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ON

EFFECT OF WATER PROPERTIES

IN THIXOTROPIC CLAY SYSTEMS

ON BIOLOGICAL ACTIVITY

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ABSTRACT

In this report data are presented to show that suspensions of Na-clay in water are Newtonian and non-hysteretic in their shear stress-shear rate behavior below a clay content of 4 percent by weight but are non-Newtonian and hysteretic above this clay content; also, at this clay content there is a sudden increase in viscosity. Suspensions of Na/Al-clay in water are shown to be more viscous than those of Na-clay, to exhibit no sudden changes in viscosity and to be more non-Newtonian and hysteretic in their behavior. These data are interpreted, with the help of absolute-reaction rate theory, in terms of the existence of strong and weak bonds in the systems.

Data on the specific heat capacities of Na-clay and Na/Al-clay suspensions, obtained with a sensitive microcalorimeter, are discussed. These data show that the specific heat capacities of both kinds of suspensions depart markedly from those calculated from the respective specific heat capacities of the components. The departures are greatest in the case of the Na/Al-clay. An analysis of the data is made and it is shown that these departures are due to interaction between particle surfaces and the associated water, which results in a lattice-ordered water structure of appreciable integrity and extent. Even in a suspension having a clay content as low as 0.5 percent by weight the average specific heat capacity of the water differs from than of normal water by 1.4 percent.

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A report is made of the heat of compression of water in a Na-clay suspension. The heat of compression of this water is found to be much different than that of normal water and there is evidence of a distinct phase change in the water at 20-25 p.s.i.

Results on the relative partial molar free energies of NaCl and water in Na-clay and Na/Al-clay suspensions are reported and interpreted. The results are interpreted to mean that these quantities are influenced significantly by the amount and arrangement of clay particles.

Two graphs comparing data from different experiments are presented. The comparison reveals that there are two critical clay contents at which significant changes in the properties of the clay suspensions occur. These clay contents are 0.5 and 4.0 percent by weight.

The effects of disturbing clay pastes (by tapping) on the rates of germination of lettuce seeds sown on their surfaces is discussed. It is noted that disturbing the pastes in this way increases the rates of germination. Based on the available evidence, it is concluded that tapping the pastes disorients the clay particles from their equilibrium arrangements and, thereby, alters the structure and properties of the associated water. As a result, the germination rates of the seeds is affected. Thus the hypothesis that water structure and properties affect biological activity is supported.

Several investigators[1] have observed that anomalies occur in the properties of water at certain specific temperatures. These anomalies are supposed to be due to higher-order phase transitions in the structure of water. At the same temperatures, anomalies in the activity of biological systems have been noted.[2] Hence, the conclusion has been made that biological systems are sensitive to the structural configuration of water.

In this laboratory, evidence has been accumulated that the properties of water in a clay-water system change as the system gels [3,4]. The change in properties has been ascribed to a change in the structure of the water. Hence, if the observations referred to earlier are valid, biological activity in a clay-water sol should be different than in a clay-water gel. It was with this thought in mind that the present project was initiated. Results obtained on the project during 1966 are

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1/ For a review see: Drost-Hansen, W. Anomalies in the properties of water. Paper presented at the First International Symposium on Water Desalinization, Washington, D.C., October 3-9, 1965.

2/ Drost-Hansen, W. The effects on biologic systems of higher-order phase transitions in water. Annals N.Y. Academy Sci. 125:471-501, 1965.

3/ Kolaian, J. H. and Low, P. F. Thermodynamic properties of water in suspensions of montmorillonite. Clays and Clay Minerals 9:71-84, 1962.

4/ Leonard, R. A. and Low, P. F. Effect of gelation on the properties of water in clay systems. Clays and Clay Minerals. Proc. 12th Natl. Conf., pp. 311-325, 1964.

presented in the following report. These results pertain to changes in water properties occasioned by the sol-gel transition and to associated changes in the germination of seeds placed on the gel surface.

Very recently suspicions have been aroused that the properties of water near the surface of a clay having a thin film of hydrous aluminum oxide on it are different than those near the surface of the same clay without the film. Therefore, Na-clays were prepared with and without this film. Preparation of the Na-clay with the hydrous-oxide film was accomplished by passing a suspension of < 2-micron Wyoming bentonite through a H-saturated exchange resin, allowing it to stand 4 days and then titrating it with NaOH to pH 7. Previous evidence, e.g., that obtained by Low [5/], has shown that a Wyoming clay prepared in this manner has precipitated on its surfaces approximately 0.37 me. of hydrous aluminum oxide per gm. of clay. Preparation of the Na-clay without the film of hydrous aluminum oxide was by a different procedure. In this case, the suspension of < 2-micron Wyoming bentonite was passed through a Na-saturated Dowex 50 cation-exchange resin. Because this resin holds aluminum ions very strongly, the resulting clay can be expected to be essentially free of hydrous aluminum oxide. To remove the unwanted anions from both kinds of suspension, they were

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5/ Low, P. F. The role of aluminum in the titration of bentonite, Soil Sci. Soc. Amer. Proc. 19:135-139, 1955.

dialyzed until no Cl^- could be detected in the dialyzate with $AgNO_3$. Hereafter, the clay containing the hydrous aluminum oxide will be referred to as the Na/Al-clay. That containing essentially no hydrous aluminum oxide will be referred to as the Na-clay. Batches of the latter clay were prepared in 1965 and in 1966. These batches will be differentiated by calling them batch I and batch II, respectively.

To examine the mechanical properties of the different clays, data on viscosity, shear stress versus shear rate, etc., were obtained at room temperature with a Fann Viscometer (Model 35) using the R1-B1 rotor-bob combination and appropriate torsion spring. In figure 1 are plotted the data thus obtained on viscosity versus clay content for the different clays. These data show that the viscosity in suspensions of Na/Al-clay increases continuously with clay content, whereas the viscosity in suspensions of Na-clay remains very low until a clay content of about 4 percent by weight is reached, and then it increases abruptly.

In figures 2, 3 and 4 are plotted curves of shear stress versus shear rate for suspensions of Na/Al-clay and Na-clay containing 2, 4 and 6 (5.7 in the case of the Na-clay) percent clay by weight, respectively. Note that the only suspension exhibiting Newtonian behavior (shear stress $\propto$ shear rate) is that containing Na-clay at a content of 2 percent by weight. All other suspensions were non-Newtonian in their behavior. Note also that hysteresis was evident in the curves for all suspensions excepting those containing Na/Al-clay at 2 percent by weight and Na-clay at 2 and 4 percent by weight.

Curves of the type shown in figures 2, 3 and 4 can be explained on the basis of the theory of absolute reaction rates. Following Powell and Eyring [6] we suppose that there are at least two types of bonds in the clay-water system namely, strong bonds (type 1) and weak bonds (type 2). The total shear stress, f, is expressible as the sum of that required to break the strong bonds, f_1, and that required to break the weak bonds, f_2. Hence

$$f = f_1 + f_2 \tag{1}$$

But, according to the theory, the shear rate, ds_1/dt, of the type-1 bonds is given by

$$\frac{ds_1}{dt} = \frac{\lambda}{\lambda_1} k_r \, e^{f_1 \lambda_2 \lambda_3 \lambda / 2kT} \tag{2}$$

and the shear rate, ds_2/dt, of the type-2 is given by

$$\frac{ds_2}{dt} = f_2/\eta_2 \tag{3}$$

where $\lambda_2\lambda_3$ is the cross-sectional area of the flowing unit on which the shear stress acts, λ_1 is the distance between neighboring flowing units in the direction normal to shear, λ is the distance moved between adjacent equilibrium positions, k_r is the frequency with which

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[6] Powell, R. E. and Eyring, H. Mechanisms for the relaxation theory of viscosity. Nature 154:427-428, 1944.

the flowing unit crosses the energy barrier between adjacent equilibrium positions in the direction of flow at zero stress, k is the Boltzmann constant, T is the absolute temperature and η_2 is the coefficient of viscosity due to type-2 bonds. If the system is homogeneous, both types of bonds must shear at the same rate. Hence,

$$\frac{ds_1}{dt} = \frac{ds_2}{dt} = \frac{ds}{dt} \tag{4}$$

Therefore, the relation between shear stress and shear rate is

$$f = \eta_2 \frac{ds}{dt} + \frac{2kT}{\lambda_2\lambda_3\lambda} \ln\left(\frac{\lambda_1}{\lambda k_r} \frac{ds}{dt}\right) \tag{5}$$

or, in simplified form

$$f = \eta_2 \frac{ds}{dt} + a \ln\left(b \frac{ds}{dt}\right) \tag{6}$$

As shown by Dahlgren 1/, the last equation can be applied to a system containing any number of strong and weak bonds. Thus,

$$f = \Sigma\eta_i \frac{ds}{dt} + \Sigma a \ln\left(b_i \frac{ds}{dt}\right). \tag{7}$$

According to equations (6) and (7) the shear stress depends logarithmically on the shear rate at small shear rates when the term for strong bonds predominates, whereas, it depends linearly on the shear rate at large shear rates when the term for weak bonds predominates. This is what we observed in the non-Newtonian systems.

1/ Dahlgren, S. E. Eyring's model of flow applied to thixotropic equilibrium. Jour. Colloid Sci. 13:151-158, 1958.

On the basis of the foregoing figures and derivation, it seems reasonable to conclude that both strong and weak bonds exist in the suspensions of Na/Al-clay even at low clay contents. The presence of both types of bonds gives rise, not only to the observed non-Newtonian behavior, but to the enhanced viscosity of suspensions of this clay. In contrast, it appears that only weak bonds exist in the suspensions of Na-clay until a clay content of about 4 percent is reached. Then stronger bonds are formed, the viscosity increases suddenly and non-Newtonian behavior begins. The presence of hysteresis in the shear stress-shear rate curves at the two higher clay contents suggests that some of the stronger bonds, when once broken, take time to reform, i.e., thixotropy exists.

It should be noted here that numerous supplementary experiments with the Fann viscometer showed that manipulation of the clay-water suspensions by different techniques, e.g. tapping, stirring or remoulding with a spatula, produced different gel strengths and viscosities. And frequently the viscosity changed with time. Evidently, particle arrangement and bonding are very dependent on the history of the sample. Therefore, most of the experiments described hereafter were conducted on clay suspensions that had been extruded from an 18-guage hypodermic needle. As noted in last year's report, such a suspension, if it has the consistency of a paste, is in a stable equilibrium state that is reproducible.

Since the specific heat capacity of a system can be interpreted in terms of the motions of its molecules and/or particles, the specific heat capacities of suspensions of the Na- and Na/Al-clay were determined at different clay contents and 25°C. To make the clay suspensions comparable to those used for the measurement of NaCl activity, each suspension contained NaCl at a concentration in the aqueous phase of 10^{-4} N. The determinations were carried out in a Calvet microcalorimeter according to the procedure outlined by Calvet and Prat. 8/ The results are shown in figure 5 and are compared to those of Oster and Low 9/ in figure 6.

According to thermodynamic theory, the specific heat capacity of a mixture of clay and water is given by

$$c = \bar{c}_c x_c + \bar{c}_w x_w \qquad (8)$$

where c is the specific heat capacity of the mixture, $\bar{c}_c$ and $\bar{c}_w$ are the partial specific heat capacities of the clay and water, respectively, and x_c and x_w are the corresponding gram fractions. If there

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8/ Calvet, E. and Prat, H. Microcalorimétrie. Applications Physico-chimiques et Biologiques. Masson et C^{ie}, Paris, pp. 140-143, 1956.

9/ Oster, J. D. and Low, P. F. Heat capacities of clay and clay-water mixtures. Soil Sci. Soc. Amer. Proc. 28:605-609, 1964.

is no interaction between the clay and water, i.e., if the mixture is ideal, equation (8) becomes

$$c = c_c x_c + c_w x_w \qquad (9)$$

where the partial specific heat capacities of the two components have been replaced by their respective specific heat capacities. Equation (9) was used to obtain the theoretical line in figures 5 and 6. In obtaining this line a value of 0.191, reported by Oster and Low [2], was used for c_c and the conventional value of 0.998 was used for c_w. Obviously, there was pronounced interaction between each of the clays and water.

There are three kinds of interaction that could cause the experimental curves in figures 5 and 6 to depart from that for the ideal mixture. They are: (1) interaction between the particle surfaces and the water causing an increase in the fraction of the water molecules that occupy positions of minimum energy in a lattice-ordered configuration, (2) interaction between the exchangeable ions and the water causing a disruption of the existing structure of water and creating a new one in the vicinity of the ions, and (3) interaction between the clay particles (e.g., particle-particle bonding) that does not exist when the water is not present. The first two kinds of interaction could either increase or decrease the specific heat capacity depending on the integrity of the resulting structural arrangements. If the resulting structures are easily decomposed by thermal energy, then some of the thermal energy imparted to the

system, instead of increasing the kinetic energy of the molecules (and, thereby, the temperature) would be used to break the bonds that hold the structures together. Thus, more heat would be consumed per degree increase in temperature and the specific heat capacity would be enhanced. However, if the resulting structures are held together by such strong bonds that some of the water molecules in them lose certain modes of motion and are no longer able to absorb energy by those modes [10], then the specific heat capacity would be reduced. The third kind of interaction could only increase the specific heat capacity. This is so because the motion of the <u>particles</u> per se contributes so little to the specific heat capacity that loss of motion by them would make no significant difference. For example, if the particles undergo all three kinds of motion, i.e., rotational, vibrational and translational, the mathematical expression for their energy would involve, at the most, seven quadratic terms and the molar heat capacity would be of the order of 7/2 R. But the number of particles per gm of clay has been reported [4] to be approximately 54×10^{13}. Hence the number of moles, i.e., the fraction of Avogadro's number, is 9×10^{-10}. The latter number multiplied by

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[10] Recall that, according to the classical theory of heat capacity, each mode of motion having energy expressible by a quadratic term contributes 1/2 R to the molar heat capacity.

7/2 R is infinitesimal. However if thermal energy is consumed in rupturing interparticle bonds, an increase in specific heat capacity could result.

Now, we will consider the contribution to the molar heat capacity arising from the decomposition of an ordered structure, i.e., from the order-disorder effect. Let C_r represent this contribution. Following the procedure of Davis and Litovitz [11] it can be shown that

$$C_r = [(H')^2/RT^2]x_d(1 - x_d) \qquad (10)$$

where

$$H' = H_d - H_o \qquad (11)$$

and H_d is the molar heat content of the disordered state, H_o is the molar heat content of the ordered state, R is the molar gas constant, T is the absolute temperature and x_d is the mole fraction of the component in the disordered state. To calculate the maximum value of C_r (when $x_d = 0.5$) we need to know the value of H'.

To obtain the value of H' for particle-particle interaction assume, as is frequently done, that the activation process in the flow of viscous clay suspensions is the process of breaking particle-particle bonds. Also assume that no pressure-volume work is done in this process. With these assumptions H' = E, where E is the activation energy for viscous flow. Since, by the theory of absolute

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[11] Davis, C. M. Jr. and Litovitz, T. A. Two-state theory of the structure of water. Jour. Chem. Phys. 42:2563-2576, 1965.

reaction rates [12]

$$\log \eta = \log A + \frac{E}{2.3RT} \qquad (12)$$

where η is the viscosity and A is a constant, we can obtain a value of E by plotting log η against 1/T for a clay suspension and calculating the slope of the resulting line.

Shown in figures 7 and 8, respectively, are plots of η versus T and log η versus 1/T. The slope of the line in figure 8 yields a value for E and, hence, of H' of 880 cal. per mole. When this value is inserted into equation (10) the maximum value of C_r at 298°K is found to be 1.09 cal per mole. But, as already noted, there are only about 9×10^{-10} moles of particles per gm. of clay and in no case did a gm of suspension contain as much as a gm of clay. Consequently, the contribution of particle-particle interaction to the specific heat capacity can be ignored. Even if the value of H' far exceeds that obtained from the measured activation energy this conclusion would be unchanged. The same conclusion is reached by noting from figure 5 that the maximum positive departure from the theoretical line occurs at a clay content of 0.5 percent. As will be shown later, particle-particle interaction does not occur appreciably below this clay content.

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[12] Glasstone, S., Laidler, K. J. and Eyring, H. The Theory of Rate Processes. McGraw-Hill Book Co., New York, 1941.

To assess the role of ion-water interaction in contributing to the specific heat capacity we will refer to data obtained for aqueous solutions. Several investigators [13-17] have calculated the apparent or partial molar heat capacity of Na^+ in solution at constant pressure. Their data range from -9.3 to +37 cal./deg./mole at infinite dilution, depending on the assumptions used in dividing the apparent or partial molar heat capacity of a reference electrolyte into the contributions of the component ions. But, regardless of the value adopted, only a small fraction of the difference between the measured and theoretical specific heat capacities presented in figures 5 and 6

13/ Rossini, F. D. Apparent and partial molal heat capacities in aqueous solutions of 19 uni-univalent strong electrolytes. Jour. Res. Nat. Bur. Stand. 7:47-55, 1931.

14/ Ackermann, Th. Hydration of H^+ and OH^- ions in water from heat capacity measurements. Faraday Soc. Discussions 24:180-193, 1957.

15/ Lewis, G. N. and Randall, M. Thermodynamics. 2nd ed. (Revised by K. S. Pitzer and L. Brewer) McGraw-Hill Book Co., New York, pp. 400-401, 1961.

16/ Noyes, R. M. Assignment of individual ionic contributions to properties of aqueous ions. Jour. Amer. Chem. Soc. 971-979, 1964.

17/ Criss, C. M. and Cobble, J. W. The thermodynamic properties of high temperature aqueous solutions. V. The calculation of ionic heat capacities up to 200°. Entropies and heat capacities above 200°. Jour. Amer. Chem. Soc. 86:5390-5393, 1964.

can be accounted for by the presence of exchangeable Na^+. This fact becomes evident by the following reasoning. When we add clay to water the following reaction takes place

$$\text{Na-clay} \longrightarrow \text{Na}^+ + \text{clay}$$

Thus, in effect, we are adding Na^+ ions and clay from which these ions have been dissociated instead of the undissociated clay. And both Na^+ and dissociated clay may interact with the water to change its properties. But we obtained the theoretical lines in figures 5 and 6 using data for pure dry clay and pure water. If we call the difference between the observed and theoretical values (obtained by equation (9)) the excess specific heat capacity, c_e, then

$$c_e = x'_c \varphi_c + x'_+ \frac{\Phi_+}{M_+} - x_c c_c \qquad (13)$$

where x'_c, x'_+ and x_c are the gram fractions of the dissociated clay, dissociated Na^+ ions and total clay, respectively; φ_c is the apparent specific heat capacity of dissociated clay; Φ is the apparent molar heat capacity of Na^+ ions in solution, M_+ is the molecular weight of Na^+ and c_c is the specific heat capacity of the pure dry clay. However, <u>if no interaction occurs between clay and water</u>,

$$x_c c_c - x'_c \varphi_c \cong x'_+ \cdot \frac{3R}{M_+} \qquad (14)$$

because, in the dissociation process, x'_+/M_+ moles of ions are removed from particle surfaces where they oscillate about the sites of surface charge and contribute, according to classical theory, 3R cal/

mole/deg to the heat capacity. Hence, equation (13) can be written

$$c_e = \frac{x'_+}{M_+}(\Phi_+ - 3R) \tag{15}$$

But $x'_+ = \alpha\, x_+$ where α is the degree of dissociation and x_+ is the gram fraction of all Na^+, dissociated and undissociated, in the system. Therefore,

$$c_e = \alpha \frac{x_+}{M_+}(\Phi_+ - 3R) \tag{16}$$

The NaCl activity data in the Na- and Na/Al-clay suspensions, which will be discussed later, suggests that α is less than 0.3. Using this value and the maximum positive value reported for Φ_+ (i.e., 37 cal/deg/mole) we find that c_e in the suspension containing 0.5 percent clay is 4.6×10^{-5} cal/deg/gm if the base exchange capacity is of the order of 1 me per gm of clay. Actually the Na-clay has a base exchange capacity of 0.954 me per gm and the Na/Al-clay has a base exchange capacity of 0.745 me per gm. Thus it is evident that the Na^+ ions cannot account for the discrepancy between the observed and theoretical values at this clay content. Similar calculations using any of the reported values for Φ_+ and any experimental clay content invoke the same conclusion.

Evidently, the discrepancies between the experimental and theoretical curves in figures 5 and 6 can best be accounted for on the basis of interaction between the water and the particle surfaces. This being the case, it is of interest to examine the relationship between the apparent specific heat capacity of the water,

Φ_w, and the clay content. The appropriate equation for Φ_w is

$$\Phi_w = \frac{c - c_c x_c}{x_w} . \qquad (17)$$

This equation was utilized to obtain the curves in figure 9.

The curves in figure (9) emphasize the departures from ideality observed in figures 5 and 6. Evidently, interaction between the clay surfaces and the water alters the thermal properties of the water to a marked degree. The extent of this alteration cannot be fully appreciated unless it is realized that the apparent specific heat capacity is an average quantity. Thus, in the 0.5-percent suspension of Na/Al-clay, which is more effective in influencing the water than the Na-clay, the average specific heat capacity of the water is as much as 1.4 percent greater than that for pure bulk water. And it is as much as 1.5 percent lower than that for pure bulk water in the 12-percent suspension. Probably, the curves derived from the data of Oster and Low [9] represent extensions of those for the Na/Al-clay in this figure and figure 6. Oster and Low passed their clays through an H-exchange resin and then titrated them with NaOH. Since the curves in figures 5, 6 and 9 show the same effects with different emphasis, a common explanation should apply to all of them. A plausible explanation follows.

Attention was called earlier to the fact that order-disorder effects can contribute appreciably to the heat capacity. In pure bulk water as much as 12 of the 18 cal/deg/mole can be ascribed to these effects. [11] Therefore, it is reasonable to believe that, in

those suspensions where there is an excess specific heat capacity compared to the theoretical one, the particle surfaces induce an ordered structure in the vicinal water and that this structure, at least in those regions farthest removed from the surfaces, is thermally unstable. Further, attention was called to the fact that the "freezing out" of degrees of freedom or modes of motion can detract from the heat capacity. Consequently, it is reasonable to believe that, in those suspensions where the specific heat capacity is less than the theoretical one, the integrity of this or a similar water structure becomes great enough that some of the water molecules lose freedom of motion and do not contribute to the specific heat capacity. Now, for a given clay, the suspensions differed only in clay content and, hence, in the angular relationship and proximity of their surfaces. Of course, these factors can affect the nature and intensity of force fields and bonds. With these thoughts in mind, it is proposed that, at clay contents less than 0.5 percent, the clay particles are largely independent of each other and that, associated with each one, is an extensive hydration shall which is thermally unstable in its outermost layers. At a clay content of 0.5 percent, or thereabouts, the clay particles begin to interact with each other to form clusters or domains. Interaction at this clay content has been shown by measurements of viscosity and optical density [18]. Probably, the clusters are

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[18] van Olphen, H. and Waxman, M. H. Surface conductance of sodium bentonite in water. Proc. 5th Nat. Conf. on Clays and Clay Minerals, pp. 61-80, 1958.

composed of parallel ribbons formed by the edge-to-edge linking of particles [19]. The water structure within the clusters, under the mutual influence of adjacent surfaces, acquires greater integrity and the "slushy" regions are absent. As the clusters increase in number the fraction of the water involved therein increases. At a clay content of about 12 percent the spacial requirements of the clusters can no longer be met and a face-to-face arrangement of the particles begins to occur. The latter arrangement predominates at higher clay contents. In the face-to-face arrangement there is less integrity in the water structure. The loss in integrity is probably aggravated by the exchangeable ions which, at the higher clay contents, have appreciable concentrations. Whether or not there is an abrupt change in water structure in the Na-clay suspensions at a clay content of 4 percent, corresponding to the abrupt change in viscosity, cannot be ascertained at the present time because of insufficient data on specific heat capacities.

In figure 10 are plotted data on the heat of compression of a suspension of Na-clay. These data were obtained in the following manner. A clay paste, which had been prepared by placing dry clay inside a filter candle and wetting it under vacuum with a degassed

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19/ M'Evan, M. B. and Mould, D. L. The gelation of montmorillonite. Part 2. The nature of the interparticle forces in sols of Wyoming bentonite. Faraday Soc. Transactions, 53:548-564, 1957.

0.0001 N NaCl solution, was extruded into a hypodermic syringe which was subsequently evacuated, with the plunger in place, through the needle. Then the paste was introduced into the inner cylinder of a special calorimetric cell by inserting the needle (from which the air had been displaced by extrusion of a small part of the paste) through a rubber stopper capping the cylinder and depressing the plunger. The cylinder into which the clay was introduced had previously been filled with degassed water through a long narrow stainless-steel tube connected to it. The water that was displaced by the paste escaped through this tube. Next, the rubber stopper was removed from the inner cylinder and, while this cylinder was inverted, the concentric outer cylinder was screwed into place. The outer cylinder also had a long narrow stainless-steel tube connected to it and the final evacuation and filling of the cell was accomplished through this tube. Then the cell was placed in an upright position in the calorimeter and pressure was applied on the water in the stainless-steel tubes. The resulting heat of compression was registered as a peak on the recorder chart.

The calculated curve, which is presented for the purpose of comparison, was obtained by first filling the special calorimetric cell with pure water and obtaining the peak height-pressure curve, and then filling it with pure water and glass beads and obtaining this curve again. Obviously the difference between the two curves represented the heat of compression of the water displaced by the glass beads. Since the volume of the glass beads had been determined previously in a pycnometer, the weight of water they displaced was calculable.

At any given pressure the difference between the two peak height-pressure curves divided by the weight of displaced water gave the peak height per gm of water at that pressure. The values thus obtained were multiplied by the weight of water displaced by the clay, which was calculated using a clay density of 2.8 gm per cm^3, and subtracted from the values obtained when only water was present in the cell. The resulting values were used to plot the calculated curve.

It is evident from figure 9 that the water in the clay had a different heat of compression than the same amount of pure bulk water. The heat of compression at constant temperature $(\partial Q/\partial P)_T$ is related to the thermal dilatation at constant pressure $(\partial V/\partial T)_P$ by the following equation from Bridgman [20]

$$\left(\frac{\partial Q}{\partial P}\right)_T = - T\left(\frac{\partial V}{\partial T}\right)_P \qquad (18)$$

where Q is the heat lost, P is the pressure, T is the temperature and V is the volume. Therefore, it is also evident that the thermal dilatation of the water in the clay suspension is different from that of pure bulk water. Further, the pronounced break in the observed curve at 20-25 p.s.i. is indicative of a higher-order phase change in the water associated with the clay particles. It appears that below this

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[20] Bridgman, P. W. Thermodynamic properties of liquid water to 80° and 12000 KGM. Collected Experimental Papers 1:379-432, 1964.

pressure interval the heat of compression of the water in suspension is lower than that for pure water, whereas, above this pressure interval it is greater than that for pure water. The same applies to the magnitude of the thermal dilatation which, in this case, is a negative quantity. The data on heat of compression support those on specific heat capacity in that they show that clay surfaces alter the properties of the adjacent water.

Presented in figure 11 are curves of water tension versus clay content for suspensions of Na- and Na/Al-clay. The tension data were obtained using a tensiometer in which pure water in contact with the diaphragm of a sensitive pressure transducer, which served as one wall of a closed compartment, was in contact with the suspension through a Visking dialysis membrane. For an arrangement of this kind, the relative partial molar free energy of the water in the suspension at atmospheric pressure $(\overline{F} - F^{o})_{p}$ can be related to the tension, τ, by the following expression, derived by Leonard and Low [4]

$$(\overline{F} - F^{o})_{p} = -M g \tau. \qquad (19)$$

In this expression M is the molecular weight of water and g is the acceleration of gravity. It should be mentioned here that equation (19) applies only if the membrane is permeable only to the water and not to the clay particles, and this may not be strictly the case for the Visking membrane [21]. Nevertheless, the tension data indicate that

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[21] Banin, A., Davey, B. G. and Low, P. F. Effect of membrane pore size on the measurement of water tension in clay systems. Soil Sci. Soc. Amer. Proc. In press.

the relative partial molar free energy of the water in suspensions of Na/Al-clay is less than that in comparable suspensions of Na-clay. Probably, this can be accounted for on the basis of the previous observations which indicated that the water in suspensions of the former clay had greater structural integrity and, hence, a lower escaping tendency. Special note should be taken of the fact that, in the Na-clay suspensions, the water tension was zero until the clay content reached 4 percent--the clay content at which the viscosity suddenly increased. Thereafter it assumed finite values.

The curves in figure 12 show the relationship between the relative partial molar free energy of NaCl in suspensions of the two clays and clay content. The relative partial molar free energy $(\overline{F} - F^{o})_{NaCl}$ was obtained by measuring the electromotive force, E, between a Ag-AgCl and a sodium glass electrode inserted in the suspension and utilizing the result in the equation

$$E = E^{o} + \frac{(\overline{F} - F^{o})_{NaCl}}{F} \qquad (20)$$

where E^{o} is the standard potential and F is the faraday. Since the sodium glass electrode ages and, therefore, E^{o} changes, the electrodes were calibrated periodically in a NaCl solution having a known value for $(\overline{F} - F^{o})_{NaCl}$. A striking thing about these results is the drop in $(\overline{F} - F^{o})_{NaCl}$ between 0 and 0.5 percent clay. This drop is all the more striking in view of the fact that Na^{+} is being added with the clay. The addition of Na^{+} would normally increase $(\overline{F} - F^{o})_{NaCl}$,

as shown by the following equations:

$$(\overline{F} - F^{o})_{NaCl} = 2RT \ln a_{\pm} \tag{21}$$

$$a_{\pm}^{2} = a_{+}\, a_{-} \tag{22}$$

in which $a_{\pm}$ is the mean ionic activity of NaCl, a_{+} is the activity of Na^{+} and a_{-} is the activity of Cl^{-}. Apparently, there is interaction between the force fields emanating from the surfaces of the particles, or between the shells of altered water associated with these surfaces, which affects the activity of NaCl before significant particle-particle interaction or clustering begins. At a clay content of 0.5 percent, where particle-particle interaction becomes evident [18], the trend in $(\overline{F} - F^{o})_{NaCl}$ is reversed. Whether this reversal is due to the change in the intensity of the force fields as the particles form clusters, or to the change in the nature of the water in these clusters, is not known. The formation of a coherent, intensely-bonded water structure could tend to exclude ions, as ice does, and raise their activities. It is interesting to note, however, that a sharp break in the rate of increase of $(\overline{F} - F^{o})_{NaCl}$ with clay content occurred at a clay content slightly above 4 percent in the Na-clay suspensions--the clay content at which the stronger bonds formed and the viscosity rose suddenly. Since such a sharp break was not evident at this point in the curves of specific heat capacity, it is not improbable that the activities of Na^{+} and Cl^{-} are reduced because of their involvement in the bonding process. Obviously, more research must be done before these problems are resolved.

Now,

$$\gamma_{\pm} = \frac{a_{\pm}}{c_{\pm}} \tag{23}$$

and

$$c_{\pm}^2 = c_+ \, c_- \tag{24}$$

where $\gamma_{\pm}$ is the mean ionic activity coefficient, $c_{\pm}$ is the mean ionic concentration, c_+ is the concentration of Na^+ and c_- is the concentration of Cl^-. Therefore, we conclude that, since the exchangeable Na^+ contents for the Na- and Na/Al-clay are 0.954 and 0.745 me per gm, respectively, the mean ionic activity coefficients of NaCl in suspensions of Na/Al-clay must be greater than those in comparable suspensions of Na-clay. An analysis of the magnitude of these coefficients indicates that they are generally less than 0.3, as noted earlier. But, if it is assumed that the Cl^- ion acts ideally, because it is present in such a low concentration, then

$$\gamma_{\pm}^2 = \frac{a_+}{c_+} = \gamma_+ \tag{25}$$

and γ_+ becomes less than 0.1. Hence, it appears that Na^+ is only slightly dissociated from the particle surfaces.

Figures 13 and 14 are presented to illustrate the fact that different kinds of data, obtained by us and others, are consistent in exhibiting dramatic changes at or near clay contents of 0.5 and 4.0 percent in the Na-clay suspensions. In these figures c_p indicates the specific heat capacity at constant pressure; K_c/c indicates the

weight conductance, i.e., the specific conductance divided by the concentration of clay in gm per 100 cm^3; η_{sp}/c indicates the specific viscosity divided by the clay concentration; and, as before, $(\overline{F} - F^o)_{NaCl}$ indicates the partial molar free energy of NaCl. The η_{sp}/c data in figure 13 were taken from van Olphen and Waxman [18]. The K_c/c data in both figures were taken from Jorgensen [22]. The remainder of the data were obtained in this study. All of these data have already been discussed in this report excepting the weight conductance data. As regards these data, it should be pointed out that the weight conductance decreases with a decrease in $(\overline{F} - F^o)_{NaCl}$ and vice versa, which is to be expected since the latter quantity is a measure of the escaping tendency of the salt. Also, attention is called to the precipitous drop in weight conductance between clay contents of 3.2 and 3.7 percent. This drop is to be associated with the loss in particle mobility that occurs at this point. It is the break that occurs at a clay content of 4.2 percent that is likely to be associated with the corresponding break in $(\overline{F} - F^o)_{NaCl}$.

Figures 15, 16 and 17 show the effects of different kinds, contents and treatments of clay suspensions on the germination of lettuce seeds. In the relevant experiments, Na- and Na/Al-clay suspensions having clay contents of 4 percent (figure 15), 6 percent (figure 16) and 8 percent (figure 17) were extruded from a hypodermic syringe

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[22] Jorgensen, P. Density, conductance and infrared studies of clay-water systems. Unpublished Ph.D. thesis, Purdue University, January, 1967.

through an 18-guage needle into petri dishes. Each of these suspensions had the consistency of a paste. Two petri dishes were prepared in this manner for each kind of clay at each clay content. Then one of each was jarred slightly by tapping it on the laboratory bench. Following this the surfaces of the pastes were smoothed gently with a spatula and 100 lettuce seeds were placed on each one. Thereafter, the lettuce seeds were examined periodically for the appearance of radicles. Between examinations the covered petri dishes were kept in the dark. At each examination those seeds exhibiting radicles were removed with tweezers and counted. Thus, the data in the figures were obtained.

Inspection of these figures reveals that, consistently, the lettuce seeds germinated faster on the extruded and tapped pastes than on the corresponding pastes that were extruded only. This difference in germination rates increased with increasing clay content in the Na-clay pastes but decreased in the Na/Al-clay pastes. Also, the rate of germination was higher on the former kind of paste than on the latter when both pastes were treated similarly. And there was usually, but not always, a tendency for the rate of seed germination to decrease with increasing clay content.

These observations can be explained on the basis of the data reported earlier which indicated a strong dependence of water properties in a clay system on particle arrangement. Evidently, tapping the pastes disoriented the particles from the parallel arrangement existing as a result of extrusion through the hypodermic needle and, thereby,

changed the properties of the water so that the germination of the seeds was enhanced. Since previous evidence [3,4] showed that mechanical disturbance of a clay gel in its equilibrium state reduces the tension of the water in it, the enhancement of seed germination may have been the result of a reduction in water tension alone. Germination of seeds is very sensitive to water tension.[23] But other changes in water properties may have played a role [24]. In any event, unique data have been obtained that support the hypothesis on which this study is based, namely, that a change in the structure and properties of water affects the activity of biological entities associated with it.

Possibly, the reason why the effect of tapping the pastes on seed germination became more pronounced with increasing clay content for the Na-clay but not for the Na/Al-clay is the following. The Na-clay particles, forming weaker inter-particle bonds, were disoriented by the tapping more easily but returned to their equilibrium orientation more readily. As the clay content increased, because of increased steric hindrance and enhanced energy barriers, reorientation of the

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[23] Collis-George, N. and Sands, J. E. Comparison of the effects of the physical and chemical components of soil water energy on seed germination. Australian Jour. Agric. Res. 13:575-584, 1962.

[24] Low, P. F. Effect of quasi-crystalline water on rate processes involved in plant nutrition. Soil Sci. 93:6-15, 1962.

particles required a longer time. Hence, restoration of the original water structure was delayed and the altered water structure, with its attendant properties, had a longer time to affect seed germination. Thus, in this case, an increase in clay content decreased the rate of return to the initial state and, thereby, increased the difference in seed germination between the tapped and un-tapped systems. This explanation is supported by the observation that hysteretic and non-Newtonian behavior increased with an increase in the content of Na-clay. On the other hand, the Na/Al-clay particles, forming stronger inter-particle bonds, were disoriented by the tapping less easily and returned to their equilibrium orientation with difficulty. As the clay content increased, the number of strong inter-particle bonds increased and tapping had less effect on disorientation of the particles. Thus the tapped and un-tapped systems became less discrepant in particle arrangement. As a result, the structure and properties of the water in them became less dissimilar. Thus, as regards the Na/Al-clay pastes, an increase in clay content decreased the degree of particle disorientation occasioned by tapping and, thereby, decreased the difference in the rate of seed germination between the tapped and un-tapped systems. In support of this explanation, recall that the Na/Al-clay systems exhibited pronounced non-Newtonian behavior at all clay contents, but to a greater degree at the higher ones.

The observation that the rate of seed germination was always higher on the Na-clay pastes than on the Na/Al-clay pastes of comparable treatment is easily explained by the fact that the latter clay

induced a structure in the associated water of greater integrity, and from which the water molecules escaped with more difficulty. Of course, as the clay content of both kinds of paste increased, the integrity of the associated water structures increased and the rate of seed germination decreased.

The research reported herein was under the direction of the author but was carried out largely by Dr. B. G. Davey, to whom the author expresses his appreciation.

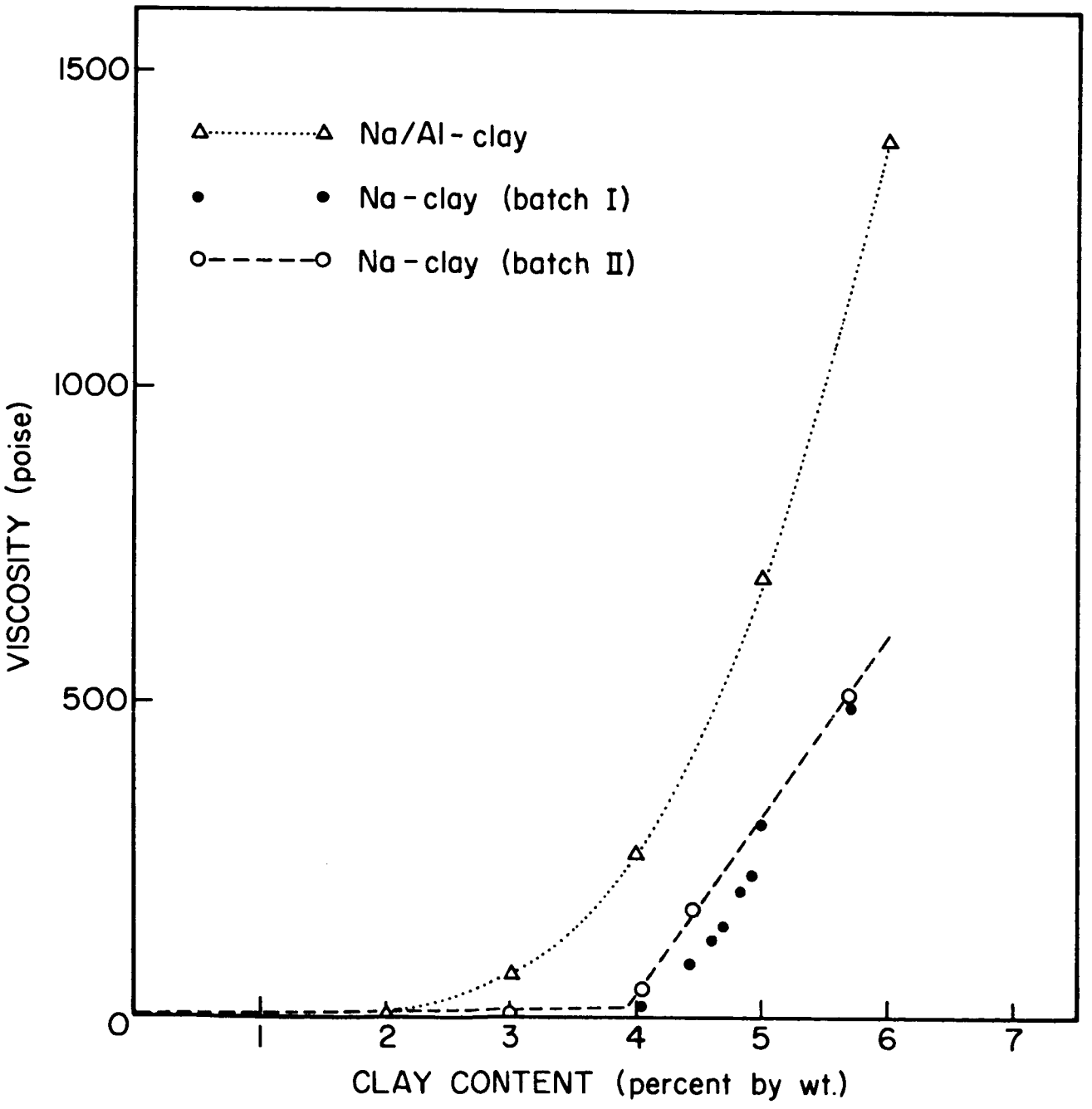
1500
1000
500
0
VISCOSITY (poise)
Na/Al - clay
Na - clay (batch I)
Na - clay (batch II)
1
2
3
4
5
6
7
CLAY CONTENT (percent by wt.)

Fig 1

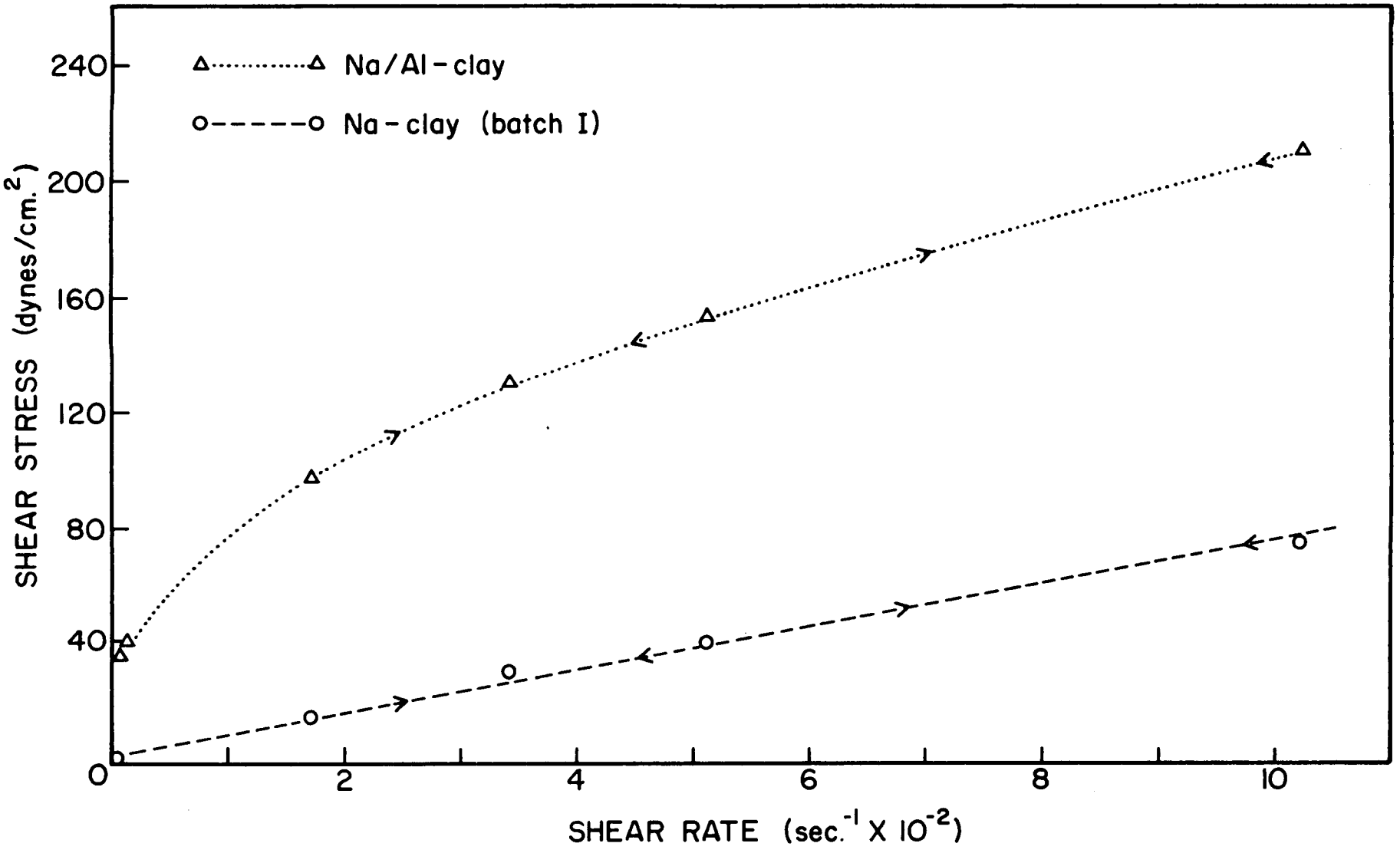
Na/Al-clay
Na-clay (batch I)
SHEAR STRESS (dynes/cm.^{2})
240
200
160
120
80
40
0
2
4
6
8
10
SHEAR RATE (sec.$^{-1}$ X 10^{-2})

Fig 2

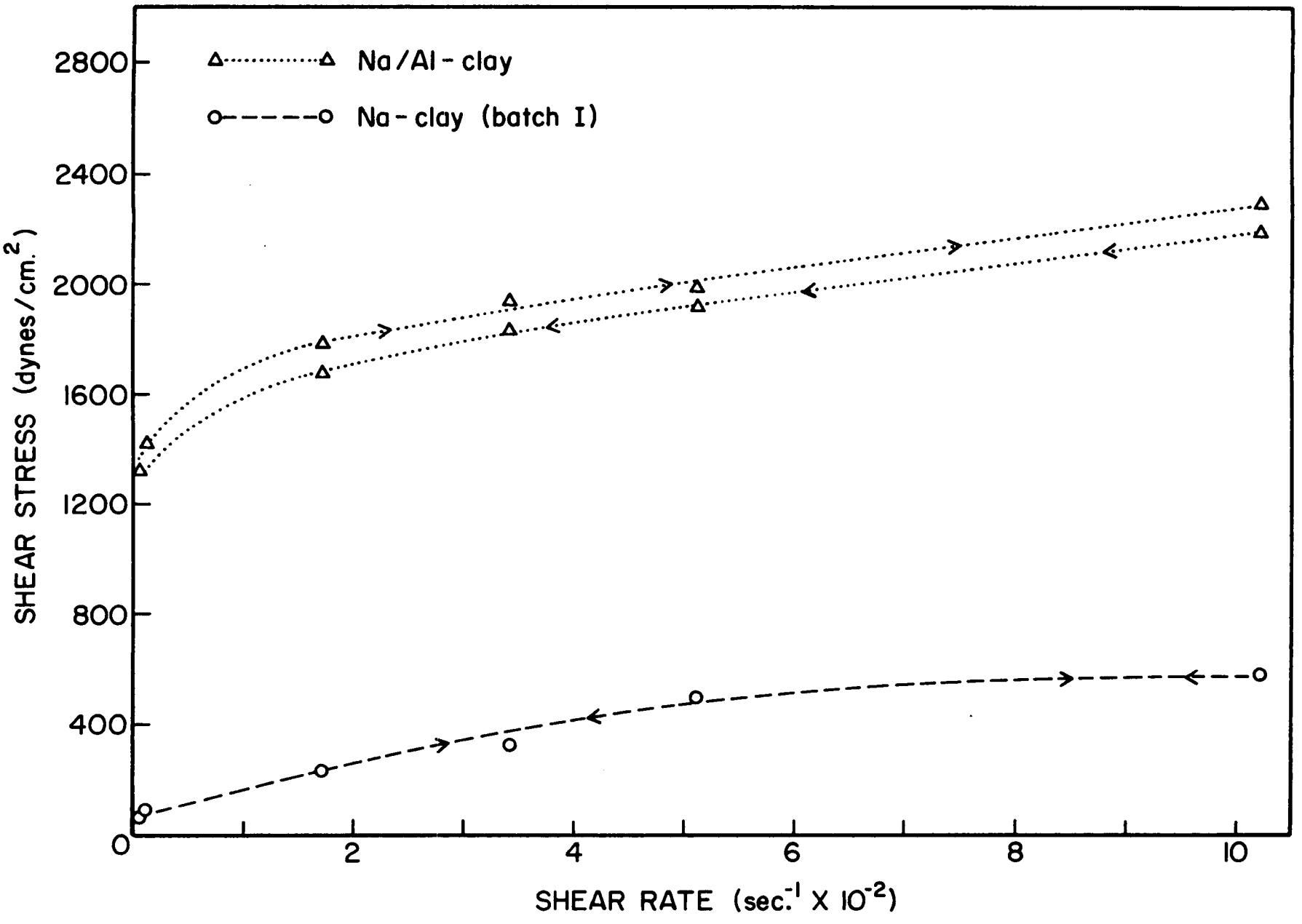
Na/Al - clay
Na - clay (batch I)
SHEAR STRESS (dynes/cm.^{2})
2800
2400
2000
1600
1200
800
400
0
2
4
6
8
10
SHEAR RATE (sec.$^{-1}$ X 10^{-2})

Fig 3

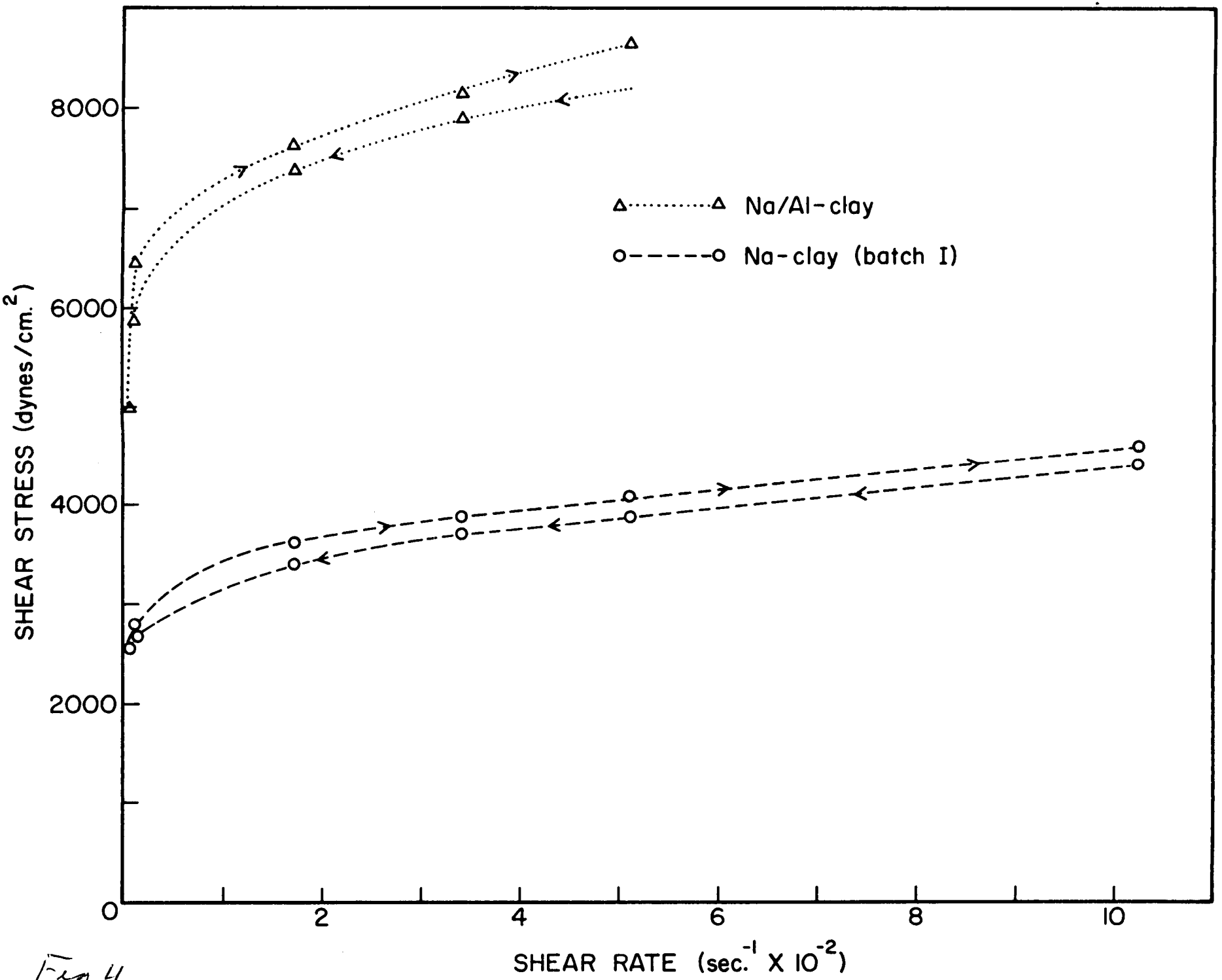
8000
6000
4000
2000
0
SHEAR STRESS (dynes/cm.^{2})
2
4
6
8
10
SHEAR RATE (sec.$^{-1}$ X 10^{-2})
Na/Al-clay
Na-clay (batch I)

Fig 4

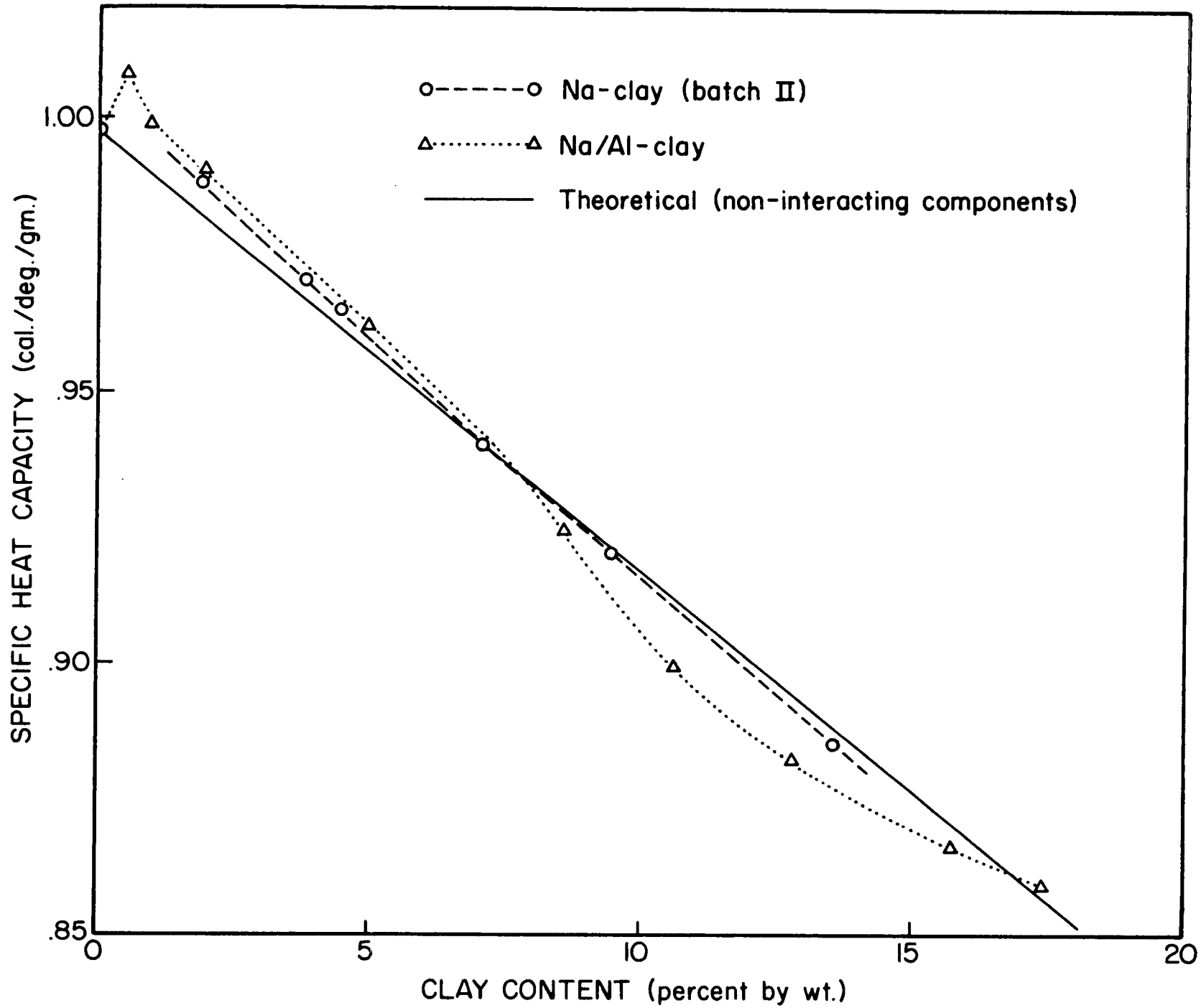
o-----o Na-clay (batch II)
Δ·····Δ Na/Al-clay
——— Theoretical (non-interacting components)
SPECIFIC HEAT CAPACITY (cal./deg./gm.)
1.00
.95
.90
.85
0
5
10
15
20
CLAY CONTENT (percent by wt.)

Fig 5

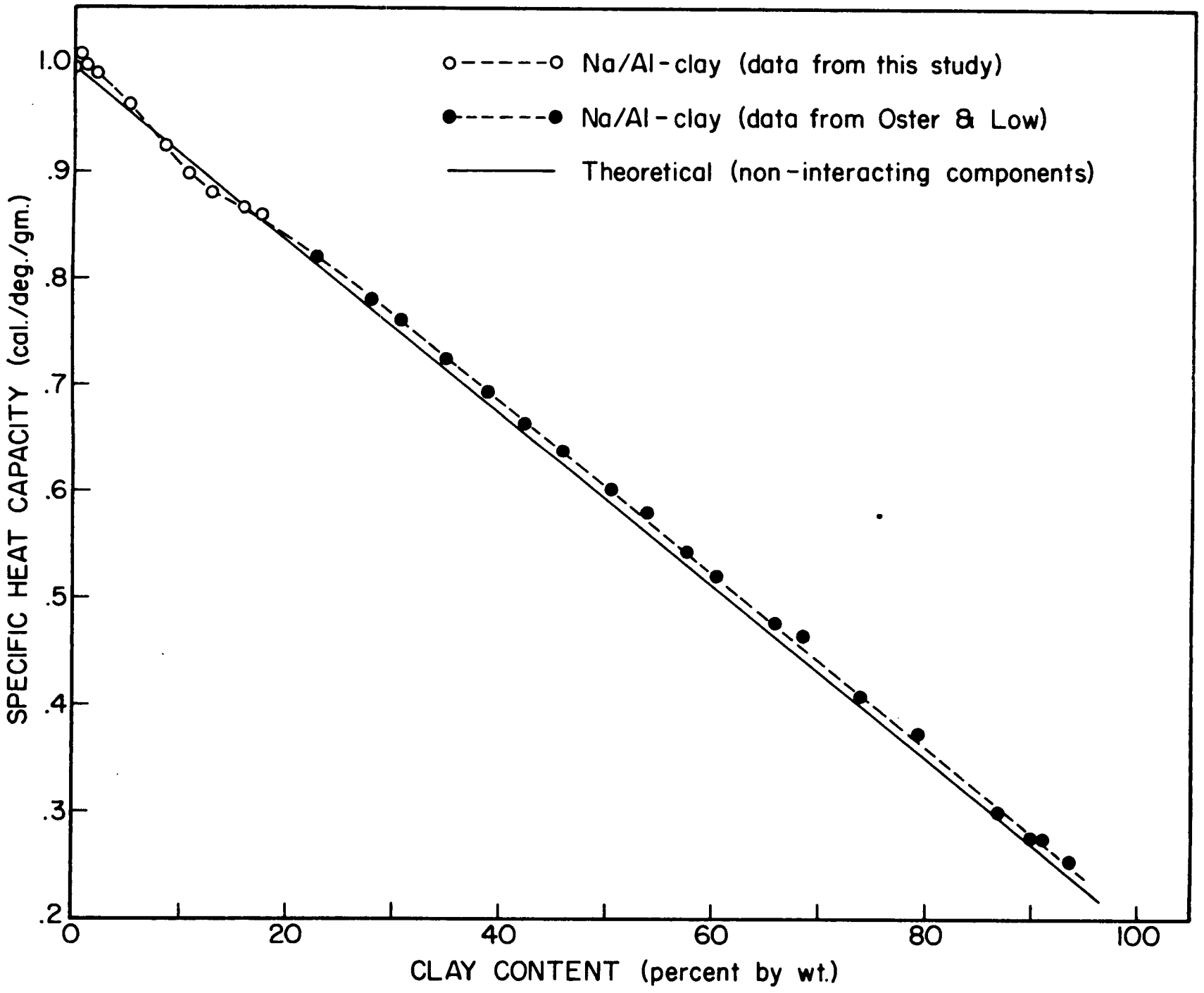
o-----o Na/Al-clay (data from this study)
●-----● Na/Al-clay (data from Oster & Low)
——— Theoretical (non-interacting components)
SPECIFIC HEAT CAPACITY (cal./deg./gm.)
1.0
.9
.8
.7
.6
.5
.4
.3
.2
0
20
40
60
80
100
CLAY CONTENT (percent by wt.)

Fig 6

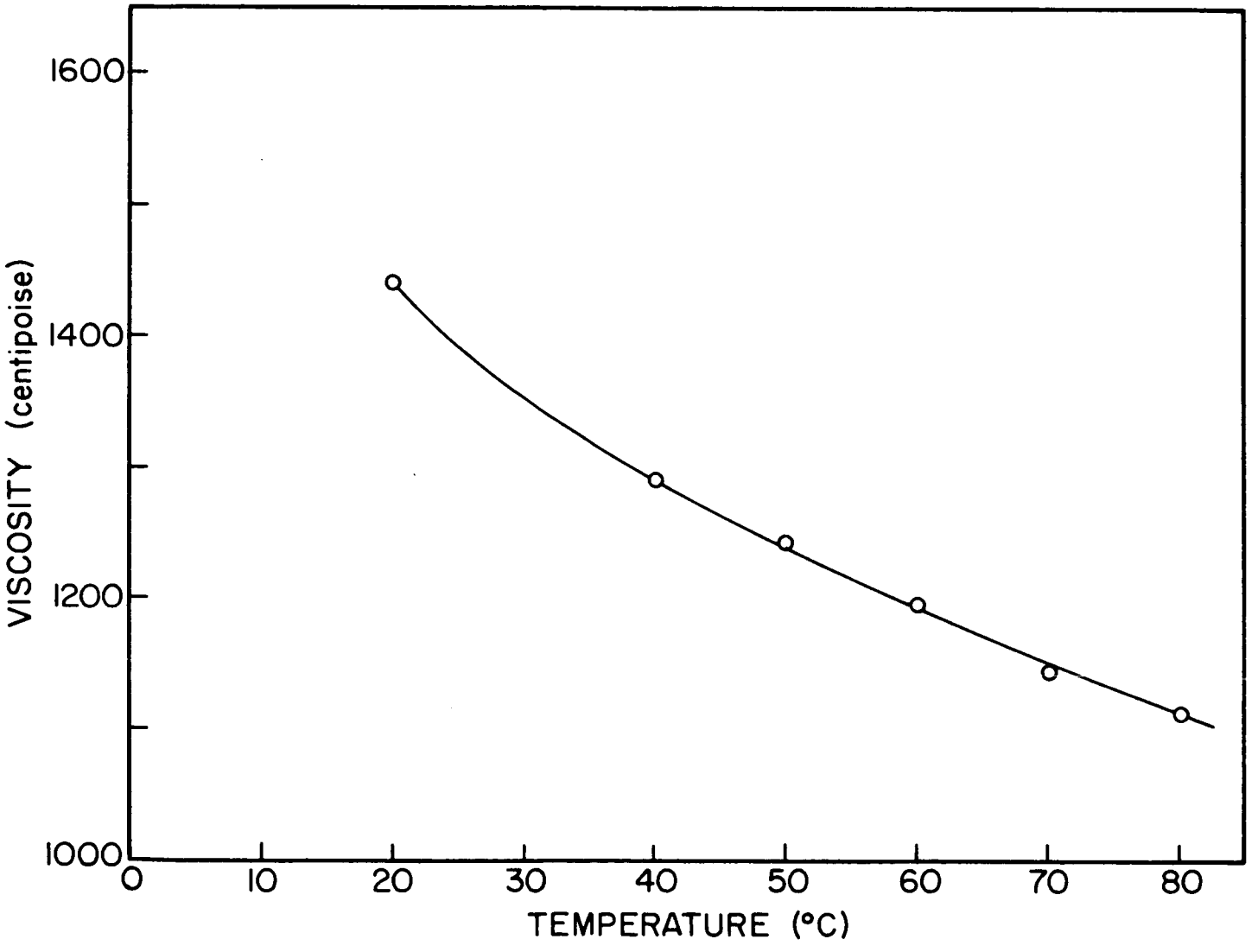
VISCOSITY (centipoise)
1600
1400
1200
1000
0
10
20
30
40
50
60
70
80
TEMPERATURE (°C)

Fig 7

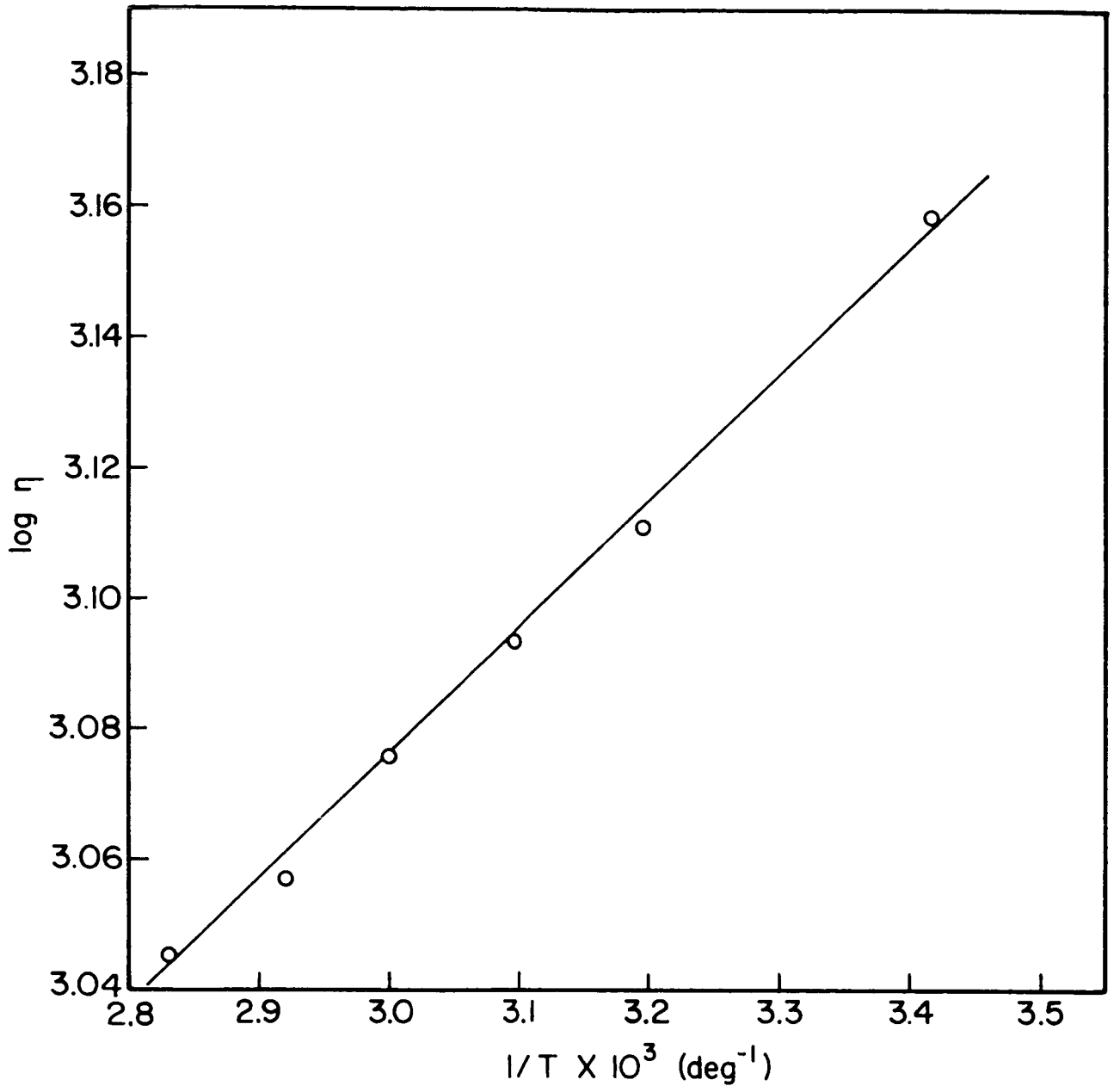
3.18
3.16
3.14
3.12
3.10
3.08
3.06
3.04
log η
2.8
2.9
3.0
3.1
3.2
3.3
3.4
3.5
1/T X 10³ (deg⁻¹)

Fig 8

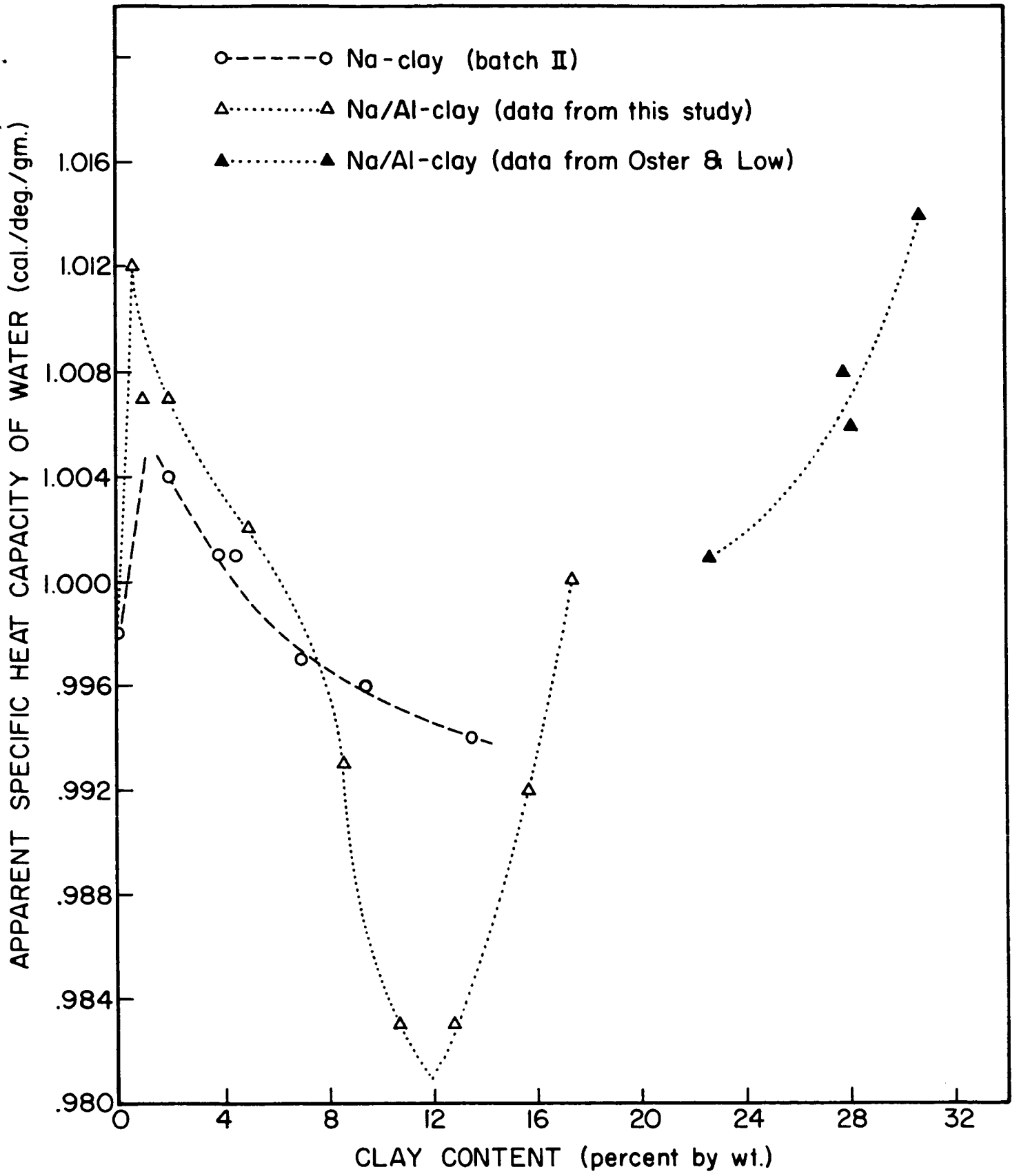
Na-clay (batch II)
Na/Al-clay (data from this study)
Na/Al-clay (data from Oster & Low)
APPARENT SPECIFIC HEAT CAPACITY OF WATER (cal./deg./gm.)
1.016
1.012
1.008
1.004
1.000
.996
.992
.988
.984
.980
0
4
8
12
16
20
24
28
32
CLAY CONTENT (percent by wt.)

Fig 9

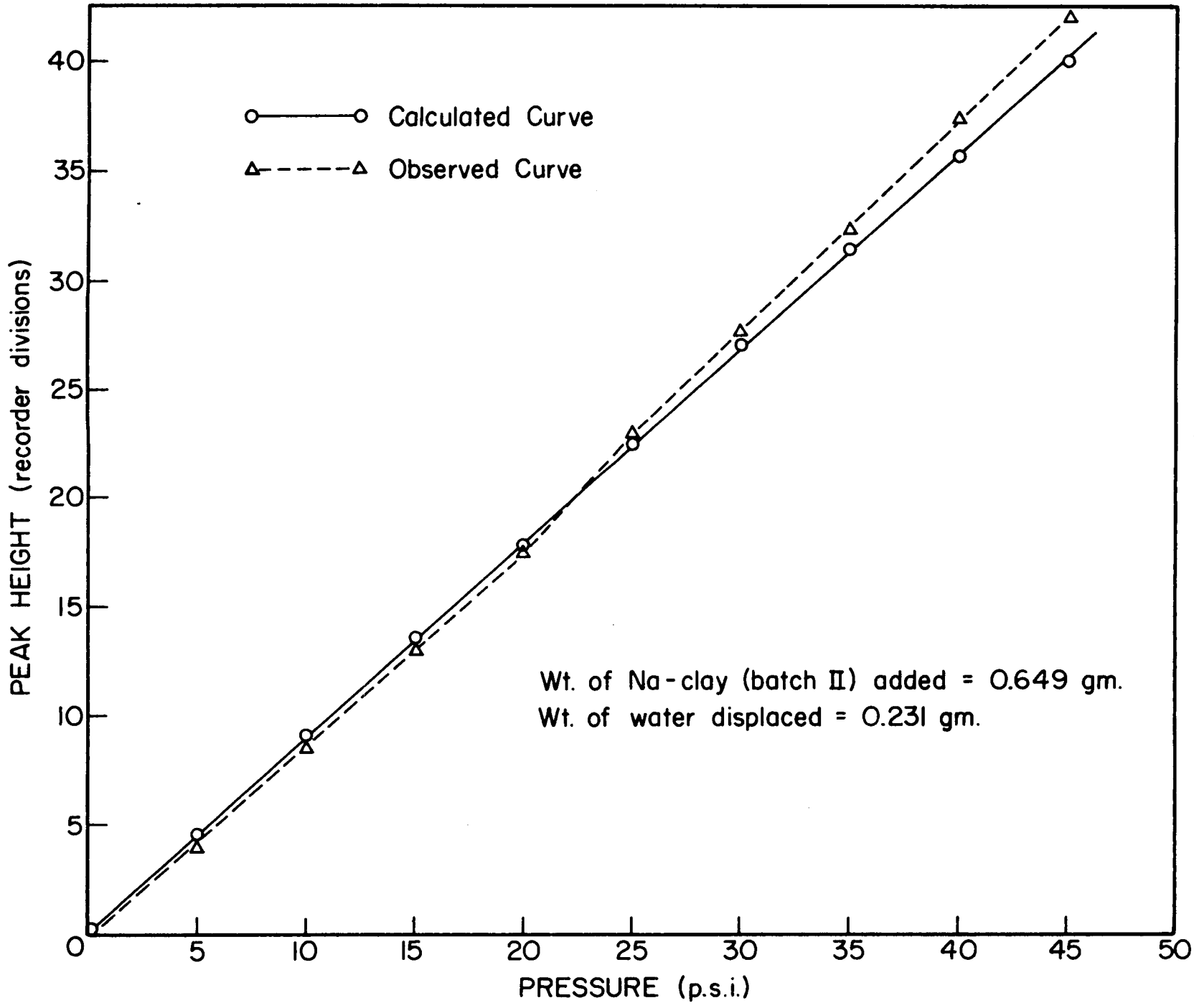
Calculated Curve
Observed Curve
Wt. of Na-clay (batch II) added = 0.649 gm.
Wt. of water displaced = 0.231 gm.
PEAK HEIGHT (recorder divisions)
PRESSURE (p.s.i.)
0
5
10
15
20
25
30
35
40
45
50

Fig 10

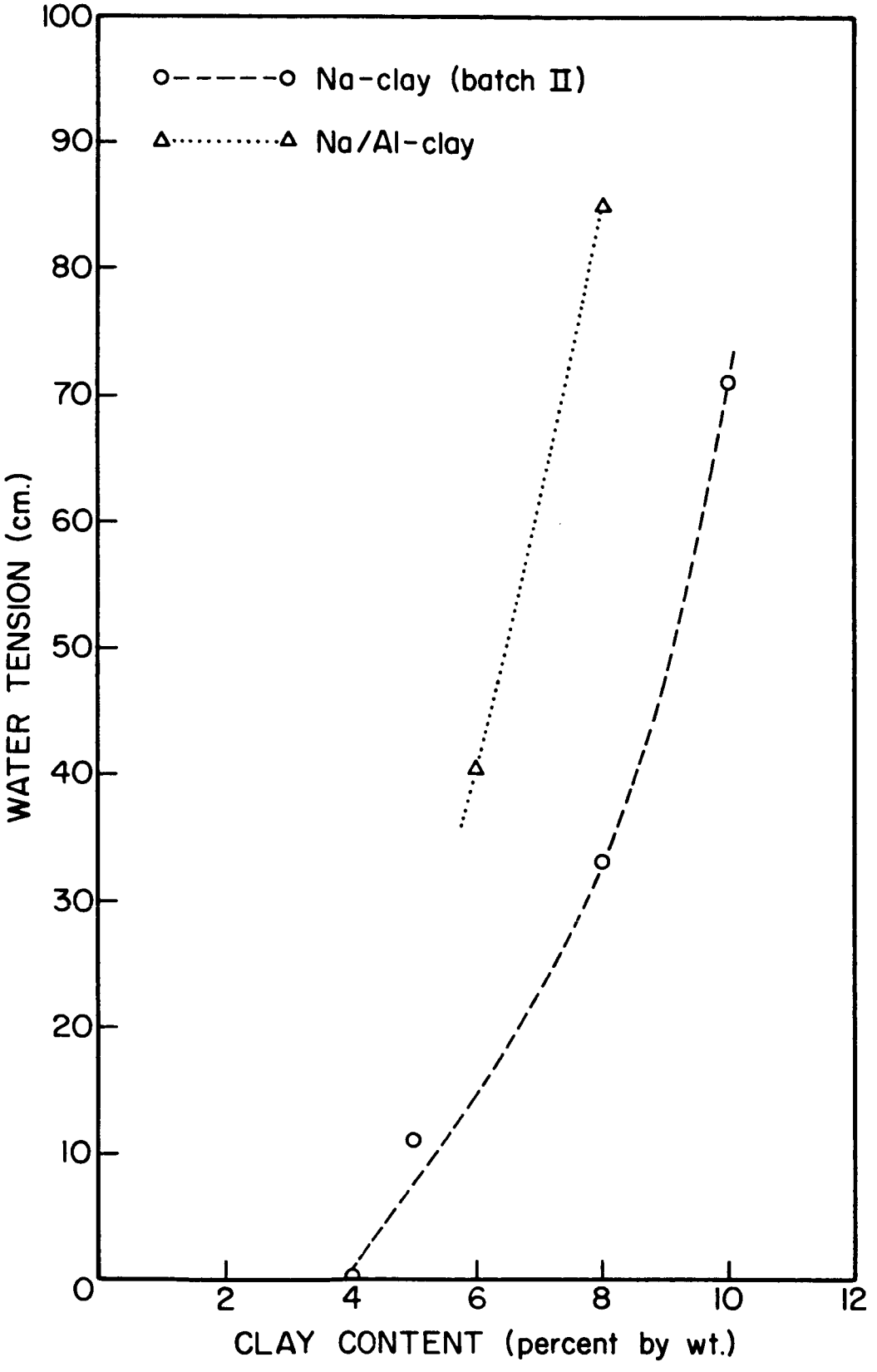
Na-clay (batch II)
Na/Al-clay
WATER TENSION (cm.)
CLAY CONTENT (percent by wt.)
0
10
20
30
40
50
60
70
80
90
100
2
4
6
8
10
12

Fig 11

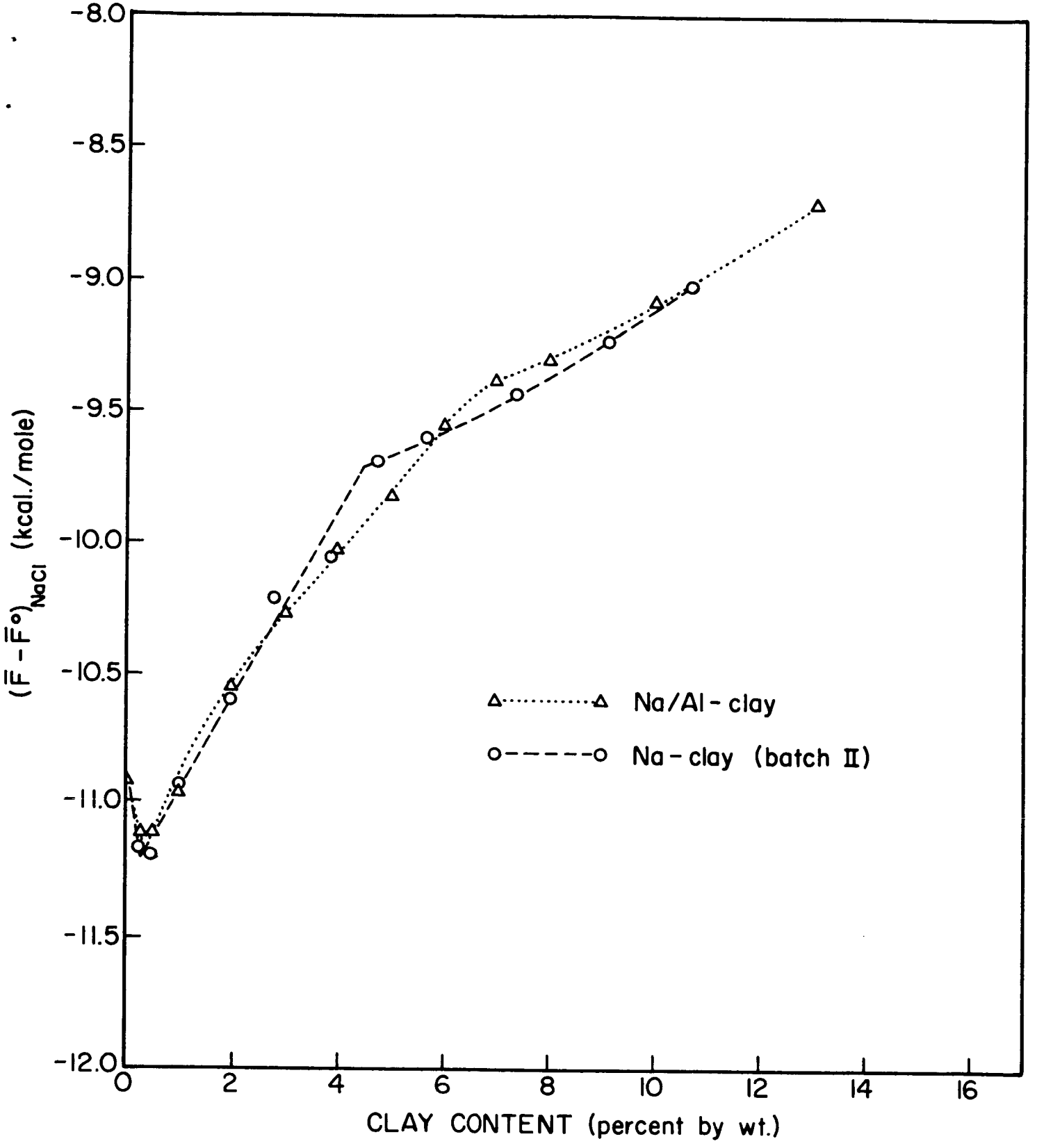
-8.0
-8.5
-9.0
-9.5
-10.0
-10.5
-11.0
-11.5
-12.0
0
2
4
6
8
10
12
14
16
$(\bar{F}-\bar{F}^{\circ})_{NaCl}$ (kcal./mole)
CLAY CONTENT (percent by wt.)
Na/Al - clay
Na - clay (batch II)

Fig. 12

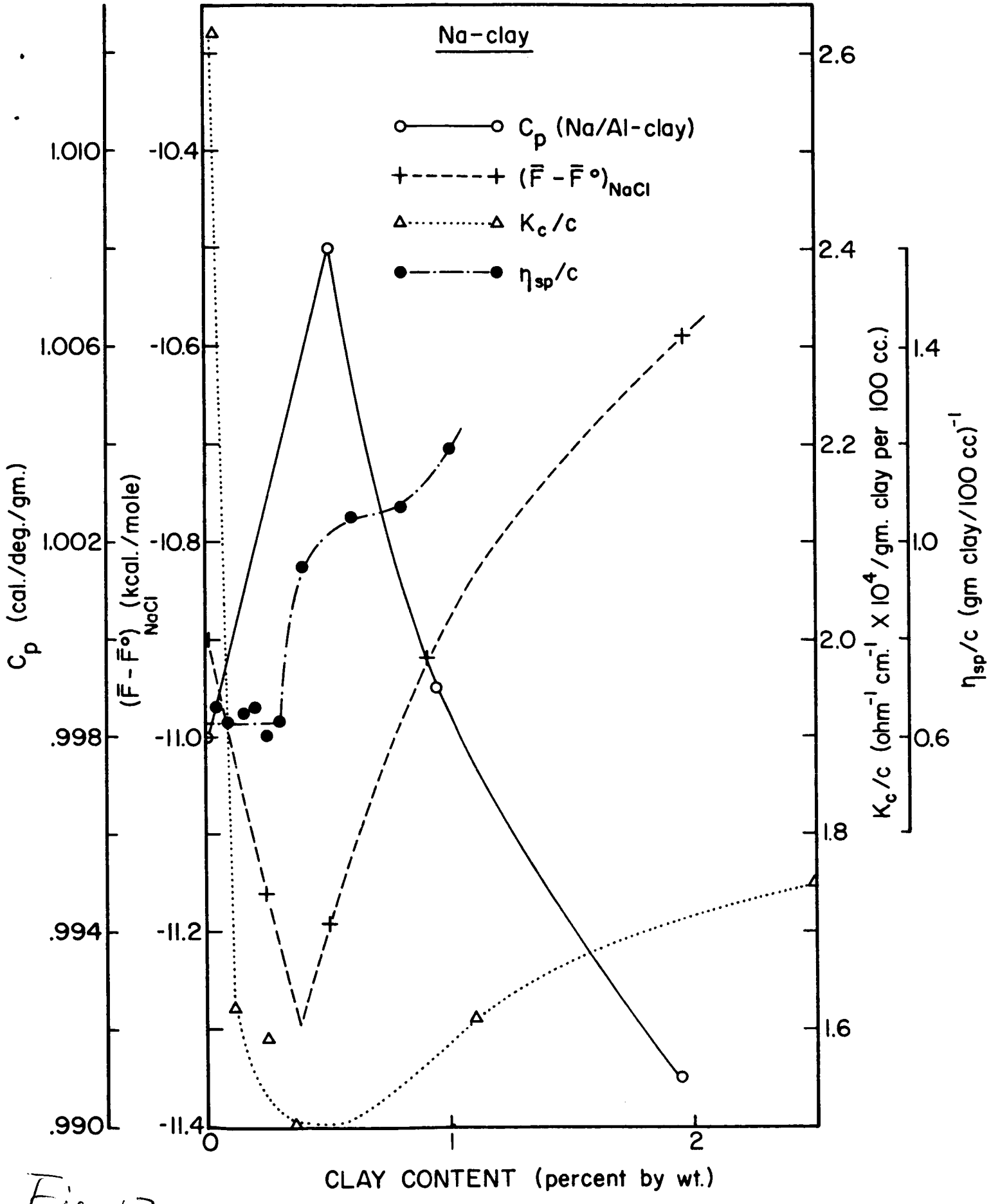
Na-clay
C_p (Na/Al-clay)
$(\bar{F} - \bar{F}°)_{NaCl}$
K_c/c
η_{sp}/c
C_p (cal./deg./gm.)
$(\bar{F} - \bar{F}°)_{NaCl}$ (kcal./mole)
K_c/c (ohm^{-1} cm.$^{-1}$ X 10^4/gm. clay per 100 cc.)
η_{sp}/c (gm clay/100 cc)$^{-1}$
1.010
1.006
1.002
.998
.994
.990
-10.4
-10.6
-10.8
-11.0
-11.2
-11.4
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.0
0.6
0
1
2
CLAY CONTENT (percent by wt.)

Fig 13

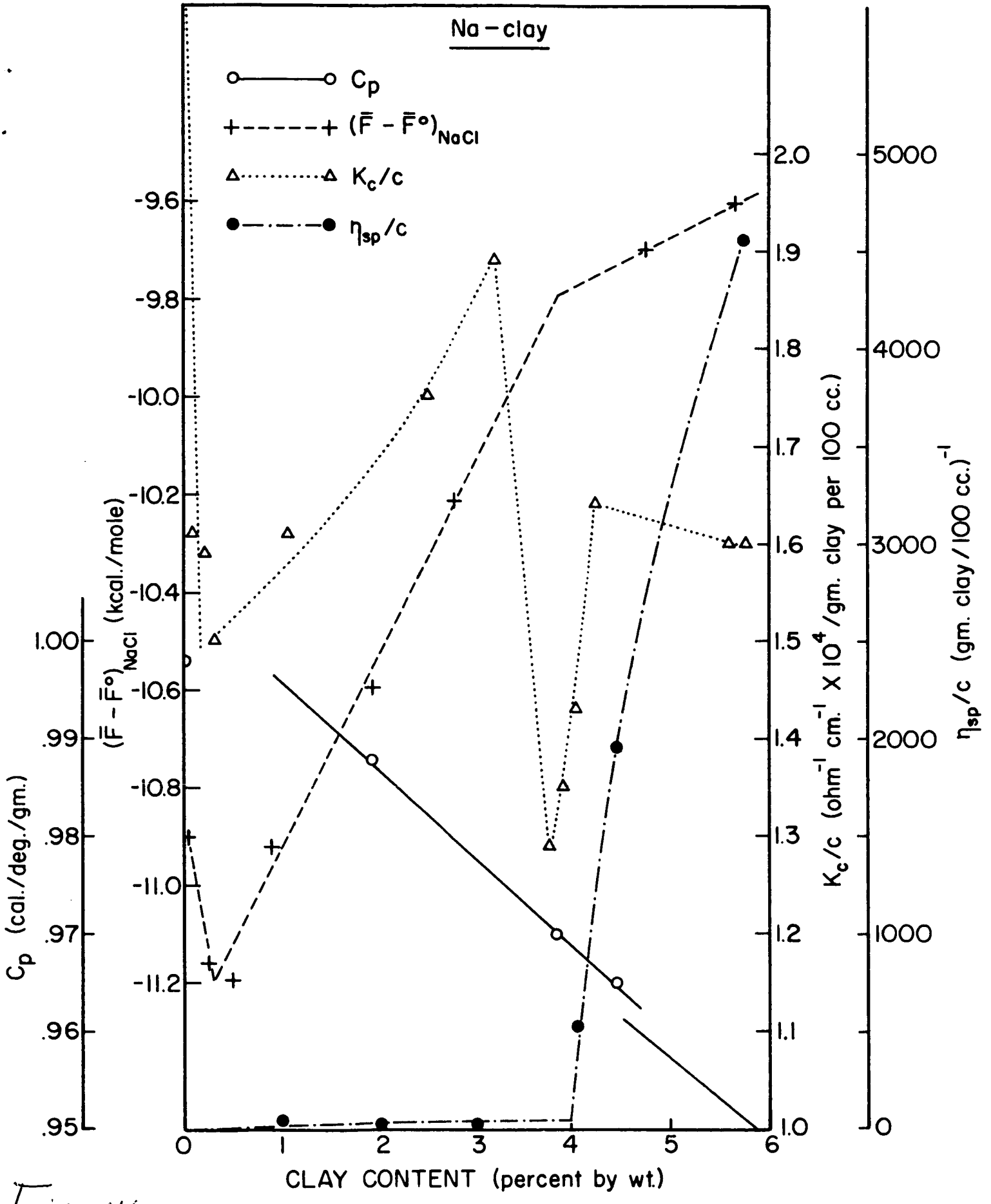
Na – clay
C_p
$(\bar{F} - \bar{F}^\circ)_{NaCl}$
K_c/c
η_{sp}/c
C_p (cal./deg./gm.)
$(\bar{F} - \bar{F}^\circ)_{NaCl}$ (kcal./mole)
K_c/c (ohm^{-1} cm.$^{-1}$ X 10^4/gm. clay per 100 cc.)
η_{sp}/c (gm. clay/100 cc.)$^{-1}$
CLAY CONTENT (percent by wt.)

Fig 1X

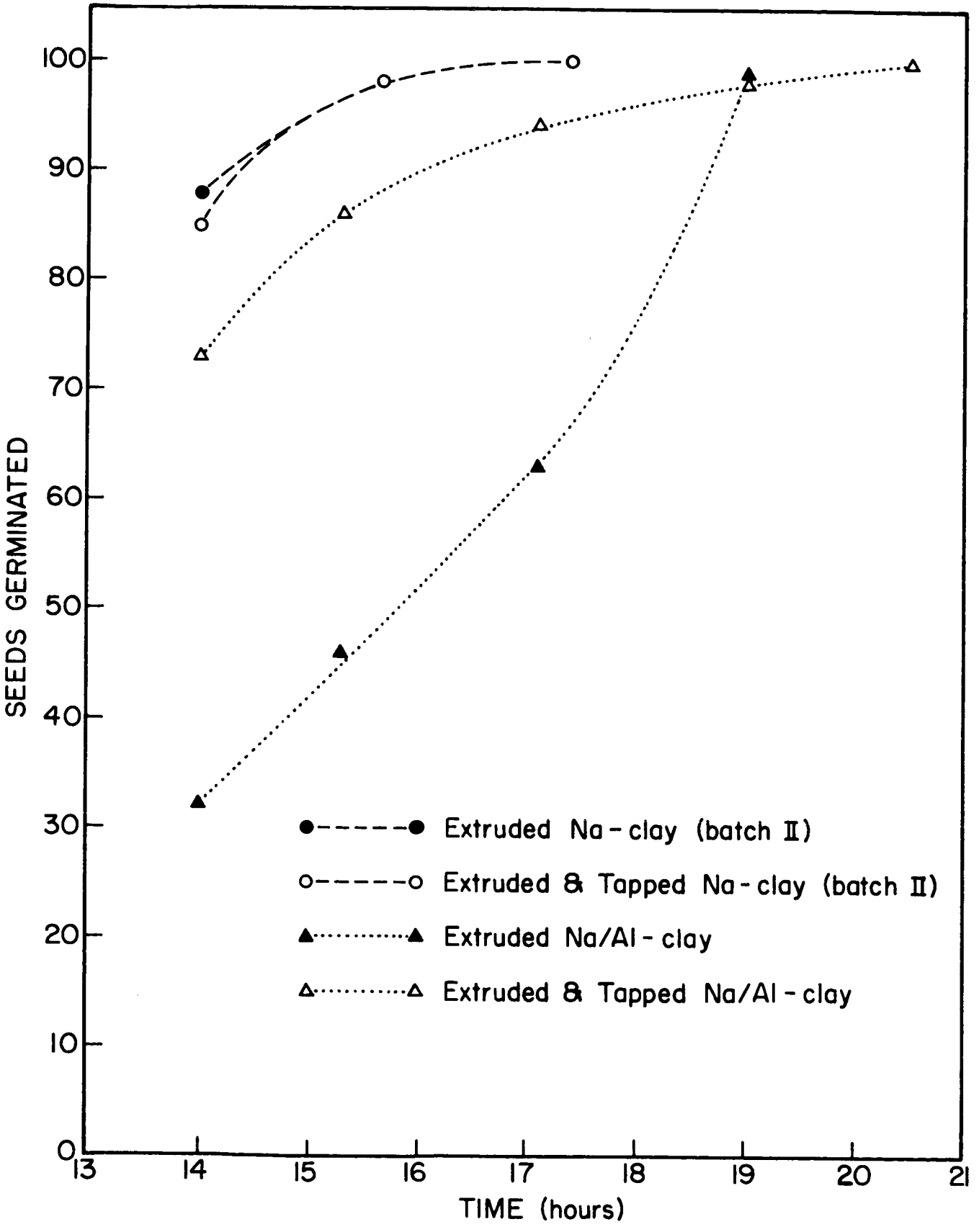
SEEDS GERMINATED
100
90
80
70
60
50
40
30
20
10
0
13
14
15
16
17
18
19
20
21
TIME (hours)
Extruded Na - clay (batch II)
Extruded & Tapped Na - clay (batch II)
Extruded Na/Al - clay
Extruded & Tapped Na/Al - clay

Fig. 15

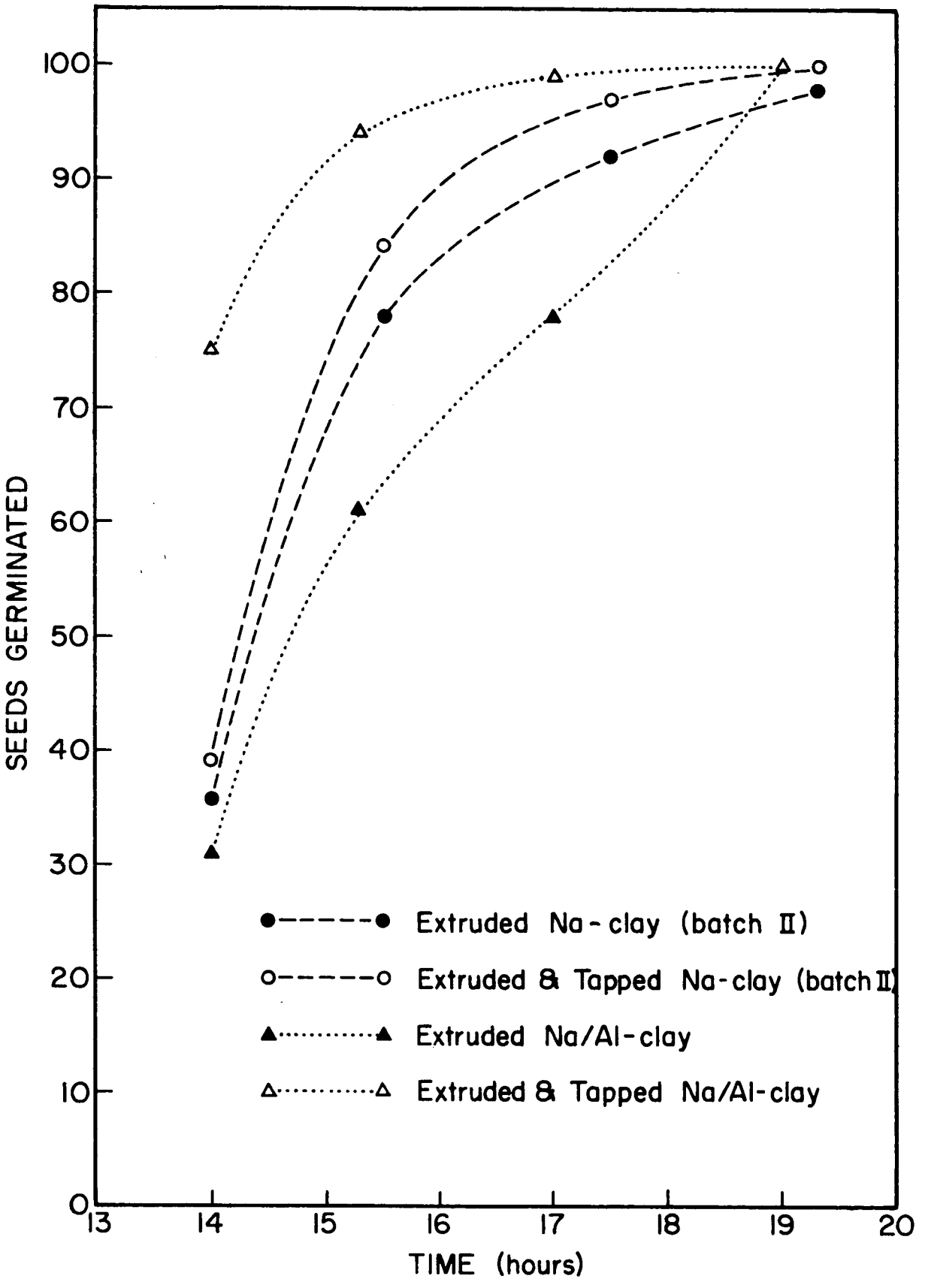
SEEDS GERMINATED
100
90
80
70
60
50
40
30
20
10
0
13
14
15
16
17
18
19
20
TIME (hours)
Extruded Na-clay (batch II)
Extruded & Tapped Na-clay (batch II)
Extruded Na/Al-clay
Extruded & Tapped Na/Al-clay

Fig. 16

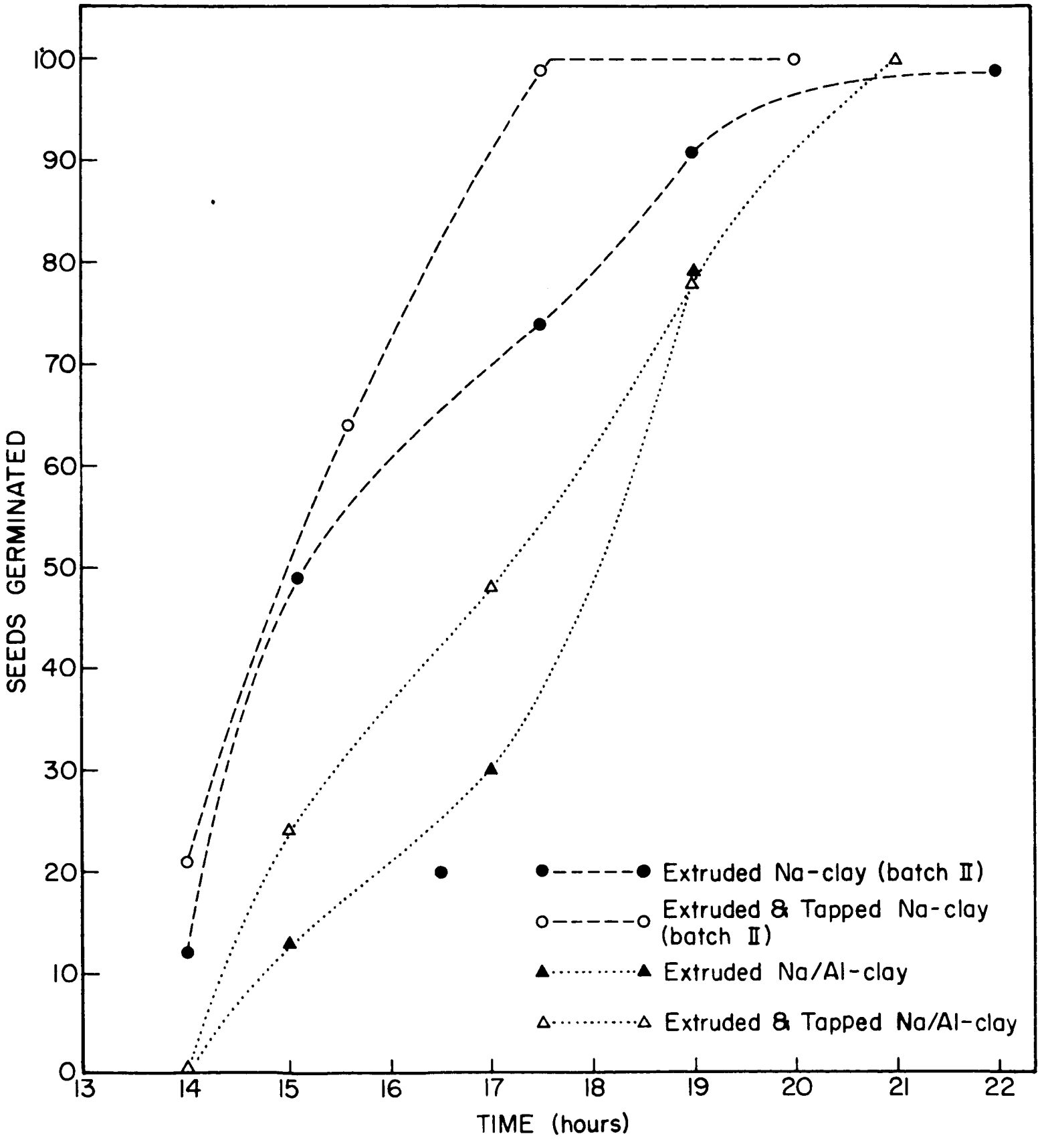
SEEDS GERMINATED
0
10
20
30
40
50
60
70
80
90
100
13
14
15
16
17
18
19
20
21
22
TIME (hours)
Extruded Na-clay (batch II)
Extruded & Tapped Na-clay (batch II)
Extruded Na/Al-clay
Extruded & Tapped Na/Al-clay

Fig. 17