

SWELLING PRESSURES OF DILUTE Na-MONTMORILLONITE PASTES¹

by

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ABSTRACT

Swelling pressures calculated from diffuse double-layer theory previously had been experimentally verified for Na-montmorillonite at clay concentrations above 10 percent, but published data at clay concentrations less than 5 percent consistently showed osmotic pressures much lower than the maximum of about 40 cm water calculated from theory. Swelling pressures of Na-montmorillonite in 4–5 percent orientated suspensions were therefore measured in a specially constructed osmometer in various solutions of NaCl up to 1.25 mN. The osmometer construction allowed solutions of desired concentration to be flushed continually across the membrane separating solution from clay. It was found that soluble impurities present in the clay decreased swelling pressures to about 1 cm of water. When these were removed during sample preparation, most efficiently by ultrafiltration through a dialysis membrane, swelling pressures measured were in satisfactory agreement with calculated values. The impurities were not identified chemically, but buffer curves of the solution toward HCl were determined.

INTRODUCTION

Swelling pressures of a clay suspension can be calculated from diffuse double-layer theory if the suspension corresponds to the model of electrically charged plates in parallel orientation. From the combined Poisson–Boltzmann equation the concentration of ions at the point midway between two charged plates in a solution can be calculated. Assuming ideal behavior of the ions, the swelling pressure can then be taken as the van't Hoff pressure due to the difference between this concentration and the ion concentration in the dialyzate or outside solution (Langmuir, 1938; Schofield, 1946). The swelling pressure thus calculated decreases with decreasing clay concentration or increasing distance between particles, and decreases with increasing electrolyte concentration in the suspension. A 4 percent (by weight) suspension of Na-montmorillonite has a calculated swelling pressure of 25 cm water in distilled water and 3 cm water in 1 mN NaCl.

To determine whether the model on which these calculations were based was applicable to dilute Na-montmorillonite suspensions, swelling pressures were measured at 4–5 percent clay concentration. The clay particles were orientated by drying, and the pressures measured at low electrolyte concentration where errors of the van't Hoff approximation would not be serious.

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EXPERIMENTAL METHOD

An osmometer to measure swelling pressures of clay suspensions was designed to allow filling with orientated flakes of clay and to allow continuous flushing with the dialysis solution against which the pressure was to be measured. The functional parts, constructed of clear plastic, are shown in Fig. 1. The osmometer cavity was about 2 in. \times 2 in. \times $\frac{1}{4}$ in. deep.

The clays used in this study were $< 0.2\mu$ fractions of Wyoming bentonite, saturated with sodium by percolating a 1 percent suspension through a column of sodium-saturated cation exchange resin. Sample *A* was obtained

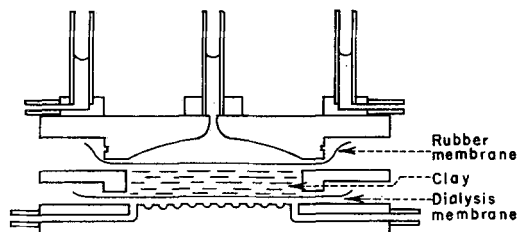


FIGURE 1.—Components of osmometer to measure swelling pressure of clay pastes.

through the courtesy of F. W. Berk & Co. Ltd., London, and sample *B* through the courtesy of American Colloid Co., Chicago.

Orientated flakes of clay were prepared by drying a 0.1 percent suspension at 60°C in an evaporating dish 1 cm deep. These were placed in the osmometer cavity, each flake being covered with dialysis solution before adding the next, to exclude air bubbles. When the required weight of clay had been introduced it was covered by a thin rubber membrane, with the exclusion of air, and the osmometer was bolted together.

The standpipes on either side of the osmometer were connected to the inflow and outflow tubes through which the dialysis solution passed. De-aerated dialysis solution at constant head was flushed under the dialysis membrane during measurements. The concentration of the dialyzate could thus be varied easily without disturbing the clay sample. Water was introduced into the central standpipe and adjusted to the levels of the dialysis solution in the inflow and outflow standpipes. As swelling of the clay proceeded, air pressure applied from a controlled source was adjusted to maintain this level. At equilibrium the applied pressure balanced the swelling pressure.

The concentration of clay in the suspension was determined after measurements were made, by drying the sample at 110°C.

CALCULATIONS

The half distance of separation of the clay plates (d) was calculated assuming uniform parallel orientation and a surface area of 800 m²/g from the relationship :

$$d = \frac{V}{W_s S} = \frac{100 - W}{W} \times 12.5$$

where V = volume of free liquid ;

W_s = weight of clay ;

W = weight percent of clay in the suspension ;

S = specific surface area of clay.

The swelling pressure (P) of a clay suspension in distilled water was calculated from the relationship :

$$P = \frac{RT\pi^2}{\nu^2 \beta X_{\max}^2} \quad (\text{Schofield, 1946})$$

where :

$$X_{\max} = d + \frac{4}{\nu\beta\Gamma} = d + 4 \text{ \AA} \text{ for Na-montmorillonite}$$

ν = valence of exchangeable ion on clay

$$\nu^2 \beta = \frac{\nu^2 \pi F^2 8}{1000 \epsilon RT} = \nu^2 \times 1.06 \times 10^{15} \text{ cm/m-mole.}$$

In dialyzate solutions of NaCl the swelling pressure was calculated, with the aid of Table 1, from the relationship :

$$P = 4RTm \cot^2 \theta_0 \quad (\text{Schofield, 1946})$$

where :

m = concentration of electrolyte in moles/liter.

TABLE 1.—VALUES OF θ_0 (IN DEGREES) AS A FUNCTION OF THE PRODUCT $X_{\max} \cdot \sqrt{m}$ (IN $\text{\AA} \cdot \sqrt{(mN)}$), FOR CALCULATING SWELLING PRESSURES

$X_{\max} \cdot \sqrt{m}$	θ_0	$X_{\max} \cdot \sqrt{m}$	θ_0
40.2	15	163.0	55
53.9	20	181.2	60
67.7	25	203.5	65
81.9	30	228.7	70
96.5	35	260	75
111.6	40	302	80
127.7	45	371	85
144.0	50		

RESULTS

Measurements on sample *A* introduced as a slurry gave pressures which were at least an order of magnitude lower than those calculated, even though distilled water was flushed through the osmometer for long periods to remove any soluble materials that moved through the membrane. Pressures of the

order of 1 cm H₂O were measured for 5 percent clay suspensions. These values were similar to swelling pressures observed for Na-montmorillonite slurries (Coleman and Jakobi, 1954).

Since impurities in the clay or initial arrangement of particles could affect swelling pressures, a further sample of clay *A* was purified by repeated washing in methyl alcohol until the clay began to disperse, and drying at 100°C to drive off the alcohol. Orientated flakes were prepared after redispersion in distilled water. The swelling pressures measured were lower than the calculated pressures, as shown in Table 2, but much higher than the values

TABLE 2.—SWELLING PRESSURES OF PURIFIED Na-MONTMORILLONITE SUSPENSIONS

Clay and Method of Purification	Clay Concentration (wt. %)	Half Distance of Separation of Clay Plates (<i>d</i>) (Å)	Concentration of NaCl in Dialyzate (<i>mN</i>)	θ_0 (Deg.)	Swelling Pressure Calculated (cm H ₂ O)	Swelling Pressure Measured (cm H ₂ O)
Sample <i>B</i> repeated ultrafiltration	5.3	223	0.062	21	41	38
			0.62	59.5	22	27
	4.7	253	0.062	24	31	26.5
			0.62	65	13	13
			1.25	78.5	5	6
	Sample <i>A</i> washing with methyl alcohol	3.8	316	0.062	29.5	19
0					35	21
4.65		256	0.1	30	29	18
			1.0	75	7	5
4.1		292	0		27	13
			0.1	34	22	11

obtained for unwashed clays. At concentrations of 5–15 percent of this clay measured swelling pressures were equal to calculated pressures.

A sample of clay *B* was purified by repeated dispersion in distilled water and pressure filtration through a dialysis membrane, until the conductivity of the filtrate corresponded to 0.3 mN salt. The measured swelling pressures of this sample are given in Table 2. There is some variation between calculated and measured swelling pressure, especially at the highest clay concentration, but the general agreement is acceptable. At the lowest NaCl concentration the measured pressures may be lower than the calculated pressures, whereas at the higher NaCl concentrations the measured values may exceed the calculated values. At 1 mN NaCl the errors in the van't Hoff approximation may no longer be negligible.

These differences between measured and calculated pressures may have resulted from the experimental difficulty in rapidly and accurately removing the sample to determine clay concentration. A quantitative agreement was also made difficult because the measurements were subject to two opposing errors, nonorientation increasing the swelling pressure (Warkentin, Bolt and Miller, 1957) and impurities decreasing it. Small differences in orientation of the samples as finally placed in the osmometer and in the degree of removal of impurities would cause variations in measured swelling pressures.

The measured values in Table 2 were reversible. At pressures of 0.5–1 cm water lower or higher, swelling or shrinkage of the clay suspension was measured. The swelling pressures were also independent of the order in which the series of dialysis solutions were used. At equilibrium, the swelling pressure in 0.1 mN NaCl was the same regardless of whether the clay previously had been equilibrated with distilled water or with 1 mN NaCl.

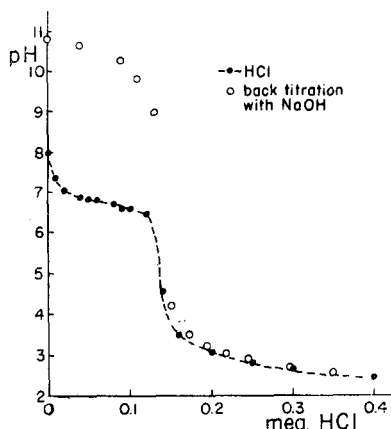


FIGURE 2.—Potentiometric titration curve of supernatant liquid of 0.5 percent Na-montmorillonite in 0.2 N NaCl, 50 ml. of solution was titrated with 0.1 N HCl, and then immediately back-titrated with 0.1 N NaOH.

The impurities that apparently caused the decrease in swelling pressures were not identified chemically. They may consist of low molecular weight silicates (Nutting, 1943) and traces of aluminate ion. Fig. 2 shows the titration curve of the supernatant liquid obtained from a suspension of unpurified clay *A* in 0.2 N NaCl. On adding HCl a fine white precipitate appeared which was not dissolved on adding NaOH. As seen from the back titration curve in Fig. 2, the precipitate adsorbed only small amounts of base.

CONCLUSIONS

Measured swelling pressures of dilute Na-montmorillonite suspensions were influenced by soluble impurities in the sample and by particle orientation. When these impurities were removed by ultrafiltration and the clay particles were orientated, the correspondence between measured and calculated swell-

ing pressures indicated that at low electrolyte concentrations these suspensions corresponded to the model of charged planar surfaces in parallel orientation for which the repulsive osmotic pressure could be calculated correctly from the diffuse double-layer theory.

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DISCUSSION

by

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Attention may be drawn to the fact that, in principle, the measured equilibrium pressure is not identical with the osmotic swelling pressure of the clay. The latter is a fluid pressure whereas the equilibrium pressure is the sum of the grain pressure and the fluid pressure. Therefore, the osmotic swelling pressure is lower than the equilibrium pressure. The contribution of the grain pressure is difficult to evaluate quantitatively. One would expect this contribution to increase with increasing clay concentration, but even in 4 percent sodium bentonite suspensions a coherent network of clay, which can take up elastic stresses, still exists. The locally higher clay concentration in the filter cake on the permeable membrane also might need to be considered in evaluation of the contribution of grain pressure.

If indeed there is a grain pressure term in the equilibrium pressure, the observation that the osmotic pressure (i.e. unit layer repulsion) predicted by the Gouy theory is about equal to the equilibrium pressure indicates that the values predicted from the Gouy theory are too high. The swelling experiments of Norrish (1954), in which equilibrium layer distances in a swelling clay flake are measured, lead to the same conclusion. As suggested before (van Olphen, 1954), utilizing the Stern model and assuming specific counter ion adsorption would lead to a smaller repulsion between the unit layers than that predicted by the Gouy model.

It is not intended to discuss the applicability of any double layer model in this note. This comment is only meant to call attention to the contribution of the grain pressure in the swelling pressure experiments which has been neglected in the literature.

¹ Shell Development Company, Exploration and Production Research Division, Houston, Texas.

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REPLY

by

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There is probably a grain pressure component in many of the equilibrium pressures measured in clay-water systems. This can explain the higher pressures measured during the first compression of a Na-montmorillonite slurry (Warkentin, Bolt and Miller, 1957), and also the higher pressures measured on compression compared with rebound or swelling for Ca-montmorillonite (Warkentin, Bolt and Miller, 1957). However, in the present experiments the clay was introduced at a low moisture content and allowed to take up water and swell against an outside pressure. Swelling pressure was taken as the ambient pressure which stopped swelling. Grain pressure would not be expected to cause a volume increase. There is also little hysteresis between the swelling and compression parts of the cycle in these experiments, and between swelling and all but the first compression in the previous experiments (Warkentin, Bolt and Miller, 1957). Grain pressure should contribute to total equilibrium pressure during compression but not during swelling. The observation that these two pressures are so nearly equal indicates that in pure Na-montmorillonite at low salt concentrations there is little evidence of a grain pressure.

In solutions of high salt concentration, where these Na-montmorillonites will not disperse on unconfined swelling, equilibrium layer distances probably exist. Here an osmotic swelling pressure calculated only from the simple Gouy theory combined with the van't Hoff relationship might not explain swelling pressures.

REFERENCE

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