HEATS OF COMPRESSION OF
CLAY–WATER MIXTURES*

B. D. Kay† and Philip F. Low

Department of Agronomy, Purdue University, Lafayette, Indiana 47907, U.S.A.

Abstract—Heats of compression of glass bead–water and clay–water mixtures were determined from the peak heights of the thermograms produced when these mixtures were subjected to pressure in a Calvet differential microcalorimeter. It is known that the heat of compression is directly proportional to the peak height. When the latter quantity was plotted against the pressure applied to any mixture, two intersecting straight lines were obtained. The change in slope at the point of intersection was interpreted as being the result of a pressure-induced higher-order phase transition in the water.

The differential peak height, ϵ, was defined as the rate of change of peak height with pressure/g of water present in the mixture. Hence, it is directly proportional to the rate of change of the heat of compression with pressure/g of water. Values of ϵ were determined for both glass bead–water and clay–water mixtures containing different proportions of solids. It was found that ϵ remained nearly constant with increasing proportions of glass beads, whereas, it varied in a non-uniform way with increasing proportions of clay. Also, its values in the clay–water mixtures were relatively high. Calculations showed that the difference in ϵ values for the two mixtures could not be ascribed to the exchangeable cations associated with the clay particles. Consequently, it was ascribed to the effect of the particle surfaces on the structure of the vicinal water.

The nature of water in clay–water systems has been discussed in several reviews (Low, 1961; Martin, 1962; Graham, 1964; Low and White, 1970). From these reviews it is evident that a controversy exists. The available evidence has been interpreted as being in favor of long-range order in the interlayer water, as being opposed to such order, or as being inconclusive. To help resolve the controversy, the authors conducted experiments on the heat of compression of water in aqueous systems of Na–montmorillonite. Our hypothesis was that the structure of this water is different from that of bulk water. Therefore, it should respond differently to the application of pressure and yield a different heat of compression.

Some of our results have already been published (Kay and Low, 1972). They show that the heat of compression of the water–montmorillonite system, its electrical resistance and the e.m.f. between reversible electrodes inserted in it, undergo an abrupt change at 20–30 psi. This abrupt change occurs only if the concentration of montmorillonite is above $\sim 3.0\%$ by vol and if a small amount of adsorbed hydrous aluminum oxide is present. It was interpreted as being the result of a pressure-induced, higher-order structural transition in the water.

Additional tests of our hypothesis are reported in the present paper. In particular, it is our intention to show how the heat of compression of an aqueous Na–montmorillonite system changes with the concentration of Na–montmorillonite and with the amount of adsorbed hydrous aluminum oxide at pressures up to 7000 psi.

MATERIALS AND METHODS

Sodium–montmorillonites containing 0, 0·37 and 0·7 m-equiv. of hydrous aluminum oxide/g montmorillonite were prepared from the $<2\,\mu m$ fraction of Wyoming bentonite (Volclay 200 from the American Colloid Co.) as described by Kay and Low (1972). These montmorillonites, which will be referred to hereafter as Na–clay, Na/Al–clay and Na/Al*–clay, respectively, were mixed in different proportions with water. Then, the heats of compression of the mixtures were determined at 25°C. The procedure was as follows.

A weighed amount of freeze-dried clay was placed in the barrel of a hypodermic syringe, the plunger of the syringe was inserted far enough to confine the clay to the desired volume, the syringe was evacuated and degassed deionized water was admitted through its open tip, under vacuum. After 3–5 days of equilibration, the resulting consistent mixture was extruded through an 18-gauge hypodermic needle into a special stainless-steel cell (3·66 ml capacity) containing degassed, deionized water. Thus, it displaced the water in the cell and remained gas-free.

Simpler ways could have been devised for preparing a clay–water mixture and introducing it into the calorimeter cell. However, the present technique was adopted to preclude any significant heat effects due to particle rearrangement with time. Earlier, Davey and Low (1968, 1971) showed that extrusion of a consistent clay–water mixture through an 18-gauge hypo-

---

dermic needle orients the particles into a stable, probably parallel arrangement.

When the cell was full of the mixture, a copper gasket was placed on its rim and it was screwed onto a stainless-steel cap that was connected by means of a stainless-steel delivery tube to a Bourdon gauge and a hand-operated hydraulic pump. Then it was inserted into one microcalorimetric element of a Calvet differential microcalorimeter (Calvet and Prat, 1956, 1963). Since the delivery tube had been filled previously with degassed, deionized water, a measured pressure could be transmitted hydraulically from the pump to the mixture. A conventional cell was filled with water, capped and inserted into the opposing microcalorimetric element. It was not connected to a source of pressure and served as a reference.

The heat of compression of the mixture in the cell was not measured until thermal stability was achieved. Generally, a minimum of 12 hr elapsed between the introduction of the cell into the microcalorimeter and the application of pressure. Then pressure was applied in successive increments over a period of 24 hr. Each increment, which was measured to the nearest 25 psi, caused the release of heat and produced a thermogram (e.m.f. in μV vs time). The thermogram was recorded by a Keithley Model 150 AR microvoltmeter connected to a Sargent Model MR recorder. When the first series of measurements was completed, the pressure was reduced to zero and the process was repeated. Hence, there were two series of measurements on each mixture.

The thermogram consisted essentially of a ballistic-type peak. Both theory and experiment (Calvet and Prat, 1956; 1963) indicate that, for a thermogram of this kind,

$$E_m = -\alpha Q \qquad (1)$$

where E_m is the peak height, i.e. the maximum pen displacement on the recorder chart, Q is the heat released and α is a proportionality constant. The negative sign is included to indicate that when heat is released (Q is negative) the pen displacement is positive. Since the value of α is difficult to determine experimentally, we expressed the heat released in terms of the peak height in microvolts. The peak height for any pressure consisting of the sum of several increments was obtained by adding the respective peak heights for those increments. At the conclusion of the experiment, the clay content of the sample was determined gravimetrically. To convert weight to volume, a density of 2·8 g/cm³ was used for the clay.

Heats of compression were also determined on glass bead–water mixtures. Prior to introducing the glass-beads into the water-filled cell, they were boiled in deionized water to eliminate adsorbed air. The procedure used was the glass bead–water mixtures was the same as that used with the clay–water mixtures.

In order to examine in greater detail the heats of compression at relatively low pressures, i.e. up to 400 psi, the pressure delivery system discribed previously (Kay and Low, 1972) was employed. With this system, applied pressures could be measured to within 0·5 psi.

RESULTS AND DISCUSSION

The interstitial water in a glass bead–water mixture should have the properties of bulk water if the specific surface of the glass beads is small. In addition, the glass beads should have a negligible heat of compression. Therefore, to determine the effect of the volume percentage of *inert* solids on the heat of compression of a mixture of such solids and water, compression studies were conducted on glass bead–water mixtures. The glass beads in these mixtures had an average weight of 0·089 g and an average volume, determined by means of a pycnometer, of 0·040 cm³. Hence, the average values of their density, radius and specific surface were 2·225 g/cm³, 0·212 cm and 6·34 × 10⁻⁴ m²/g, respectively. The latter value is insignificant in comparison with the specific surface of the clay, i.e. ~800 m²/g. The results of the compression studies with the glass bead–water mixtures are reported in Fig. 1. In this figure, the data points represent both the first and second series of measurements because there was no difference between them.

Note that the curves consist of two linear segments, with different slopes, which intersect at a pressure of about 3000 psi. The relative positions depend on the amounts of water in the corresponding mixtures. Because replacement of the water in the system by mercury resulted in a constant linear relation between peak height and pressure over the entire pressure range, the breaks in the curves must be characteristic of the water. Regression equations and S.D. from regression were calculated for each curve for the pressure ranges of 400–2000 psi and 4000–6000 psi, i.e. for the linear segments on either side of the breaks. The results are given in Table 1.

To our knowledge, there has been no previous report of a sudden change in any property of pure bulk water at a pressure of ~3000 psi. In order to see if there is any additional evidence for such a change, data from the National Engineering Laboratory Steam Tables (1964) were used to plot the speci-
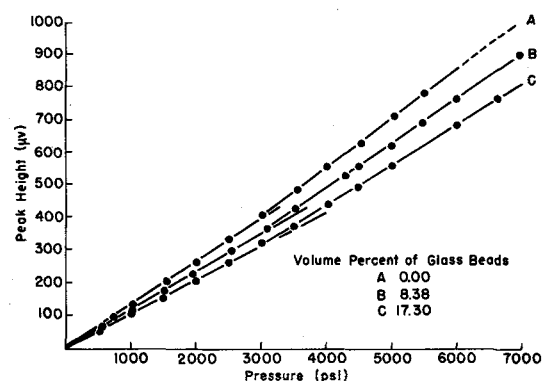

Fig. 1. Change of peak height, E_m, with pressure in the range 0–7000 psi for glass bead–water mixtures containing different proportions of glass beads.

Table 1. Regression equations and standard deviations from regression, S_b, for the dependence of peak height, E_m, on applied pressure, P, for glass bead–water mixtures containing different concentrations of glass beads.

Concentration of glass beads (% by vol)	Regression Equation (400–2000 psi)	S_b ($\times 10^6$)	Regression Equation (4000–6000 psi)	S_b ($\times 10^6$)
0.00	$E_m=0.1327P-1.3$	0.302	$E_m=0.1516P-53.1$	0.563
8.38	$E_m=0.1176P-0.9$	0.246	$E_m=0.1386P-65.7$	0.487
17.30	$E_m=0.1047P-1.2$	0.313	$E_m=0.1251P-61.0$	0.749

fic entropy and specific enthalpy of water vs pressure at different temperatures and the specific volume of water vs temperature at different pressures. These plots are relevant because, for a reversible process in a closed system, the following thermodynamic relations hold:

$$(\partial Q/\partial P)_T = T(\partial S/\partial P)_T = (\partial H/\partial P)_T - V$$
$$= -T(\partial V/\partial T)_P \quad (2)$$

where Q is the heat released or absorbed, S is the entropy, H is the enthalpy, V is the volume, P is the pressure and T is the absolute temperature of the system. The plots of specific entropy and specific enthalpy vs pressure appeared to consist of two linear segments of slightly different slope which intersected or merged at a pressure depending on temperature. At 25°C, this pressure was near 3000 psi. The plots of specific volume vs temperature at different pressures were straight lines which appeared to change slope slightly at a pressure near 3000 psi. However, since the study of pure bulk water was not our objective, we did not attempt to confirm our visual observations by a detailed statistical analysis of the data. In this regard it should be noted that Whalley[*] claims that his P–V data for pure bulk water (Kell and Whalley, 1965) do not support these observations. Nevertheless, we do want to call attention to them. Also, we want to point out that, if the obvious breaks in the curves of Fig. 1 are not characteristic of pure bulk water, they must be attributable to interaction of the glass bead surfaces with the water.

The peak height vs pressure curve for one of the clay–water mixtures is shown in Fig. 2. Again, the data points represent both series of measurements because they were entirely reproducible. Corresponding curves for the other mixtures were similar in shape. Each consists of two linear segments, with different slopes, which intersect at a pressure of about 3000 psi. However, their relative position did not vary uniformly with the volume percentage of solids.

It should be noted here that the process of compression was found to be completely reversible, i.e. the compression and decompression curves were coincident.

The differential peak height, ϵ, is defined by

$$\epsilon = (dE_m/dP)/m_w = -\alpha(dQ/dP)/m_w \quad (3)$$
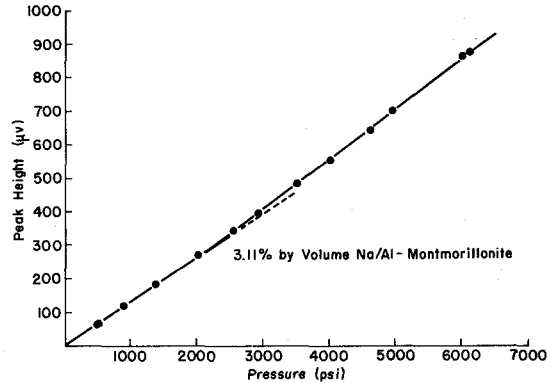
* E. Whalley, private communication.

Fig. 2. Change in peak height, E_m, with pressure in the range 0–7000 psi for a mixture of Na/Al–montmorillonite and water containing 3·11% Na/Al–montmorillonite by vol.

where m_w is the mass of water. Thus, it is the slope of the peak height vs pressure curve/unit mass of water and is proportional to the rate of change of the heat of compression with pressure/unit mass of water. Accurate values of ϵ were readily attainable because, as indicated earlier, plots of peak height vs pressure were linear and reproducible.

In Figs. 3–5, the differential peak height is plotted against the vol% of solids for glass bead–water and clay–water mixtures in pressure ranges on either side of the breaks in Figs. 1 and 2. Observe that the resulting curves for the glass beads are linear and have a small negative slope. Because glass bead–water interaction is presumed to be negligible, $(\partial Q/\partial P)/m_w$ should be constant regardless of the proportion of glass beads. Therefore, α in equation (3) must have changed slightly as the proportion of glass beads increases. The peak height of a ballistic-type thermogram is affected somewhat by the heat capacity of the cell contents (Calvet and Prat; 1956, 1963) and the change in α is attributed to the loss in heat capacity accompanying the addition of glass beads to the cell.
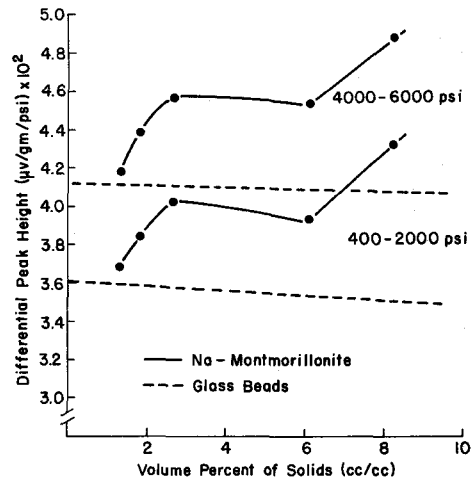

Fig. 3. Variation of the differential peak height, ϵ, with the concentration of glass beads or Na–montmorillonite in water for two pressure ranges.

Fig. 4. Variation of the differential peak height, ϵ, with the concentration of glass beads or Na/Al–montmorillonite in water for two different pressure ranges.

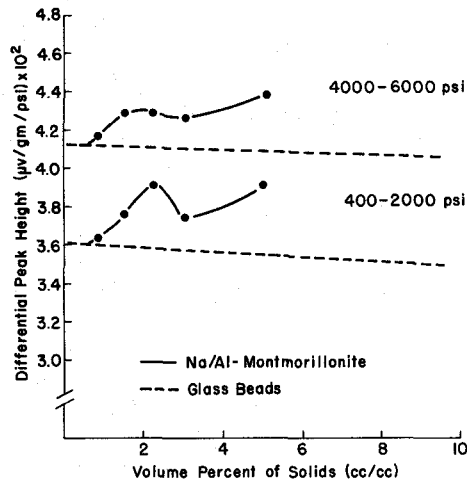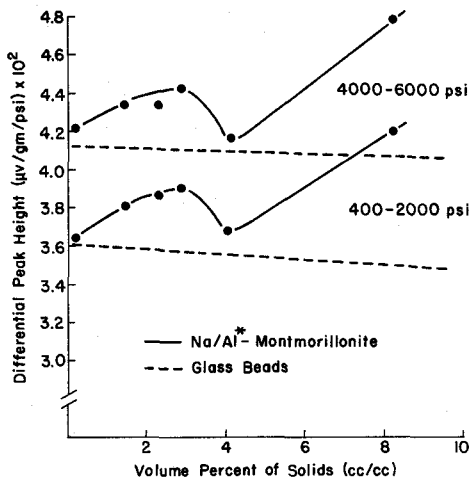

Fig. 5. Variation of the differential peak height, ϵ, with the concentration of glass beads or Na/Al*-montmorillonite in water for two different pressure ranges.

The specific heat capacity of the glass beads was not determined. However, it would be within the range of handbook values for glass, i.e. 0·199–0·117 cal/deg/g. The specific heat capacity of Na-saturated montmorillonite from Upton, Wyoming is 0·191 cal/deg/g (Oster and Low, 1964). Hence, the curves of differential peak height vs volume per cent of solids for the Na–montmorillonite should approximate those for the glass beads if the montmorillonite acts like an inert solid. It is obvious from Figs. 3–5 that this is not the case. Not only do the curves for the Na–montmorillonite deviate from those for the glass beads, but the deviation depends in a non-linear way on the montmorillonite concentration and on the amount of hydrous aluminum oxide that is present in the system. Similar curves were obtained in the pressure ranges 0–25 and 0–400 psi.

The Calvet microcalorimeter is more isothermal than adiabatic. The temperature change between sample and reference cells is usually very small. For example the peak height for each increment of pressure was usually of the order of 150 μV. This voltage corresponds to a rise in temperature of the sample cell of $\sim 0\cdot005°$C. Since thermal equilibrium was restored between pressure increments, it can be said that the temperature of the sample varied by no more than this amount. Further the process of compression was reversible. Therefore, it is reasonable to assume that equation (2) is applicable to our glass bead–water and clay–water systems. If this is true, equations (2) and (3) can be combined to yield

$$\epsilon = -\frac{\alpha T}{m_w}(\partial S/\partial P)_T = \frac{\alpha T}{m_w}(\partial V/\partial T)_P. \qquad (4)$$

Thus, at any water content and temperature, ϵ is proportional to the rate of change of entropy with pressure. Since entropy is a measure of the degree of randomness or disorder of a system, ϵ indicates the effect of pressure on its structural arrangement. In support of equation (4), it should be noted that a straight line is obtained when the ϵ values reported here are plotted against the corresponding values of $(\partial V/\partial T)_P/m_w$ which were determined by Clementz (1969).

The value of $(\partial V/\partial T)_P/m_w$ for the pure bulk water in the glass bead–water mixture *at atmospheric pressure and* 25°C can be determined from handbook data (*Handbook of Chemistry and Physics*, 1962). It is $2\cdot58 \times 10^{-4}$ cm^3/g/deg. When this value and the value for T (298 K) are substituted into equation (4), we find that $\alpha = \epsilon/1\cdot267 \times 10^{-4}$ μV/cal when the proper conversion factors are used. An appropriate value of ϵ at atmospheric pressure can be determined from the curves for the glass bead–water mixtures at 400–2000 psi in Figs. 3–5. These curves are applicable down to one atmosphere pressure because, as shown by using the data from Fig. 1 in equation (3), ϵ has a constant value (at any vol% of glass beads) from 0 to $\sim$3000 psi. Thus, α can be calculated. Because the heat capacity of a clay–water mixture should be essentially the same as that of a glass bead–water mixture at the same vol% of solids, the calculated value of α should apply to both mixtures.

It is evident from Figs. 3–5 that ϵ is greater for the clay–water mixtures than for the glass bead–water mixtures. Hence, the application of pressure must cause a larger loss of entropy in the clay–water mixtures. This relatively large loss of entropy may be due to a rearrangement of the particles in the clay matrix. However, it is doubtful that such is the case. If the compressibility of the water in a clay–water mixture is close to that of bulk water, a pressure of 6000 psi would compress it by $\sim$2 per cent which, in view of the broad potential energy minimum the particles are supposed to occupy as a result of their mutual interaction, is insufficient to cause them to move into a new potential energy minimum corresponding to another arrangement. Also, if there are $\sim 10^{14}$ particles/g <2 μm Na-saturated montmorillonite (Leonard and Low, 1964) the ratio of clay particles to water molecules in a clay–water mixture containing 3·0% clay by vol is approximately 10^{-10}. This

ratio is so small that the change in entropy due to a rearrangement of the particles must be infinitesimal compared to that due to a rearrangement of the water molecules. Moreover, the particles in a clay sol undergo random translational and rotational motion, whereas those in a clay gel are interconnected in a semi-rigid framework. If particle rearrangement contributes measureably to the change in entropy with pressure, there would have to be a distinct change in ϵ at the clay concentration at which rapid gelation occurs (1·5, 1·2 and 0·75% by vol for the Na–, Na/Al*– and Na/Al–clay, respectively). No such change was evident. Therefore, the effect of particle rearrangement on the entropy loss can be discounted.

The effect of pressure on the structural integrity of the water in a clay–water system may be influenced by the exchangeable cations and/or the particle surfaces. To see if our results can be ascribed entirely to the influence of the exchangeable cations, we relate the volume, V, of the system to the volumes of its constituents in the following way

$$V = v_w^0 m_w + v_P^0 m_P + \phi_{Na} m_{Na} \tag{5}$$

where v_w^0 and v_P^0 are the specific volumes of pure water and solid particles, respectively, ϕ_{Na} is the apparent specific volume of dissolved Na^+ and m_w, m_P and m_{Na} are the masses of the water, particles and dissolved Na^+, respectively. Thus, all effects on V of interaction between constituents are arbitrarily included in ϕ_{Na}. When equation (5) is differentiated with respect to temperature at constant pressure, the result is

$$(\partial V/\partial T)_P = (\partial v_w^0/\partial T)_P m_w + (\partial v_P^0/\partial T)_P m_P$$

$$+ (\partial \phi_{Na}/\partial T)_P m_{Na}. \tag{6}$$

In a clay–water system containing, for example, one g water and 3·0% clay (by vol) with a cation exchange capacity of one m-equiv./g, the values of m_w, m_P and m_{Na} are 1, 0·086 and 0·00197 g, respectively. At 25°C and 1 atm pressure, the values of $(\partial v_w^0/\partial T)_P$ and $(\partial v_P^0/\partial T)_P$ are 2·58 × 10^{-4} and ~10^{-5} cm³/g/deg, respectively. The former value was calculated from handbook data (Handbook of Chemistry and Physics, 1962). The latter value was taken from the thesis of Clementz (1969) who calculated the coefficients of thermal expansion of several layer-lattice minerals from their lattice parameters at different temperatures. Now, let us assume that *the particle surfaces have no effect on the vicinal water and that, therefore, the interlayer solution is identical to a bulk solution of Na^+ in water at the same average concentration.* Then $(\partial \phi_{Na}/\partial T)_P$ can be approximated closely by dividing the partial molal expansibility of Na^+ in aqueous solution at infinite dilution by its atomic weight. The value obtained in this way from the data of Millero (1968) is 1·39 × 10^{-3} cm³/g/deg. As we now have values for all the independent variables in equation (6), the value of $(\partial V/\partial T)_P$ can be calculated. It is 2·62 × 10^{-4} cm³/deg. When this value and the appropriate values of T and α (found to be 281 μV/cal

by the method described previously) are substituted into equation (4), the calculated value of ϵ is 3·61 × 10^{-2} μV/g/psi. However, the experimental value of ϵ for the same system is 4·03 × 10^{-2} μV/g/psi. The calculated value of ϵ exceeds that for the glass bead–water mixture by 1·4 per cent whereas the experimental value exceeds it by 13·2 per cent. Consequently, we can conclude that the interlayer solution is not a simple solution of Na^+ in ordinary bulk water. The structure of the water in this solution must be affected by the adjacent particle surfaces.

When water is subjected to changes in pressure or temperature, there are accompanying volume changes. The explanation for these changes depends on the model that is adopted. In general, there are two kinds of models for liquid water, namely, 'mixture' models and 'continuum' models (Eisenberg and Kauzmann, 1969). The 'mixture' models describe water as an equilibrium mixture of two or more species which differ from each other in molecular arrangement; whereas, the 'continuum' models describe water as a continuous, hydrogen-bonded species in which there is a distribution of angles, distances and bond energies. According to both models, changes in pressure and temperature cause changes in bond lengths and hence expansion or contraction of the existing structures. In addition, they cause structural rearrangement or relaxation. In the 'mixture' models, the relaxation is supposed to involve a breaking of bonds and a falling together of the resulting unbonded molecules. Thus, the more ordered, open-packed species are converted to the less ordered, close-packed species. In the 'continuum' models, the relaxation is supposed to involve only the bending of bonds. Hence, the structure is not broken down but just distorted or perturbed. In either case, there are two components to the heat of compression and related thermodynamic quantities, namely, that due to expansion or contraction of the existing structures and that due to structural rearrangement or relaxation. If we designate these components by the subscripts s and r, respectively, we can write

$$(\partial Q/\partial P)_T = [(\partial Q/\partial P)_s + (\partial Q/\partial P)_r]_T \tag{7}$$

$$(\partial S/\partial P)_T = [(\partial S/\partial P)_s + (\partial S/\partial P)_r]_T \tag{8}$$

$$(\partial V/\partial T)_P = [(\partial V/\partial T)_s + (\partial V/\partial T)_r]_P. \tag{9}$$

Now, either the breakdown or perturbation (due to bond bending) of an ordered, open packed species consumes energy, increases entropy and reduces volume. Therefore, regardless of which kind of model is applicable, the relaxational components in equations (7) and (8) are positive and the relaxational component in equation (9) is negative. Since heat and entropy are lost on compression, i.e. $(\partial Q/\partial P)_T$ and $(\partial S/\partial P)_T$ are negative, it follows that structural relaxation reduces the heat and entropy losses. Also, because the volume expands on heating, i.e. $(\partial V/\partial T)_P$ is positive, structural relaxation must reduce the thermal expansibility. Our results show that the heat and

entropy lost on compression and the volume gained on heating are greater for the water in montmorillonite–water systems than for an equal amount of bulk water. Clementz (1969) showed that the thermal expansibility of water in these systems was greater than that of bulk water. Therefore, we conclude that the water in montmorillonite–water systems is less susceptible to structural breakdown or perturbation with increasing pressure and temperature than bulk water.

Observe from Figs. 3–5 that ϵ does not increase uniformly with the proportion of clay present. The same is true of the apparent specific heat capacity (Davey and Low, 1971) and of the coefficient of thermal expansion (Clementz, 1969) of the interlayer water. Plots of these three properties vs the concentration of Na–montmorillonite have essentially the same shape. All of them exhibit a pronounced minimum at the same clay concentration. A reasonable conclusion is that the water structure undergoes a higher-order phase transition at this concentration.

The curves in Figs. 3–5 have the same shape but cannot be superimposed exactly. It seems, therefore, that the presence of hydrous aluminum oxide has a small effect on the properties of the water. This is consistent with other results (e.g. Clementz, 1969; Davey and Low, 1971) and is to be expected. If epitaxy occurs between the water and montmorillonite structures as proposed by Davidtz and Low (1970) and Ravina and Low (1972), the degree of strain introduced into the water structure and the depth to which the strain persists should depend on the nature and symmetry of the atoms composing the underlying surface. Both change when the montmorillonite surface becomes coated with a film of hydrous aluminum oxide.

In summary, the results of this study, like those of earlier studies (e.g. Anderson and Low, 1958; Oster and Low, 1964; Davey and Low, 1971; Kay and Low, 1972) show that the properties of water in clay–water systems, even at high water contents, differ significantly from those of bulk water. Further, they show that only a small part of the difference can be attributed to the effect of exchangeable cations. Most of it must be attributed to the effect of particle surfaces.

REFERENCES

Anderson, D. M. and Low, P. F. (1958) The density of water adsorbed by lithium–, sodium– and potassium–bentonite. *Soil Sci. Soc. Am. Proc.* **22**, 99–103.

Calvet, E. and Prat, H. (1956) *Microcalorimétrie, Applications Physico-Chimiques et Biologiques*, Masson, Paris.

Calvet, E. and Prat, H. (1963) *Recent Progress in Microcalorimetry.* Macmillan, New York.

Clementz, D. M. (1969) *Thermal Expansion of Water in Na–bentonite Systems.* M. Sc. Thesis, Purdue University.

Davey, B. G. and Low, P. F. (1968) Clay–water interaction as affected by hydrous aluminum oxide films. *Trans. 9th Int. Cong. Soil Sci.* **1**, 607–616.

Davey, B. G. and Low, P. F. (1971) Physico–chemical properties of sols and gels of Na–montmorillonite with and without adsorbed hydrous aluminum oxide. *Soil Sci. Soc. Am. Proc.* **35**, 230–236.

Davidtz, J. C. and Low, P. F. (1970) Relation between crystal-lattice configuration and swelling of montmorillonites. *Clays and Clay Minerals* **18**, 325–332.

Eisenberg, D. and Kauzmann, W. (1969) *The Structure and Properties of Water.* Oxford University Press, London.

Graham, J. (1964) Adsorbed water on clays. *Rev. Pure Appl. Chem.* **14**, 81–88.

Handbook of Chemistry and Physics (1962) The Chemical Rubber Publishing Co., Cleveland, Ohio.

Kay, B. D. and Low, P. F. (1972) Pressure-induced changes in the thermal and electrical properties of clay–water systems. *J. Colloid Interface Sci.* **40**, 337–343.

Kell, G. S. and Whalley, E. (1965) The PVT properties of water—I: Liquid water in the temperature range 0–150°C and at pressures up to 1 kb. *Phil. Trans. R. Soc. (London).* A, **258**, 565–617.

Leonard, R. A. and Low, P. F. (1964) Effect of gelation on the properties of water in clay systems. *Clays and Clay Minerals* **12**, 311–325.

Low, P. F. (1961) Physical chemistry of clay–water interaction, *Adv. Agron.* **13**, 269–327.

Low, P. F. and White, J. L. (1970) Hydrogen bonding and polywater in clay–water systems. *Clays and Clay Minerals* **18**, 63–66.

Martin, R. T. (1962) Adsorbed water on clay: a review. *Clays and Clay Minerals* **9**, 25–71.

Millero, F. J. (1968) Apparent molal expansibilities of some divalent chlorides in aqueous solution at 25°C. *J. Phys. Chem.* **72**, 4589–4593.

National Engineering Laboratory Steam Tables. (1964) (R. W. Bain, editor) H.M.S.O., London.

Oster, J. D. and Low, P. F. (1964) Heat capacities of clay and clay–water mixtures. *Soil Sci. Soc. Am. Proc.* **28**, 605–609.

Ravina, I. and Low, P. F. (1972) Relation between swelling, water properties and b-dimension in montmorillonite-water systems. *Clays and Clay Minerals* **20**, 109–123.