

SWELLING PRESSURES OF SODIUM MONTMORILLONITE AT DEPRESSED TEMPERATURES

by

R. YONG, L. O. TAYLOR and B. P. WARKENTIN

McGill University, Montreal, Canada

ABSTRACT

Swelling pressures of oriented samples of sodium montmorillonite at 10^{-4} and 10^{-2} M NaCl in the pore-water were measured at controlled temperatures ranging from 1°C to 23°C . The specially designed apparatus allowed swelling against a movable piston connected to a mercury manometer through which the ambient pressure was applied.

A decrease in swelling pressure with decrease in temperature is predicted theoretically from the Gouy–Chapman theory, taking the variation of temperature and dielectric constant into account. At a salt concentration of 10^{-4} M NaCl, the measured swelling pressure at 120 Å average interparticle distance decreased from 48 cm of mercury at 23°C to 35 cm at 1°C , while the corresponding calculated pressure decrease was from 48 to 40 cm. While the measured pressures fell below calculated values at higher distances, the influence of temperature remained consistent.

At 10^{-2} M NaCl, a decrease in measured swelling pressure with decreasing temperature also occurred, but the measured swelling pressures were much higher than those predicted theoretically. Corrections were calculated, based upon the salt concentrations required by the theory to give the experimentally measured swelling pressures at room temperature. These were substituted into the approximate Langmuir solution of the combined Poisson–Boltzmann equation to describe the swelling pressure at 10^{-2} M NaCl. With these corrections, the calculated swelling pressure at 120 Å average interparticle distance decreased from 30 cm at 23°C to 26 cm at 1°C while the measured pressure decreased from 30 to 23 cm. This agreement between the corrected, calculated pressure and measured pressure held from 100 to 250 Å interparticle spacing.

INTRODUCTION

Measured swelling pressures of sodium montmorillonite at room temperature have been reported by several investigators (e.g. Hemwall and Low, 1956; Warkentin *et al.*, 1957; Warkentin and Schofield, 1962). In general, good agreement has been found between measured values and swelling pressures predicted from the diffuse ion-layer theory of Gouy and Chapman. The combined Poisson–Boltzmann equation gives the concentration of ions at the midplane between two parallel charged plates. The ion concentration difference between the midplane and the surrounding pore-water solution is used to calculate the van't Hoff pressure. With the assumption of ideal

behavior of ions and assuming that attractive forces between the particles may be neglected, the van't Hoff pressure may then be taken as the computed swelling pressure. Where laboratory specimens correspond to the model used in the theoretical analysis, acceptable correspondence is found between measured and calculated swelling pressures.

The conditions necessary for good agreement between measured and computed swelling pressures at room temperature are: (1) clay particles must be plate-shaped with lateral dimensions far exceeding their thickness, (2) particle sizes must be within the colloidal range and their surfaces free from irregularities, (3) surface charge of the particle is of constant sign (negative) and uniformly distributed, (4) clay must be homoionic and free from impurities, (5) particles must be oriented parallel to each other, (6) pore-water solution should consist of univalent ions of a single species (NaCl in this instance), and (7) the resulting clay-water system should be homogeneous.

The purpose of this study was to check the predictions of diffuse ion-layer theory for the effect of temperature on swelling, bearing in mind that decreasing temperature results in compression of the diffuse ion-layer, but that the resultant dielectric constant increase will cause the thickness of the ion-layer to increase. While no detailed measurements have been reported on variation of swelling pressure with temperature, it was found in consolidation tests as performed in soil mechanics (Lambe, 1960), that cooling caused the sample in the oedometer to swell and warming caused it to expand.

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EXPERIMENTAL PROCEDURE

Change in swelling pressure of clay arising from temperature depression can be measured by first allowing samples to attain equilibrium volume under an applied pressure, and then either:

- (a) maintaining each equilibrium volume constant while lowering the temperature of the sample by predetermined increments; [The pressure required to maintain the equilibrium volume for each temperature may then be measured to determine pressure change with temperature at constant volume] or
- (b) maintaining the applied pressure constant while lowering the temperature of the sample by predetermined increments. [The resulting volume change that occurs under constant applied pressure for each temperature increment is then determined.]

The apparatus, designed to accommodate either of the two methods, is shown in Figs. 1 and 2. It consisted of a Plexiglas chamber enclosed in an

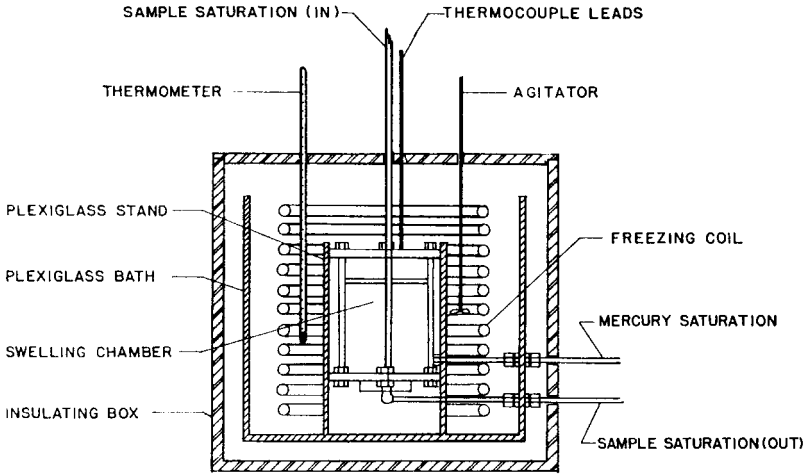


FIGURE 1.—Sectional view of assembled swelling chamber in bath.

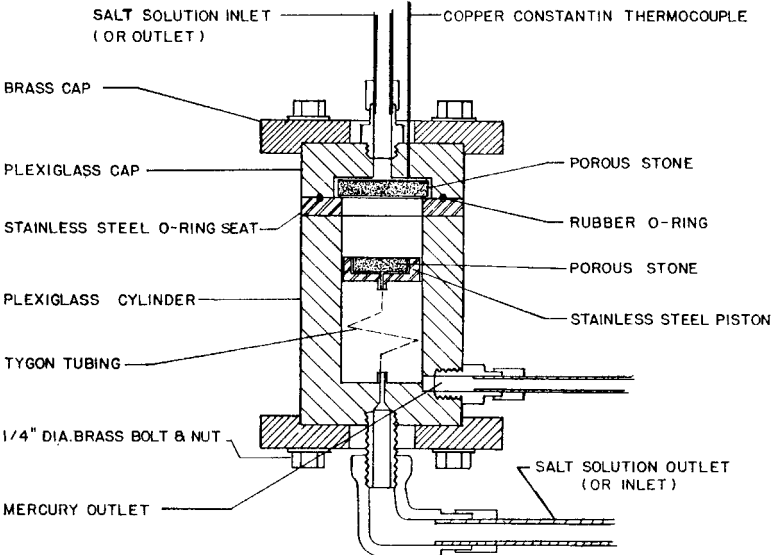


FIGURE 2.—Cross-section of swelling chamber.

insulating box to restrict heat transfer to the surroundings. Within the Plexiglas chamber, an agitator kept the fluid in the constant temperature bath circulating around the cooling coils and the swelling chamber. The details of the swelling chamber itself are given in Fig. 2, and the measuring system is detailed in Fig. 3. Temperature measurements within the swelling chamber were made with a copper-constantan thermocouple which passed through the rubber O-ring at the top and sat at the face of the porous stone. A Leeds Northrup type No. 8662 potentiometer was used in conjunction with the thermocouple. The junction of the thermocouple leads was protected by several coats of epoxy resin to prevent reaction with salts in the pore-water.

A mercury piston was connected to the swelling chamber in such a way that it could both exert a pressure on the stainless steel piston, and also measure volume changes of the sample. The stainless steel piston with an embedded porous stone provided a level face with the sample, and eliminated meniscus effects of the mercury face in the chamber. Mercury was not expected to slip past the sides of the piston since the pressure differential across the face of the piston was zero.

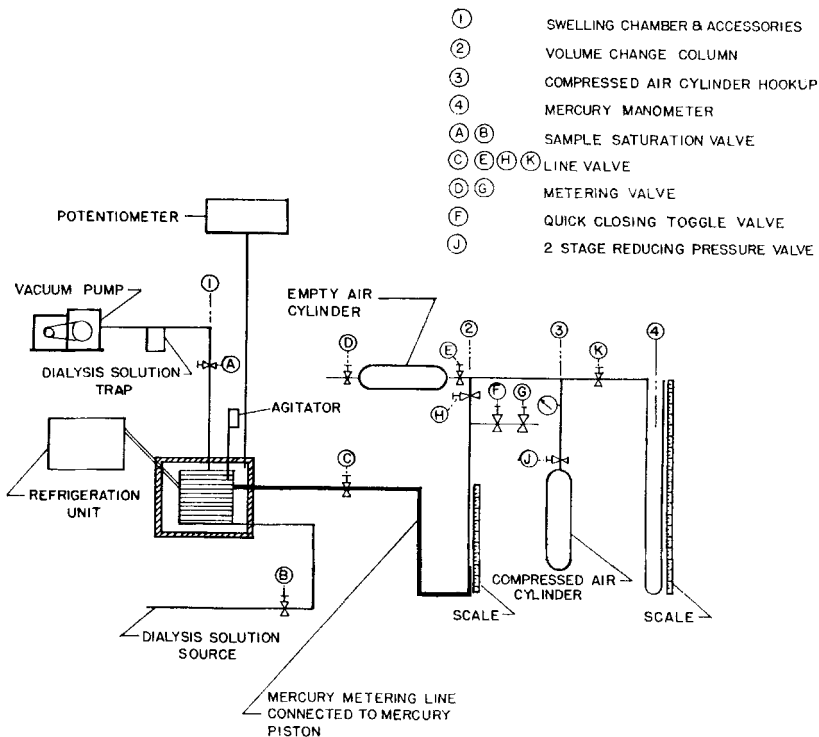


FIGURE 3.—Schematic layout—swelling pressure apparatus and measurement system.

In Fig. 3, the heavy lines indicate the portion of the measuring system saturated with mercury. Any change of volume occurring in the chamber as a result of pressure change was indicated by a corresponding change in the level of mercury in column (2). The ratio of the cross-sectional area of the chamber to that of column (2) is such that a small volume change of the sample in the swelling chamber causes a large change in the measuring column. This allows for an accurate measurement of small volume changes. The error in determination of volume change of the sample, based on column readings, was ± 1 per cent with readable volume changes of 0.04 ml. Ambient pressures applied to the sample were measured by a mercury manometer in the connection between the compressed air cylinder and column (2).

In order to reduce the sensitivity of the apparatus to small leaks that might cause a rapid loss of pressure, and at the same time to increase the volume of the system, an empty air cylinder was incorporated. A slow release of air through valves (F) and (G) (shown in Fig. 3) allowed a slow expansion of the sample. A more gradual expansion of the sample was obtained by partly filling the air cylinder with oil and slowly bleeding the oil through valve (D). The loss of oil caused a decrease in pressure and allowed the sample to swell. If small leaks developed, the uncertainty in the applied pressure could amount to ± 3 per cent in pressure variation. This, however, stabilized during the time taken for the sample to reach equilibrium volume at a constant temperature.

The measuring system was calibrated for temperature effects by measuring the change of mercury level in the cell with changes in cell temperature, and the change in level of mercury in the measuring column with changes in room temperature.

Oriented specimens of homoionic sodium montmorillonite were prepared by slow sedimentation and drying of weak suspensions of the purified clay. Clay suspensions containing less than one per cent clay by weight were allowed to settle slowly in small Plexiglas tubes which were sealed at the bottom with cellophane membranes. This technique of slow evaporation and sedimentation to produce waferlike clay plates had previously been used successfully (Warkentin and Schofield, 1962).

Five clay plates, weighing about 0.6 g, were placed individually in the flooded swelling chamber. "Millipore" membranes were used at the faces of the top and bottom porous stones. Sample placement in the chamber and general assembly of the swelling apparatus was performed under water so that no air was introduced. The sample was allowed to swell under a small pressure restraint which determined its initial equilibrium volume. Since the applied pressure was transmitted through the mercury piston which also served as a scale for volume change measurements (shown in Fig. 3 as the line passing through valve C), initial zero readings for equilibrium volume at room temperature could be made before introduction of the cooling fluid. A period of from three to six days was required to allow the sample to swell and come to equilibrium volume at room temperature. The time taken for samples to reach equilibrium under applied pressure at any one temperature

varied from 900 min to 4000 min. The variation in equilibrium time depended upon both applied pressure and temperature.

Following the initial equilibrium, a series of resultant volume changes were measured as a function of temperature depression. A complete test series on any one sample consisted of measurement of volume changes occurring as a result of temperature variation from 23°C to 1°C for a range of applied pressures. Since sample area is constant, volume changes can also be reported as changes in the average distance between particles, neglecting edge area. The void ratio may be obtained by multiplying the half-distance between particles by the factor 0.22.

RESULTS AND CALCULATIONS

Measured swelling at depressed temperatures.—The measured decrease of interparticle spacing with depressed temperatures at constant pressure is shown in Fig. 4 for three series of tests at 10^{-4} M NaCl and in Fig. 5 for one series at 10^{-2} M NaCl. The numbers on each line are the pressures in cm of mercury under which the volume decreases were measured. At all pressures, volume or interparticle spacing decreased linearly with decreasing temperature.

Calculation of swelling pressures.—From diffuse ion-layer theory, the swelling pressure can be calculated for any interparticle spacing if the surface area and charge of the clay, and the nature and number of ions present are known. These calculations have been set out in several papers (e.g. Bolt and Miller, 1955; Warkentin and Schofield, 1962). At 10^{-4} M NaCl the Langmuir solution (Langmuir, 1938) can be used. This assumes that the concentration of anions between clay particles can be neglected.

Swelling pressure measurements for both 10^{-4} M NaCl and 10^{-2} M NaCl have been plotted in Fig. 6 for the test series at 23°C.* The correspondence between measured and computed swelling pressure above 10 cm mercury is satisfactory for 10^{-4} M NaCl. At 10^{-2} M, measured values are consistently higher than predicted from the equations. This is expected since the Boltzmann and van't Hoff equations become less valid with increasing electrolyte concentration. At concentrations less than 10^{-3} M NaCl, the agreement between experimental and calculated swelling pressures indicate that the error involved in calculating osmotic pressure by the difference in ion concentration is not large (Warkentin and Schofield, 1962). At higher concentrations, however, the error due to use of ionic concentrations rather than activities becomes significant.

It is, therefore, not possible to compare the measured influence of temperature with that predicted by the equations until some corrections have been

* The pressures in Fig. 6 are not identical with the points plotted in Figs. 4 and 5; they have been corrected for the effects of membrane plugging. After about two weeks, increasing pressures were required to force water through the "Millipore" membranes. This was measured in separate experiments as a function of time and the results corrected. These corrections did not change the measured volume decrease with decreasing temperature.

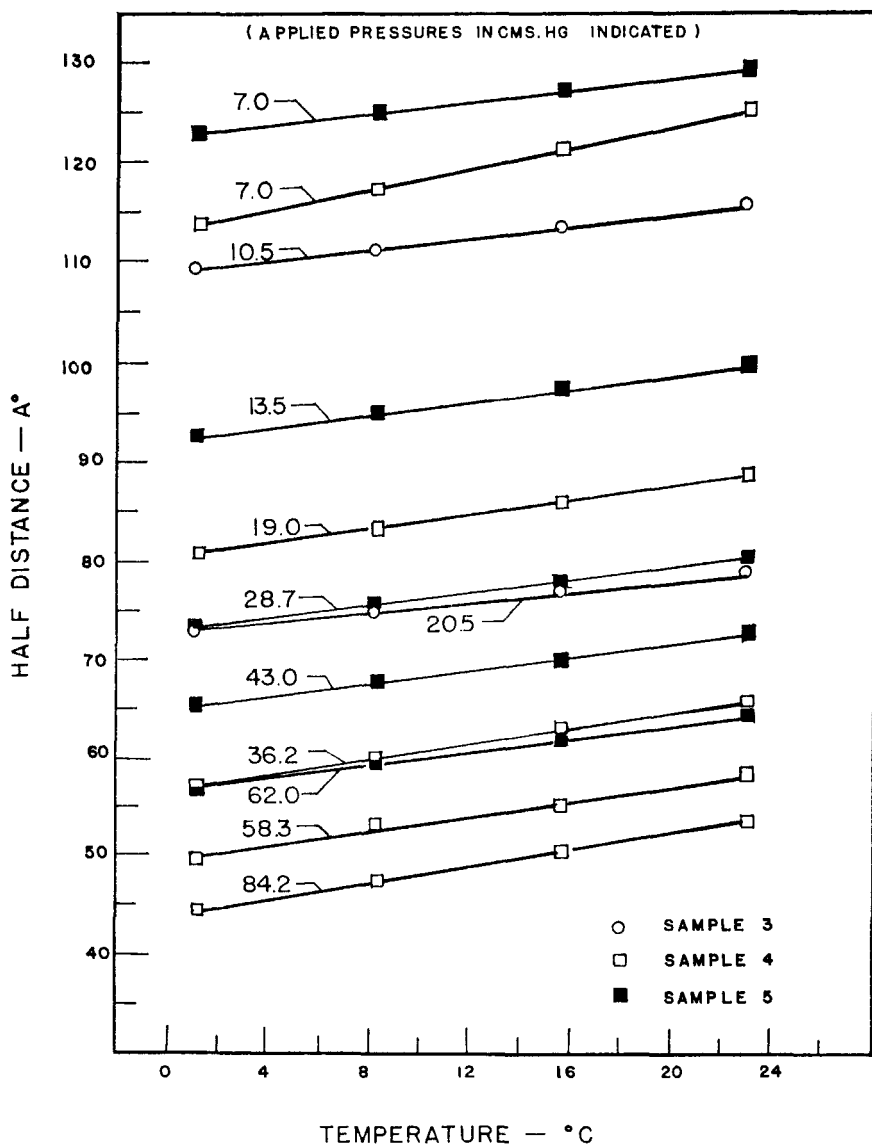


FIGURE 4.—Variation of interparticle spacing with temperature at 10^{-4} M NaCl.

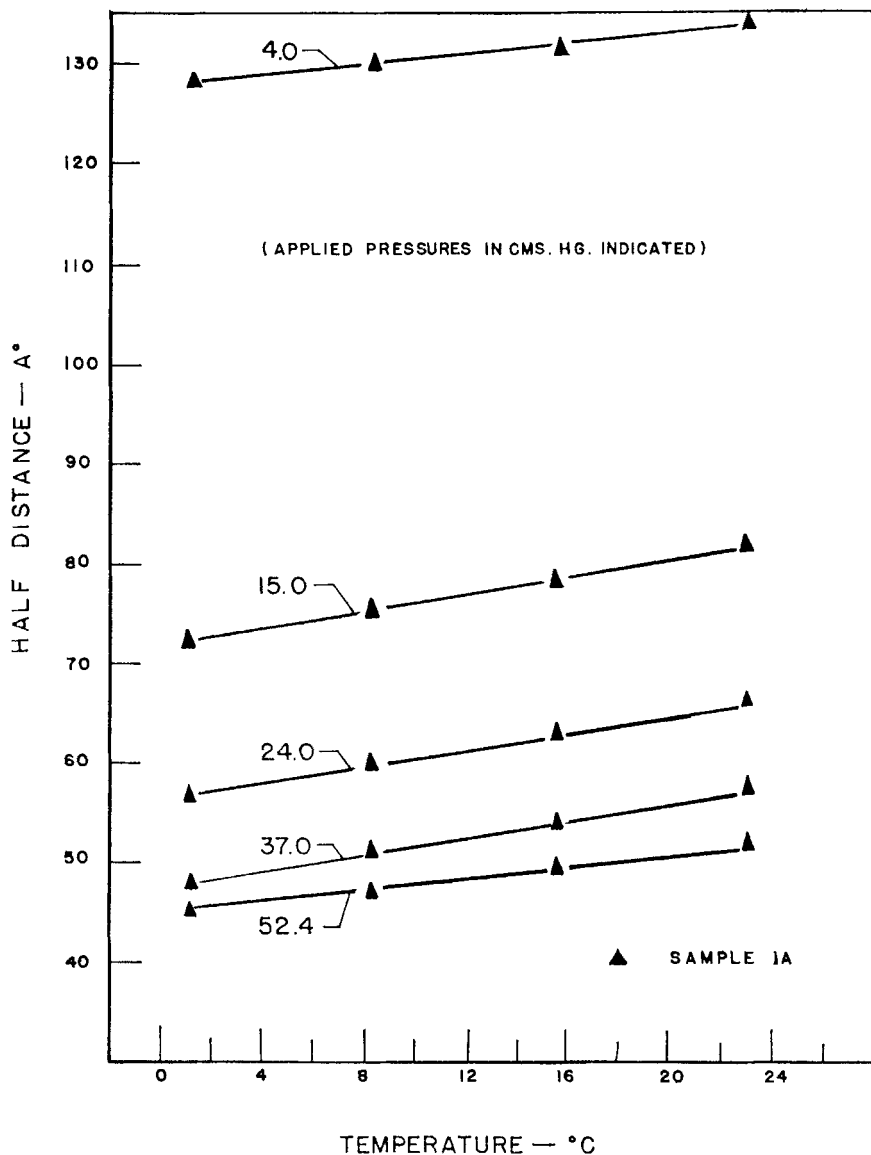


FIGURE 5.—Variation of interparticle spacing with temperature at 10^{-2} M NaCl.

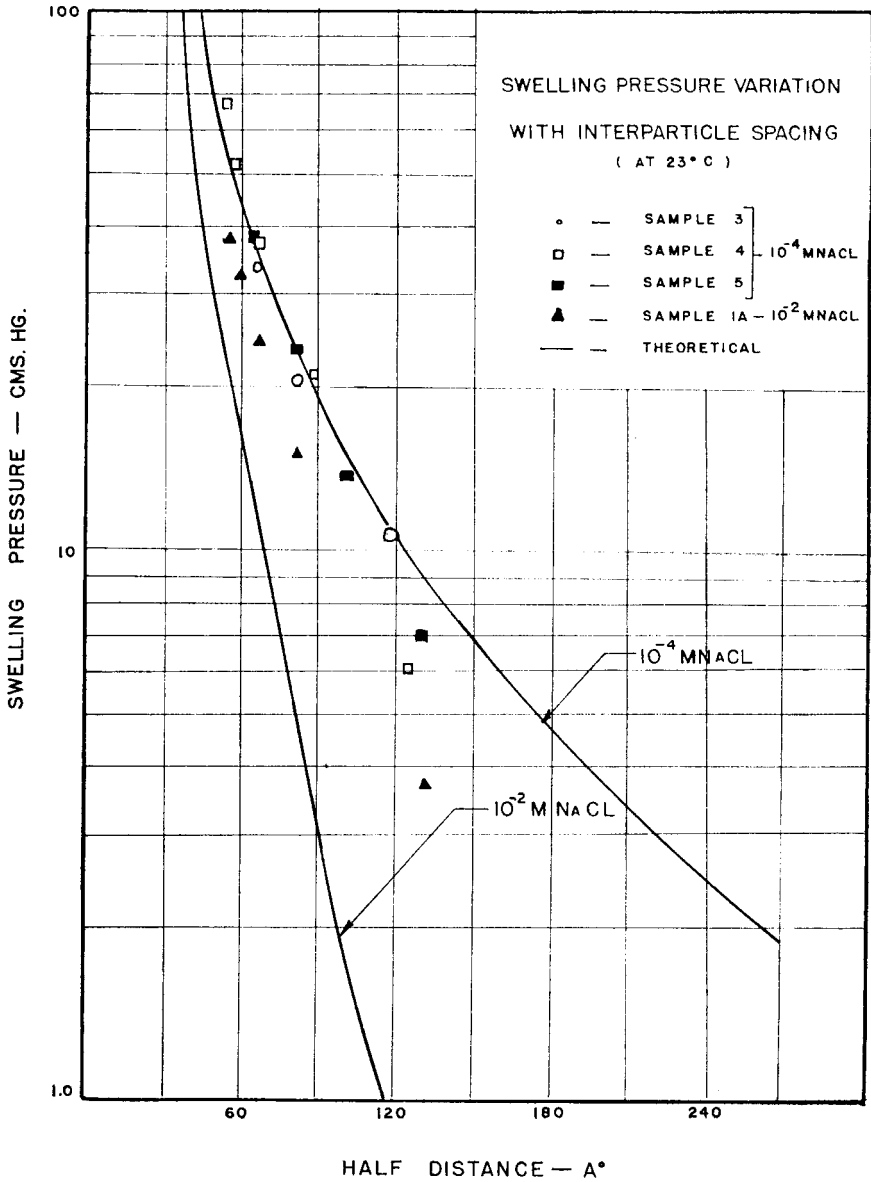


FIGURE 6.—Swelling pressure variation with interparticle spacing (at 23°C).

made. While efforts to allow for ionic activity in diffuse ion-layer calculations have been made by Loeb (1951) and Bolt (1955), it does seem that because of the difficulties involved in determination of the activity coefficients for ions between adjacent clay plates, calculation of corrected osmotic pressure based upon ionic activities is not possible. Approximate expressions accounting for the influence of dielectric saturation, polarization of ions, and ionic interactions in the structure of the electric double layer have been incorporated in the generalized Poisson-Boltzmann equation (Bolt, 1955). These corrections, when applied to the Gouy-Chapman equations at low concentration of co-ions in colloidal suspensions, are small if the surface charge density does not exceed 2×10^{-7} meq/cm².

Instead of the difficult theoretical approach for correction of osmotic pressure at higher electrolyte concentrations, an empirical treatment will be given, substituting the real concentration by an effective salt concentration.

Calculation of effective salt concentration.—The Langmuir equation for ψ_c , the electric potential at the midplane between particles, can be written to include effective salt concentration as:

$$\psi_c = \frac{2kT}{ze} \ln \frac{Kx\sqrt{S}}{\pi} \quad (1)$$

where:

$$K = \sqrt{\frac{8\pi z^2 e^2 n_0}{\epsilon kT}}$$

z = valence of ions

e = electronic charge

n_0 = number of ions per unit volume in bulk solution

ϵ = dielectric constant

k = Boltzmann constant

T = absolute temperature

x = half distance between adjacent clay particles

S = coefficient of effective salt concentration

Sn_0 = effective salt concentration

The Langmuir approximation, neglecting the anion concentration, is not valid at 10^{-2} M NaCl above interparticle half-distance of about 70 Å. However, it is used here because of the simplicity of the calculation and because a correction to concentration is being calculated anyway.

When substituted into the van't Hoff equation, the swelling pressure, P , can be calculated:

$$P = 2kT Sn_0 \left(\cosh \frac{2e\psi_c}{kT} - 1 \right) \quad (2)$$

where P = force per unit area required externally to keep adjacent particles at a spacing of $2x$.

The effective salt concentration in the pore-water which produces the same

value for ψ_c in equation (1) and (2) was then determined. For 10^{-4} M NaCl, the correction varied from 0.85 to 1.0

When the same correction was calculated for 10^{-2} M NaCl it was found that S was not constant but increased toward unity as interparticle spacing decreased. The correction for 10^{-2} M NaCl was, therefore, calculated from equations (1) and (2) with S equal unity. The value of ψ_c was calculated for different measured swelling pressures, P , at arbitrary values for salt concentration. The value of S required for the concentration at which ψ_c values calculated from equations (1) and (2) were equal was then plotted against the interparticle spacing corresponding to the measured swelling pressure. This was repeated for all measured swelling pressures. The points on this graph could be fitted by the equation:

$$Sx = \frac{x^2}{244} - 0.77x + 60.7 \quad (3)$$

The change in dielectric constant with temperature was calculated from the relationship established by Sirvastava and Varshni (1956).

$$\epsilon = \frac{62445}{T + 120} - 70.91 \quad (4)$$

The dielectric constant was assumed to be that of the solvent. While it is recognized that the dielectric constant of the water phase in clay soils and of adsorbed water may be significantly different (Pickett and Lemcoe, 1959), the assumptions involved in the initial equations of the Gouy-Chapman theory dictate the use of the solvent value for the dielectric constant.

It was found that the temperature dependence of the dielectric constant had only a small influence on the comparisons. With the uncertainties involved, similar results could be obtained by simply using a constant value for the dielectric constant.

From these equations the swelling pressure at different temperatures was calculated for the interparticle spacings measured. In Fig. 7, the measured change in interparticle spacing is plotted against swelling pressure to allow a comparison with predicted swelling pressure changes. These values have been corrected for membrane plugging as in Fig. 6. As seen from the graphs, there is reasonably close agreement between measured swelling pressures and calculated values for smaller interparticle spacings for the 10^{-4} M NaCl. While measured pressures at higher spacings fell below the calculated values, the influence of temperature on swelling pressure remained consistent.

When the calculated swelling pressures at 10^{-2} M NaCl are corrected at room temperature by using the effective salt concentration, the measured and calculated values agree at the lower temperature.

DISCUSSION

In accordance with the theoretical predictions, measured values of swelling pressure decreased with decreasing temperatures. The physical model of the

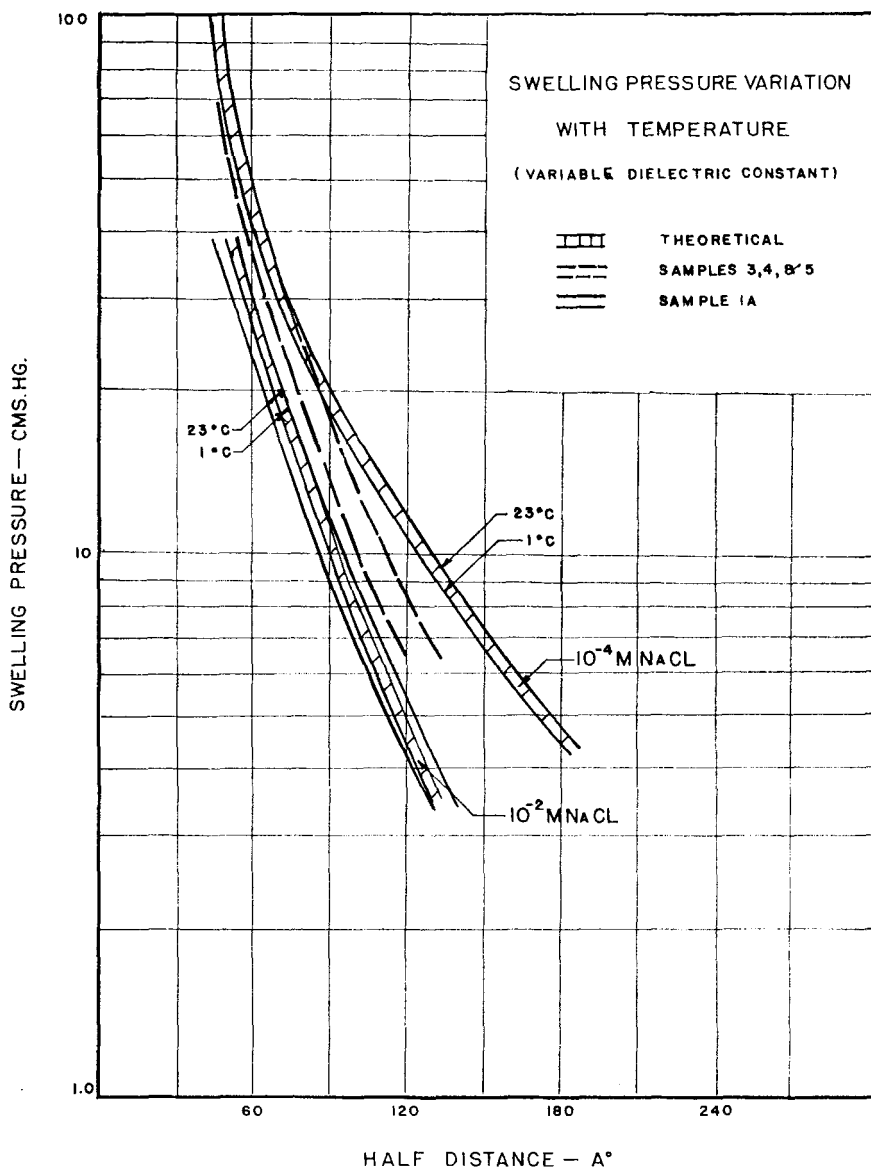


FIGURE 7.—Swelling pressure variation with temperature (Variable dielectric constant).

diffuse ion-layer assumes that the thermal energy of the ions restricts orientation in the field of charged plates, thus causing the layer to extend over large distances from the charged surface. It is expected that if the thermal energy of the ions is decreased, the capacity of the ions to resist orientation will decrease, and accordingly, the diffuse ion-layer thickness will also decrease. With a temperature depression, however, the dielectric constant will increase, which will increase the thickness of the diffuse ion-layer. The net effect, as shown in the calculations, is a decrease in thickness.

The divergence at higher interparticle spacings of measured and calculated swelling pressures at 10^{-4} M NaCl at room temperature (Fig. 6) is significant. Possibly the correction for effective salt concentration could be used to advantage here if it was necessary to describe the swelling pressures more precisely. Better agreement would then be achieved between calculated and measured pressures under depressed temperatures.

While the use of an effective salt concentration serves to adjust the physical equations to conform with measured values, it does not explain the differences between measured and calculated values. The reasons for the differences are not quite clear, but they are thought to lie in the limitations of the diffuse ion-layer theory which uses ionic concentrations rather than activities (Warkentin and Schofield, 1962), and possibly the lack of particle orientation at higher interparticle spacings.

CONCLUSIONS

Consistent with theoretical predictions, measured values of swelling pressure decreased as the temperature was decreased. With the use of a correction expressed in terms of the effective salt concentration in the pore-water, the approximate Langmuir solution of the combined Poisson-Boltzmann equation may be used to describe swelling pressure of sodium montmorillonite within certain restricted limits. The magnitude of the decrease in swelling pressure at different interparticle spacings for temperature changes between 23°C and 1°C and in the swelling pressure range of 0.1 to 1.0 atmospheres may be adequately predicted from diffuse ion-layer calculations.

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