole range of study, the integration can be performed analytically. However, this is rarely so, and it is usually necessary to resort to a graphical method by determining the area under the semi-log isotherm. The greatest difficulty in the computation lies in the low-pressure region.

Jura and Harkins (1944) found that at relative pressures below approximately 0.001, the film behaves like a gas. Thus, it is simple to extrapolate the curve to zero pressure. This extrapolation (which gives a straight line) might cause a serious error in the spreading pressure values at low relative humidities, and the error decreases with the increase in the relative humidity.

The integral enthalpies change, ΔH_s , and the entropies change, ΔS_s , may be calculated from two adsorption isotherms at two temperatures by the following equations (Hill *et al.*, 1951):

$$\Delta H_s = (H_s - H_\ell) = \frac{T_1 \cdot T_2}{T_2 - T_1} R \ln \left| \frac{X_1}{X_2} \right|_\phi \quad (4)$$

$$\Delta S_s = (S_s - S_\ell) = R/2 \left[\frac{T_1 + T_2}{T_1 - T_2} \ln \frac{X_2}{X_1} - \ln(X_1 \cdot X_2) \right]_\phi \quad (5)$$

where H_s and H_ℓ are the average molar enthalpy of the adsorbed phase, and pure bulk water, respectively; S_s and S_ℓ are the average molar entropy of the adsorbed phase and the pure bulk water, respectively; X_1 and X_2 are the vapor pressure ratio P/P_0 at temperatures T_1 and T_2 , respectively; and the other terms have been defined.

To calculate the thermodynamic properties of adsorbed water from combination of calorimetric heat of immersion data and one adsorption isotherm at the

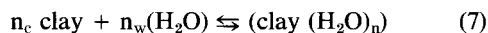
same temperature, the following relations, derived by Jura and Hill (1952) may be used. According to these authors,

$$T(S_s - S_l) = (U - U_0)/n + \frac{\phi}{\Gamma} - RT \ln P/P_0 \quad (6)$$

where S_s and S_l are the integral entropy of the adsorbed phase and the pure bulk water, respectively; U_0 is the heat of immersion of the dry clay in water (cal/g); U is the heat of immersion of the clay with n moles of water per gram pre-adsorbed on it; and P/P_0 is the relative humidity corresponding to the equilibrium amount of water adsorbed on the clay; all the other terms have been defined.

It is clear that the thermodynamic functions for water calculated by this method do not involve any assumptions as to the behavior of the system. The thermodynamic quantities derived from the experimental observations reflect the net effect of all the forces acting in the system. The derivation of Eq. (6) was based on statistical mechanical considerations for an ideal gas adsorbed on an inert solid surface. The same equation can be derived from simple thermodynamic relations. In doing so, it may be easier to check the assumptions involved.

Consider the adsorption reaction for n_w moles of water adsorbed on n_c moles of clay:



The energy of the reactants, E^r , is derived from a combination of the first and second laws of thermodynamics (see, for example, Eq. 3.115 in Daniels and Alberty, 1967):

$$E^r = TS^r - PV^r + n_c \mu_c^r + n_w \mu_w^r + \gamma^r A \quad (8)$$

where the superscript r stands for reactants, μ_c and μ_w are the chemical potential of the dry clay and pure bulk water, respectively, γ is the surface tension of the dry surface (= surface free energy in ergs/cm²), and A is the interface area. Similarly, the energy of the products is given by Eq. (9):

$$E^p = TS^p - PV^p + n_c \mu_c^p + n_w \mu_w^p + \gamma^p A \quad (9)$$

where the superscript p stands for products and the other symbols have been defined.

The energy change for the reaction described by Eq. (7) at constant temperature and pressure is:

$$\Delta E = E^p - E^r = T(S^p - S^r) - p(V^p - V^r) + n_c(\mu_c^p - \mu_c^r) + n_w(\mu_w^p - \mu_w^r) + A(\gamma^p - \gamma^r) \quad (10)$$

In deriving Eq. (10) it is assumed that the surface area does not change during the adsorption reaction. This energy change is also equal to

$$\Delta E = q - p(V^p - V^r) \quad (11)$$

where q is the heat of the reaction.

By combining Eq. (10) and (11), one obtains

$$q = T(S^p - S^r) + n_c(\mu_c^p - \mu_c^r) + n_w(\mu_w^p - \mu_w^r) + A(\gamma^p - \gamma^r) \quad (12)$$

where:

(1) $(\mu_w^p - \mu_w^r)$ is the change in chemical potential between water adsorbed on the clay (μ_w^p) and pure bulk water (μ_w^r). This free energy change is obtained from the equilibrium relative humidity by Eq. (13).

$$\mu_w^p - \mu_w^r = RT \ln P/P_0 \quad (13)$$

(2) The difference in the surface tension between adsorbed and clean interface is identical with the spreading pressure given in Eq. (3)

$$\phi = (\gamma^r - \gamma^p) \quad (14)$$

where the reactant is the dry clay and the product is the solid surface covered with water molecules.

Introducing Eq. (13) and (14) in Eq. (12) gives

$$q = T(S^p - S^r) + n_c(\mu_c^p - \mu_c^r) + n_w RT \ln(P/P_0) - A\phi \quad (15)$$

Rearranging Eq. (15) and expressing the thermodynamic function for one mole of adsorbed water ($n_w = 1.0$) gives

$$T(S^p - S^r) + n_c(\mu_c^p - \mu_c^r) = q + \phi/\Gamma - RT \ln P/P_0 \quad (16)$$

The right-hand side of Eq. (16) is identical to Eq. (6). The left-hand side of Eq. (16) is identical to the left-hand side of Eq. (6) only if the following conditions are satisfied:

- (1) $\mu_c^p - \mu_c^r = 0$, which means that the chemical potential of the clay is unaffected by introducing adsorbed water between the clay platelets.
- (2) $S^p - S^r = S_w^p - S_w^r$, which means that the entropy change of the system is identical to the entropy change of the water.

Both (1) and (2) are an indication for the requirements of an inert solid phase. The interlayer adsorption process in montmorillonite clay is essentially different from the adsorption on an inert surface. During the adsorption of water on clay surfaces various reactions can take place. The water molecules may interact with the clay surfaces to change their chemical potential. Water molecules enter the interlayer space to change the lattice geometry and the position of adsorbed ion. These effects are discussed in more detail below. However, it is clear that these effects make the terms on the left-hand side of Eq. (16) more complex than has been assumed.

MATERIALS AND METHODS

The clay preparation and the experimental methods for determination of the adsorption isotherms and the

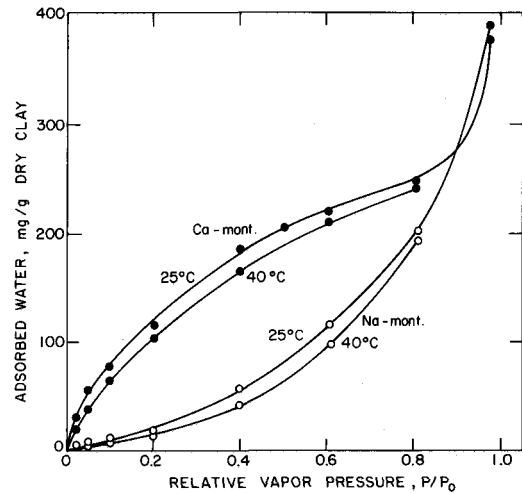


Figure 1. Adsorption isotherms of water molecules on Na- and Ca-montmorillonite at 25° and 40°C.

heat of immersion were described earlier by Keren and Shainberg (1975, 1979).

RESULTS AND DISCUSSION

The adsorption isotherms of water molecules on Na- and Ca-montmorillonite at 25° and 40°C are presented in Figure 1. The amount of water adsorbed on montmorillonite at 25°C is greater than the corresponding amount at 40°C. This phenomenon is readily explained by Le Chatelier's principle. Since vapor adsorption is an exothermic process (see below), an increase in temperature results in a decrease in the adsorbed water. For both temperatures, the Ca-isotherms are concave downward while the curves of water vapor adsorption by Na-montmorillonite are concave upward. Analysis of these shapes according to the BET theory (Keren and Shainberg, 1975) indicates that in the Ca-systems the energy of interaction between the first monolayer of adsorbed water molecules and the cations is greater than the energy of condensation of the subsequent layers of water molecules. Conversely, in Na-montmorillonite the difference between these two energy terms is not as big, indicating that the hydration forces in Na-montmorillonite are less intensive than those in Ca-montmorillonite.

Based on the Clausius-Clapeyron equation, it is possible to calculate the integral and differential change in enthalpy and entropy from these two adsorption isotherms. The assumptions involved in these calculations are: (1) an inert adsorbent; (2) Clausius-Clapeyron equation approximation; and (3) linear extrapolation of Eq. (3) to $p = 0$. Since the properties of adsorbed water (order, mobility etc.) are related to the integral change in the thermodynamic properties, only these functions are presented in detail.

The integral enthalpy of adsorbed water on Na- and

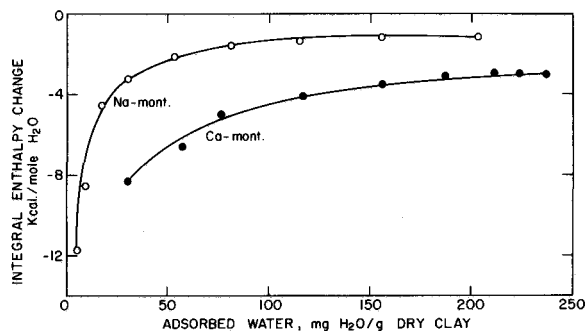


Figure 2. Integral enthalpy changes of water adsorbed on Na- and Ca-montmorillonite (calculated from the two adsorption isotherms; Eq. (4)).

Ca-montmorillonite obtained from water adsorption isotherms at two temperatures (Eq. (4)) and from one adsorption isotherm and calorimetric measurements (Eq. (6)) are presented in Figures 2 and 3, respectively. The experimental data used in Eq. (4) are presented in Figure 1, and those used in Eq. (6) are given in Figure 5 of Keren and Shainberg (1975). The enthalpy changes, ΔH_s , are negative for both Na- and Ca-montmorillonite. This implies that water molecules lose energy upon being transferred from bulk water into the adsorbed state. The shapes of the integral enthalpy curves calculated from the Clausius-Clapeyron equation (Figure 2) for both Na- and Ca-montmorillonite differ very much from the values calculated from the calorimetric measurement (Figure 3). It is evident that only one of the methods can be used to characterize the properties of adsorbed water (*vide infra*).

The integral entropy, ΔS_s , of adsorbed water on Na- and Ca-montmorillonite obtained from water adsorption isotherm at two temperatures (Eq. (5)) and from one adsorption isotherm and calorimetric measure-

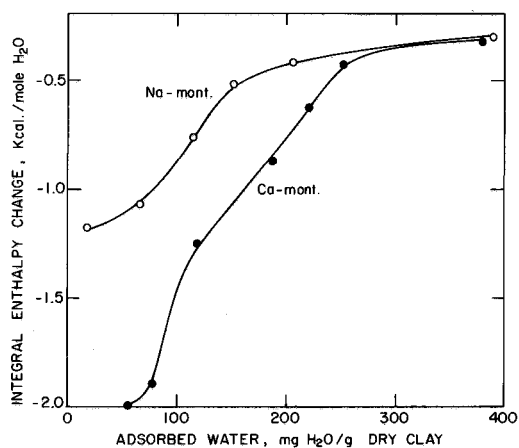


Figure 3. Integral enthalpy changes of water adsorbed on Na- and Ca-montmorillonite at 25°C (calculated from the calorimetric data; Eq. (6)).

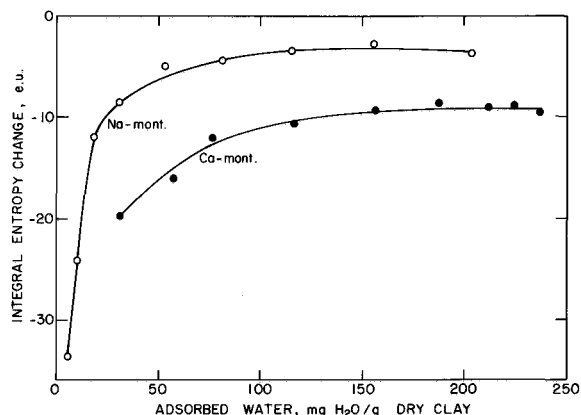


Figure 4. Integral entropy changes of water adsorbed on Na- and Ca-montmorillonite (calculated from the two adsorption isotherms; Eq. (5)).

ments (Eq. (6)) are presented in Figures 4 and 5, respectively. As with the enthalpy data, the entropy values obtained from the Clausius-Clapeyron equation are much more negative than the values calculated from Jura and Hill's equation. Moreover, whereas the entropy values of Figure 4 decrease asymptotically as the water content decreases, the integral entropy values calculated from Eq. (6) decrease and thereafter increase as the amount of adsorbed water approaches zero. In both systems the curves approach the entropy value of free water at the high content water. Kohl *et al.* (1964) and Kijne (1969) obtained similar results.

If one considers first the integral entropy change of the adsorbed water (the Clausius-Clapeyron equation and Figure 4), it is evident that the entropy of adsorbed water decreases continuously as the amount of adsorbed water decreases. It is also evident that the strong interaction with the adsorbed cations results in a high degree of orientation of the adsorbed water lead-

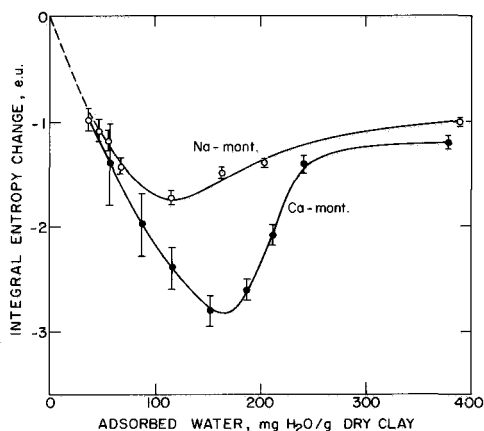


Figure 5. Integral entropy changes of water adsorbed on Na- and Ca-montmorillonite at 25°C (calculated from the calorimetric data; Eq. (6)).

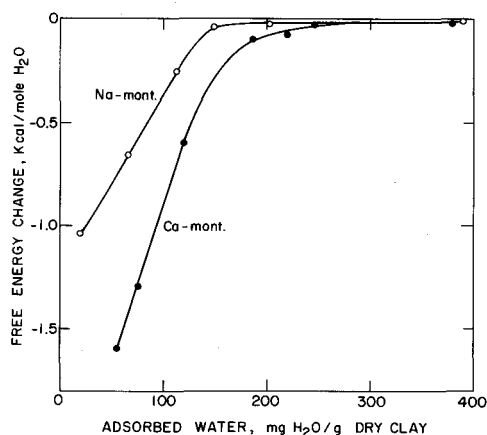


Figure 6. Integral free energy changes for water adsorbed on Na- and Ca-montmorillonite at 25°C (calculated from the calorimetric data; Eq. (6)).

ing to lower entropy. The high degree of dissociation of the adsorbed water and the high acidity of adsorbed water in the low range of moisture, both support the conclusion of strong interaction between adsorbed water and the clay-cation surface. The big difference obtained between Na- and Ca-clays suggests that the interaction is mainly with the adsorbed cation.

It is evident from the theoretical discussion in the introduction that the quantities derived from the Clausius-Clapeyron equation apply strictly to the adsorbed water. Conversely, the thermodynamic quantities derived from the calorimetric measurements depend also on other changes in the system. If the Na- and Ca-montmorillonite were completely inert during the adsorption of water, and if their surface characteristics were independent of adsorbed water, the thermodynamic quantities calculated by both methods (Eq. (5, 6)) should be identical.

The fact that the change in integral entropy calculated from the heat of immersion is much smaller than the change in integral entropy calculated from the adsorption isotherms suggests that the changes in entropy of the surfaces and the adsorbed ions counterbalance the changes in the water. It is possible that the interaction between the water molecules and the surfaces releases some of the tension and the low degree of freedom that the clay surface experiences in the dry state (Ravina and Low, 1972) and the exchangeable ions are free to move in films of water. Thus, with an increase in adsorbed water, the entropy of the surfaces increases whereas the entropy of the water decreases, as shown in Figure 5.

According to Figure 5, the minimum values for the integral entropy are found at about 115 and 180 mg H₂O/g clay for Na- and Ca-montmorillonite, respectively. These values are very close respectively to the amounts of water in one and two monolayers of water adsorbed

on montmorillonite (Keren and Shainberg, 1975). The possible arrangements of the adsorbed water is particularly restricted under these conditions, because almost all the surface is already filled and the entropy of the system is at its minimal value.

It should be pointed out that the estimated error in the integral entropy (Figure 5) is grossly exaggerated. The lower limit of the value of each point has been calculated by cutting off the integral (Eq. (3)) at the lower experimental point while the upper limit has been calculated by assuming that the integral is between the lowest experimental point and zero pressure equals twice the area of the triangle of the linear extrapolation. As can be seen, the error decreases at higher values of adsorbed water and does not affect significantly the determination of the exact minimum discussed above. The calculated errors in the entropy values presented in Figure 2 are about 10 and 30% for Na- and Ca-montmorillonite, respectively, and the errors decrease as the water content increases.

With a further increase in the amount of adsorbed water, beyond the one or two monolayers, continuous films of water with three-dimensional configuration form, and the possible arrangements of the exchangeable ions increases in these films, leading to an increase in the entropy of the system. When only one or two layers of water molecules are present, the adsorbed cations are located very close to the negative site of the clay, and their entropy is low. With a further addition of water, the average distance between the cation and the negative surface increases, leading to greater mobility and higher entropy of the adsorbed cation (Shainberg and Kemper, 1966). The entropy change of the Na-clay system is less negative than that of the Ca-clay system, probably because the Na ions are structure-breaking, whereas Ca ions are structure-making at high concentration solutions (Choppin and Buijs, 1963).

The integral free energy of Na- and Ca-montmorillonite calculated from Eq. (6) is presented in Figure 6. The free energy change decreases as the water content increases for both Na- and Ca-montmorillonite. The free energy change in the Ca-system is larger than in the Na-system at the low water content up to 220 mg H₂O per g clay. This amount of water corresponds to two monolayers of adsorbed water (Keren and Shainberg, 1975). The effect of the Ca ions on the free energy of adsorbed water is readily understood if one considers the strong electrostatic interaction between the divalent cations and the water molecules.

Above 250 mg H₂O per g clay the free energy change of adsorbed water in both Na- and Ca-montmorillonite systems is similar, and approaches zero. This indicates that as the water content increases, the adsorbed water has properties similar to those of bulk water, and the influence of the clay surface does not extend beyond a few molecular layers of adsorbed water.

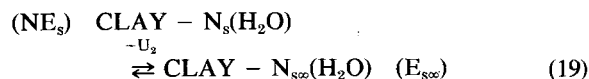
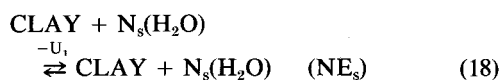
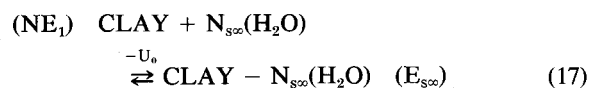
CONCLUSIONS

The differential and integral enthalpy and entropy of montmorillonite-water systems may be calculated either from water adsorption isotherms at two temperatures or from one adsorption isotherm and calorimetric measurements made at the same temperature. It was found that the two methods do not give the same results. The two adsorption isotherms give lower values for both the enthalpy and entropy of the clay-water system, compared with the values obtained by the calorimetric method. Following the derivation of the pertinent equations, it is evident that the two isotherms method gives the energy change of the water phase only, whereas the calorimetric methods give the energy change of the whole system (clay, exchangeable cation, and the adsorbed water). Only when the energy changes in the solid phase are negligible (i.e., inert surfaces), should the two methods give similar results.

APPENDIX

The relation between the heat of immersion and the enthalpy change in the water adsorption process

The reaction for getting the heat of immersion (Eq. (17)) could be split into two parts: (1) the partial wetting of the dry clay with a given amount of adsorbed water (Eq. (18)); and (2) the continued wetting of the clay with an infinite amount of water (Eq. (19)).



Where N_s and $N_{s\infty}$ are the amount of adsorbed water (in moles) at certain and infinite amounts, respectively; E_1 and E_s are the internal energy of the system at free and adsorbed water states, respectively; U_0 and U_2 are the heat evolved when, respectively, dry clay and clay adsorbed with N_s moles of water are immersed in water, and U_1 is the heat evolved when N_s moles of water are adsorbed on dry clay.

From Eq. (17), and (18), and (19) it is possible to evaluate the following equations:

$$NE_1 - U_0 = E_{s\infty} \quad (20)$$

$$NE_s - U_2 = E_{s\infty} \quad (21)$$

Combining Eq. (20) and (21) gives:

$$NE_1 - U_0 = NE_s - U_2 \quad (22)$$

$$N(E_1 - E_s) = U_0 - U_2 \quad (23)$$

$$E_1 - E_s = (U_0 - U_2)/N \quad (24)$$

$$E_s - E_1 = (U_2 - U_0)/N \quad (25)$$

thus

$$H_s - H_1 = E_s - E_1 + \phi/\Gamma = (U_2 - U_0)/N + \phi/\Gamma \quad (26)$$

where H_1 and H_s are the enthalpy of the water molecules in the free liquid water and the adsorbed phase, respectively; ϕ is the spreading pressure, and Γ is the amount of water adsorbed on one unit of adsorbent surface.

Thus

$$T(S_s - S_1) = \Delta H_s - \Delta G_s = (U_2 - U_0)/N + \phi/\Gamma - RT \ln P/P_0 \quad (27)$$

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Резюме—Высчитывались полные термодинамические количества воды, адсорбированной Na- и Ca-монтмориллонитом, по изотермам адсорбции воды Na- и Ca-монтмориллонитом при 298° и 313°K и по одной адсорбционной изотерме и калориметрическим измерениям при 298°K. Полные величины энтропии уменьшаются и затем возрастают, когда количество адсорбированной воды приближается к нулю. В обеих системах, кривые приближаются к величине энтропии свободной жидкой воды при высоком содержании воды. Обсуждаются некоторые детали термодинамики адсорбата на неинертном адсорбенте. Двух-изотермный метод дает изменение энергии только водной фазы, тогда как калориметрический метод дает изменение энергии всей системы (глины, обменных катионов, и адсорбированной воды). Только когда изменения энергии в твердой фазе незначительны (= инертной поверхности) оба метода должны показать сходные результаты. Была предложена гипотеза для объяснения изменений энтропии воды, адсорбированной на глинистых поверхностях, в которых глинистая поверхность ведет себя как неинертные адсорбенты. [N. R.]

Resümee—Die integralen thermodynamischen Mengen von an Na- und Ca-Montmorillonit adsorbiertem Wasser wurden aus den Wasseradsorptionsisothermen auf Na- und Ca-Montmorillonit bei 298° und 313°K berechnet, sowie aus einem Adsorptionsisotherm und aus kalorimetrischen Messungen bei 298°K. Die Werte der integralen Entropie nehmen ab und steigen dann wieder an, wenn die Menge des adsorbierten Wassers gegen Null geht. In beiden Systemen erreichen die Kurven den Entropiewert von freiem flüssigem Wasser bei hohem Wassergehalt. Die Thermodynamik des adsorbierten Stoffes auf einen nicht-inerten Adsorber wird detailliert diskutiert. Die Zweiisothermenmethode gibt nur die Energieänderung der Wasserphase, während die kalorimetrische Methode die Energieänderung des ganzen Systems (Ton, austauschbare Kationen, adsorbiertes Wasser) liefert. Nur wenn die Energieänderungen in der festen Phase vernachlässigen sind (= inerte Oberfläche), sollten die beiden Methoden zu ähnlichen Resultaten führen. Es wurde eine Hypothese entwickelt, um die Werte der Entropieänderung von Wasser zu erklären, das an Tonoberflächen adsorbiert ist, bei denen die Tonoberfläche als nicht-inerter Adsorber wirkt. [U. W.]

Résumé—Les quantités intégrales thermodynamiques d'eau adsorbée sur la montmorillonite-Na et -Ca ont été calculées à partir d'isothermes d'adsorption d'eau sur la montmorillonite-Na et -Ca à 298° et 313°K, et à partir d'un isotherme d'adsorption et de mesures calorimétriques à 298°K. Les valeurs intégrales d'entropie décroissent et ensuite augmentent à mesure que la quantité d'eau adsorbée approche zero. Dans les deux systèmes les courbes approchent la valeur d'entropie de l'eau liquide à haute teneur en eau. Les thermodynamiques d'un adsorbat sur un adsorbant non-inerte sont discutés en détail. La méthode à deux isothermes ne donne que le changement d'énergie de la phase eau, tandis que la méthode calorimétrique donne le changement d'énergie du système entier (argile, cations échangeables, et eau adsorbée). Les deux méthodes ne devraient donner des résultats semblables que lorsque les changements d'énergie dans la phase solide sont négligeables (surface inerte). Une hypothèse a été développée pour expliquer les données de changements d'entropie d'eau adsorbée sur les surfaces argileuses dans lesquelles la surface argileuse se comporte comme adsorbant non-inerte. [D.J.]