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PREFACE

The research work reported in this paper was performed under a continuing research grant from the Defence Research Board, in the form of a Grant-in-Aid of Research to Dr. Raymond Yong (Grant No. 9511-28 (G. & C.)). The Grant was first given in April 1958 with subsequent yearly renewals.

The authors wish to acknowledge their indebtedness to the Defence Research Board for its support and interest - without which this research study would not have been possible. This paper, prepared for presentation at the Eleventh National Clays and Clay Minerals Conference in Ottawa, concerns itself primarily with a study of the swelling pressures of a pure clay arising from temperature depression. This is considered basic to the understanding of the phenomenon of frost heaving and soil freezing.

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ABSTRACT

Swelling pressures of oriented samples of sodium-montmorillonite at pore-water salt concentration of 10^{-4} and 10^{-2} M NaCl 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.

Calculations from the combined Poisson-Boltzmann equation, taking the variation of temperature and dielectric constant into account, showed a decrease in swelling pressure with decrease in temperature. At a pore-water salt concentration of 10^{-4} M NaCl, the measured swelling pressure at 120 A average interparticle distance decreased from 48 cms. of mercury at 23°C to 35 cms. at 1°C, while the corresponding calculated pressure decrease was from 48 to 40 cms. While the measured pressures fell below calculated values at higher distances, the influence of temperature remained consistent.

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At 10^{-2} M NaCl, the measured swelling pressures were much higher than those predicted from the equation. Corrections based upon the effective salt concentrations required by the theory to give the experimentally measured swelling pressures at room temperatures were calculated. 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 this correction, the calculated swelling pressure at 120 A average interparticle distance decreased from 30 cms. at 23°C to 26 cms at 1°C while the measured pressure decreased from 30 to 23 cms. This close agreement between corrected calculated pressure and measured pressure held from 100 to 250 A interparticle spacing.

ACKNOWLEDGEMENT

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INTRODUCTION

Measurements of swelling pressure of clays saturated with sodium ions at normal room temperature have been reported in previous studies by many investigators (e.g. Warkentin et al, 1957, Blackmore 1958, Warkentin and Schofield, 1958). In general, good agreement has been found between measured values and theoretical swelling pressures computed on the basis of adaption of the Gouy-Chapman theory of the diffuse double layer. In this instance, the combined Poisson-Boltzmann equation describing the concentration of ions at the midplane of two parallel charged plates is used to compute the van't Hoff pressure arising from ion concentration difference between the midplane and the surrounding pore-water solution. With the assumption of ideal behavior of ions, the van't Hoff pressure may then be taken as the computed swelling pressure. Inasmuch as the laboratory specimens correspond to the model used in the theoretical analysis, a fair degree of correspondence is maintained between measured and calculated swelling pressures.

The solution by Verwey and Overbeek (1948) for the Poisson-Boltzmann equation for the case of overlapping diffuse double layers arising from close proximity of adjacent parallel charged plates gives:

$$M x_c = 2\exp(-Y_c/2)\int_0^{\pi} \frac{d\phi}{\sqrt{1-\exp(-2Y_c)\sin^2\phi}} \quad \ldots \quad (1)$$

where

$$M = \sqrt{\frac{8\pi z^2 e^2 n_o^2}{\epsilon k T}}$$

$$Y_c = \frac{-ze\psi}{kT} \quad \text{at midplane}$$

$$\sin^2\phi = \exp(-Y)/\exp(-Y_c)$$

z = valence of ions

e = electronic charge

n_o = number of ions per unit volume in bulk solution

ε = dielectric constant

K = Boltzmann constant

T = absolute temperature

By using the Langmuir approximation which assumes that it is possible to neglect the presence of ions carrying the same sign as the charge on the plate, a simplified solution for ψ_c the midplane potential may be derived.

$$\psi_c = \frac{2KT}{ze} \ln \left(\frac{Mx_c}{\pi} \right) \qquad \ldots (2)$$

valid only for $Y_c > 1$

Alternatively, ψ_c may also be obtained by summating the potentials due to single particles. In this instance:

$$\psi_c = - \frac{4KT}{ze} \ln \left(\coth \frac{Mx_c}{2} \right) \qquad \ldots (3)$$

The van't Hoff equation (Schofield, 1946) may then be written as

$$P = 2KTn_o \left(\cosh \frac{ze\psi_c}{KT} - 1 \right) \qquad \ldots (4)$$

where P = force per unit area required externally to keep adjacent

.. particles at a spacing of $2x_c$

It is then possible to determine from the physical equations the effects of such variables as ionic concentration, valence, and temperature of the pore-water phase of an oriented clay-water system on resultant soil-water interaction.

These equations suggest that a decrease in temperature would cause a compression of the double layer thus resulting in a decrease in osmotic swelling for the same interparticle spacing. Assuming that the conditions governing the ideal behaviour of the ions in the double layer are met reasonably well in the laboratory model, it would thus be possible to measure swelling pressure both as a function of temperature and interparticle distance. The conditions necessary for good agreement between measured values and computed swelling pressures at room temperature must evidently be satisfied; i.e. (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) the assumption that the surface charge of the particle is of constant sign (negative) and uniformly distributed should be reasonably correct, (4) particles must be homoionic and free from impurities, (5) particles must be oriented parallel to each other, (6) the 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.

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), which resolves into a correction function. This correction function when applied to the Gouy-Chapman treatment of the electric double layer shows that in the case of low concentration of co-ions in colloidal suspensions, the corrections involved are small if the surface charge density does not exceed 2×10^{-7} m.eq./cm^2.

EXPERIMENTAL PROCEDURE

Variation in swelling pressure arising from temperature depression can be obtained by first allowing samples of a well oriented clay-water system to attain their respective equilibrium volumes for specific values of applied pressure (within a predetermined pressure range), and 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 increment 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 may then be determined.

The apparatus designed to accomodate either of the two methods proposed is shown in Figures 1 and 2. This consisted of a plexiglass chamber enclosed in an insulating box to restrict heat transfer with the external surroundings. Within the plexiglass chamber, an agitator kept the fluid in the constant temperature bath circulating both around the cooling coils and the swelling chamber. The details of the swelling chamber itself is given in Figure 2 and the measurement system used is detailed in Figure 3. Temperature measurements within the swelling

ing chamber were made by means of a copper-constantin thermo-couple 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 thermo-couple. The junction of the thermo-couple leads was protected by several coats of epoxy resin to prevent reaction with the pore-water solution.

The system of measurement for volume change within the swelling chamber consisted of a mercury piston connected in such a way that it could both exert a pressure on the stainless steel piston, and also measure volume changes of the test 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 under pressure since the pressure differential across the face of the piston was zero. In the event that slippage of mercury occurred because of the tolerance limits between wall and piston, no detrimental effects were expected. Mercury in direct contact with samples of pure clay was used successfully by Hemwall and Low (1956) in previous measurements of swelling pressure.

In Figure 3, the heavy lines indicate the portion of the measurement system saturated with mercury and connected such that any change of volume occurring in the chamber as a result of pressure change is 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 minute volume changes. Ambient pressures applied to the samples were measured effectively by a mercury manometer through the connection between the compressed air cylinder and Column (2).

In order to reduce the sensitivity of the apparatus to small leaks that may develop thus causing a rapid loss of pressure, and at the same time to increase the volume of the system, an empty air cylinder was incorporated into the system. By slowly releasing air through valves (F) and (G) (shown in Figure 3), it was possible to obtain a gradual expansion of the sample. A more gradual expansion of the sample was obtained through valve (D) 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.

Oriented specimens of homoionic sodium-montmorillonite were prepared by slow sedimentation and drying of weak suspensions of the purified clay. The clay suspensions which contained less than one percent by weight of material were allowed to settle slowly in small plexiglass tubes which were sealed at the bottom with cellophane membranes. This technique of slow evaporation and sedimentation which produced waferlike clay plates has been used successfully previously (Warkentin and Schofield, 1958).

Five clay plates were placed individually in the flooded swelling chamber in the portion between the stainless steel piston and the top of the chamber. Millipore membranes were used at the faces of the top and bottom porous stones. Following sample immersion in the chamber and with both cap replaced and system de-aired, the sample was allowed to swell under a small pressure restraint. Since the applied pressure was transmitted through the mercury piston which also served as a scale for volume change measurements (shown in Figure 3 as the line passing through valve C), initial zero readings for equilibrium volume at room temperature and initial pressure restraint 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 length of time involved depended upon the initial pressure restraint. The entire system was calibrated for temperature effects previous to test measurements. With this system, a predetermined initial pressure could be applied and following equilibrium conditions, a series of resultant volume changes might be 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 be reported as changes in interparticle spacing with a simple conversion. In Figures 4 and 5 the variation in interparticle spacing resulting from temperature depression under prescribed constant applied pressures has been shown for three complete series at 10^{-4} M NaCl pore-water salt concentration, and for one complete series at 10^{-2} M NaCl.

RESULTS AND DISCUSSION

Swelling pressure measurements for both 10^{-4} M NaCl and 10^{-2} M NaCl samples have been plotted in Figure 6 for the test series at 23° C. The correspondence between measured values and computed swelling pressure indicated by the solid line for pore-water salt concentration of 10^{-4} M NaCl justifies use of both technique and apparatus. For 10^{-2} M NaCl pore-water salt concentration, the measured values are consistently higher than would be predicted from the physical 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 values and computed swelling pressures indicate that the error involved in calculating osmotic pressure by the numerical difference is not large (Warkentin and Schofield, 1962). At higher concentrations however, the error due to substitution of ionic concentrations for ionic activities becomes more significant.

While efforts to allow for ionic activity in double layer calculations have been made by Loeb (1951) and Bolt (1955), it does seem that because of the difficulties involved in determination of activity coefficients for counter-ions between adjacent clay plates, calculation of corrected osmotic pressure based upon ionic activities is not possible. A more expedient method for correction of osmotic pressure at higher electrolyte concentration would be to determine the effective pore-water salt concentration required by theory to give experimentally measured swelling pressures.

From the Poisson-Boltzmann equation, the electric potential at the midplane ψ_c may be written as

$$\psi_c = -\frac{2KT}{ze} \ln \left(\frac{\pi}{\sqrt{S}\, M x_c} \right) \qquad \ldots (5)$$

without altering the assumptions of the Gouy-Chapman theory significantly. Writing the van't Hoff equation as

$$\psi_c = -\frac{KT}{ze} \cosh^{-1} \left(\frac{p}{2KTSn_o} + 1 \right) \qquad \ldots (6)$$

where

$S =$ coefficient of effective salt concentration

$Sn_o = n' =$ effective salt concentration

the effective pore-water salt concentration which produces the same value for ψ_c in equations (5) and (6) may then be determined. For 10^{-4} M NaCl concentration, very little correction if any is needed. For 10^{-2} M NaCl concentration, this presupposes that the experimentally determined values are correct. The relationship defined for the effective salt concentration based upon equating the midplane potentials shown in equations (5) and (6) and measured swelling pressures for 10^{-2} M NaCl indicates that the effective salt concentration would be dependent on interparticle spacing.

The method of solution of the effective pore-water salt concentration for the 10^{-2} M NaCl sample consisted of determining the midplane potential for each of the measured values of swelling pressure from equations (4) and (2) using varying values of pore-water salt concentrations. For any one effective pore-water salt concentration, the value of the electric potential obtained from equation (4) must equal that obtained from equation (2). Therefore, for each chosen concentration, the algebraic differences in the mid-plane potentials were calculated from equations (4) and (2) for each ambient pressure. The relationship between algebraic difference in mid-plane potential and pore-water salt concentration may then be established for any chosen value of swelling pressure. The equation established thereby showing variation in the effective pore-water salt concentration with half distance gives:

$$S x_c = \frac{x_c^2}{244} - 0\cdot77\, x_c + 60\cdot7 \qquad \ldots (7)$$

ith temperature and dielectric constant variation, the theoretical equation may then be modified with the use of equation (7).

Based upon measurements shown in Figures 4 and 5, the variation of swelling pressure as influenced by temperature depression may then be drawn - as shown in Figures 7 and 8. The effect of a variable dielectric constant is considered in Figure 8. The relationship established by Sirvastava and Varshni (1956) for a variable dielectric constant was used in calculating variation of ε with temperature.

$$\varepsilon = \frac{62445}{T + 120} - 70\cdot91 \qquad \ldots (8)$$

The dielectric constant was assumed to be that of the solvent. While it is recognised that the dielectric constant of the water phase in clay soils and of adsorbed water may be significantly different (Pickett and Lemcoe 1959, Muir 1954), the assumptions involved in the initial equations of the Gouy-Chapman theory dictate the use of the solvent value for the dielectric constant.

The correspondence between predicted values and measured swelling pressures for the 10^{-2} M NaCl sample shows the validity of the use of the effective salt concentration for correction. As seen from the graphs, there is reasonably close agreement between 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.

In accordance with theoretical predictions, measured values of swelling pressure decreased with decreasing temperatures. The physical model of the electric double layer assumes that a large portion of its magnitude is derived from the thermal energy of the ions which tend to restrict orientation in the field of charged plates, thus causing the electric double 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 thickness of the electric double layer will also decrease. While the temperature depression decreases the thermal energy of the ions, the dielectric constant on the other hand will increase, which in turn would tend to cause the thickness of the electric double layer to increase. The net effect however is a decrease in electric double layer thickness since there is evidence that the effect of a decrease in thermal energy is greater than that of the dielectric constant. Moreover, as the temperature is depressed, the concentration and distribution of ions in general will decrease correspondingly, and a further decrease in the electric double layer may then be expected on the basis of reduction of effective volume.

The divergence of measured values from calculated swelling pressures for 10^{-4} M NaCl samples at higher interparticle spacings under room temperature conditions has been pointed out in a previous study (Yong and Warkentin 1959). However, the close agreement between measured and calculated values for swelling pressure shown in the case of the 10^{-2}M NaCl sample, suggests that correction for effective pore-water salt concentration for the 10^{-4} M NaCl samples at higher interparticle spacings may be necessary. If a similar correction is made for the 10^{-4} M NaCl samples for effective pore-water salt concentration at lower ambient pressures, as in the case of the 10^{-2} M NaCl sample carried over its entire range of pressures, better agreement would be achieved under depressed temperature conditions.

While the use of the effective pore-water salt concentration serves to adjust the physical equations to conform with initial measured values, it does not explain the reasons for the consistent differences between measured and calculated values. The reasons for the differences are not quite clear, but they are thought to lie partially in the limitations of the double layer theory, the lack of particle orientation at higher interparticle spacings and probably in the possible impurities in the clay.

CONCLUSIONS

Consistent with theoretical predictions, measured values of swelling pressure decreased with temperature depression. With the use of a correction expressed in terms of the effective pore-water salt concentration, 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 under predetermined inter-particle spacings arising from temperature changes (between 23°C and 1°C), in the pressure range of 0.1 to 1.0 atmospheres may be adequately predicted from double layer calculations.

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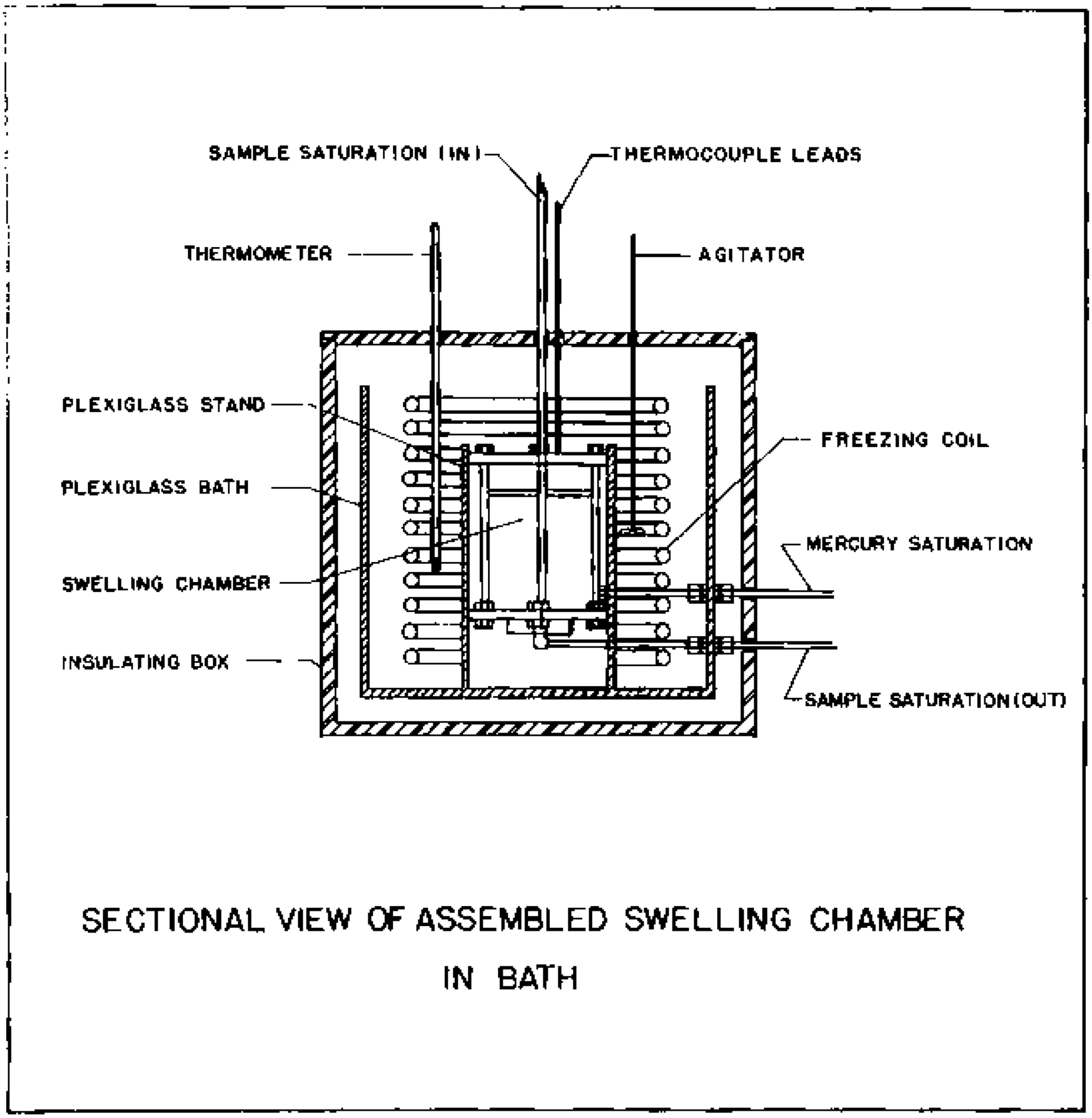

Figure 1 - SECTIONAL VIEW OF ASSEMBLED SWELLING CHAMBER

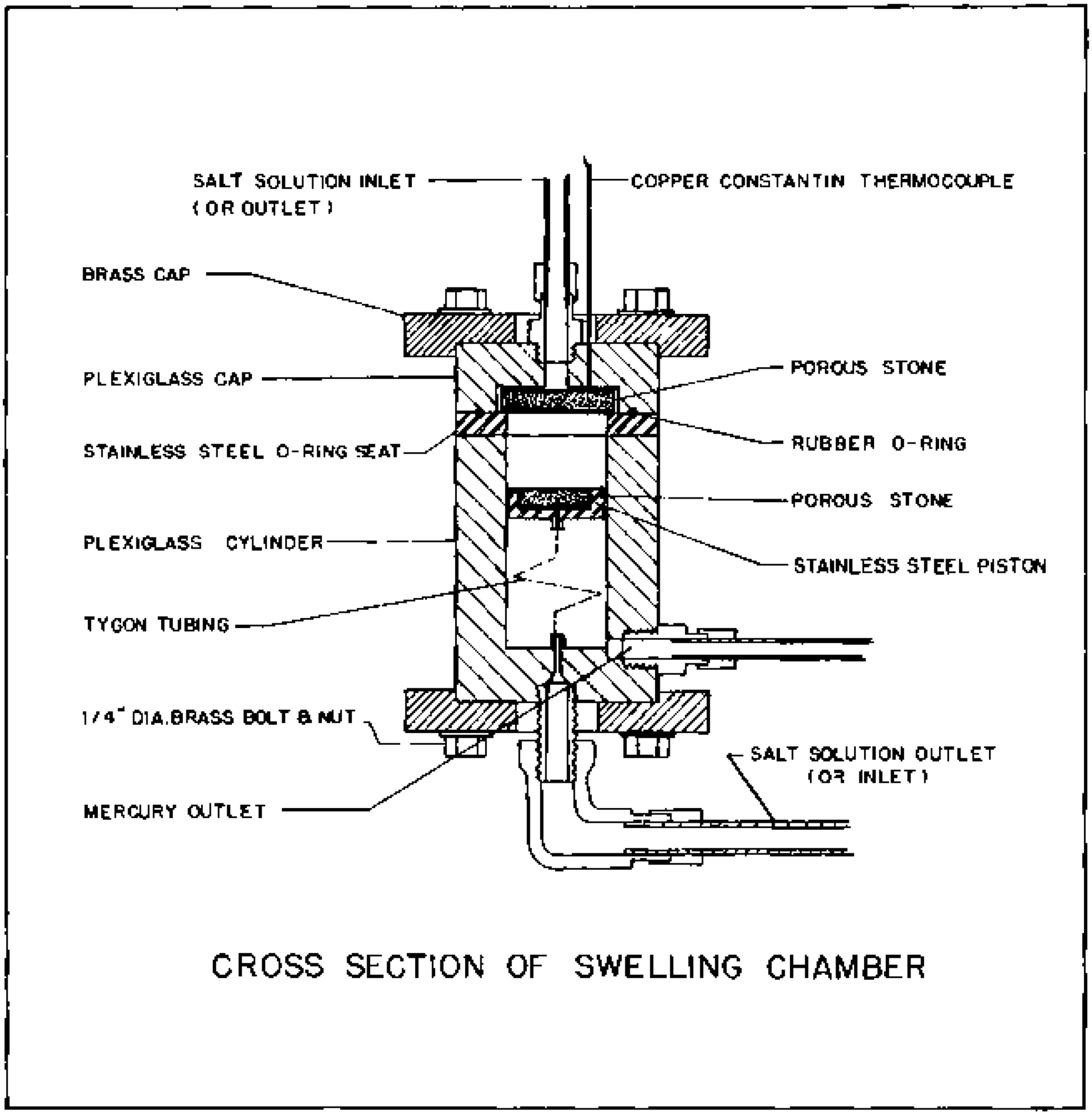

Figure 2 - CROSS SECTION OF SWELLING CHAMBER

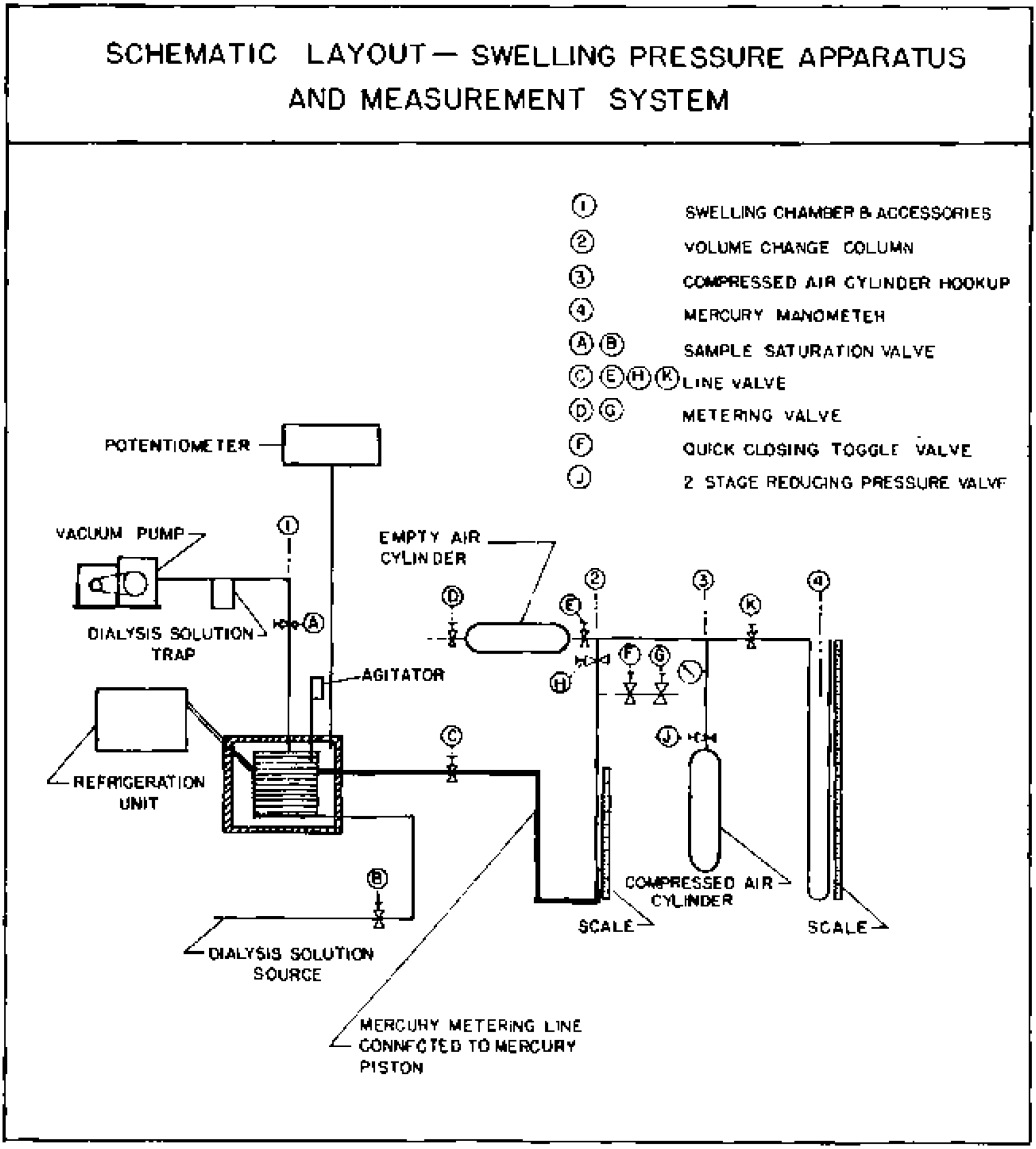

Figure 3 - SCHEMATIC LAYOUT - SWELLING PRESSURE APPARATUS AND MEASUREMENT SYSTEM

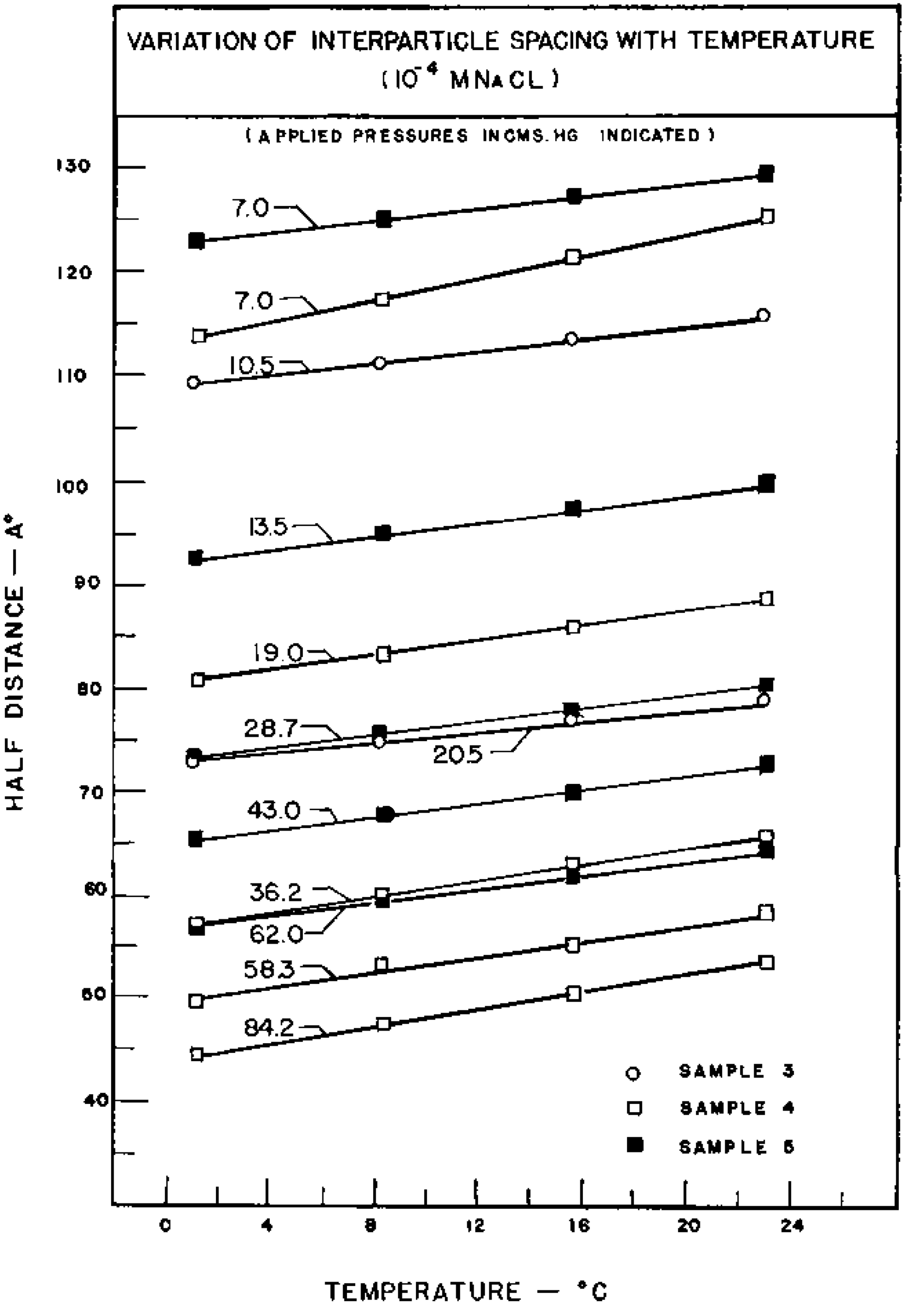

Figure 4 - VARIATION OF INTERPARTICLE SPACING WITH TEMPERATURE

(LOW SALT CONCENTRATION)

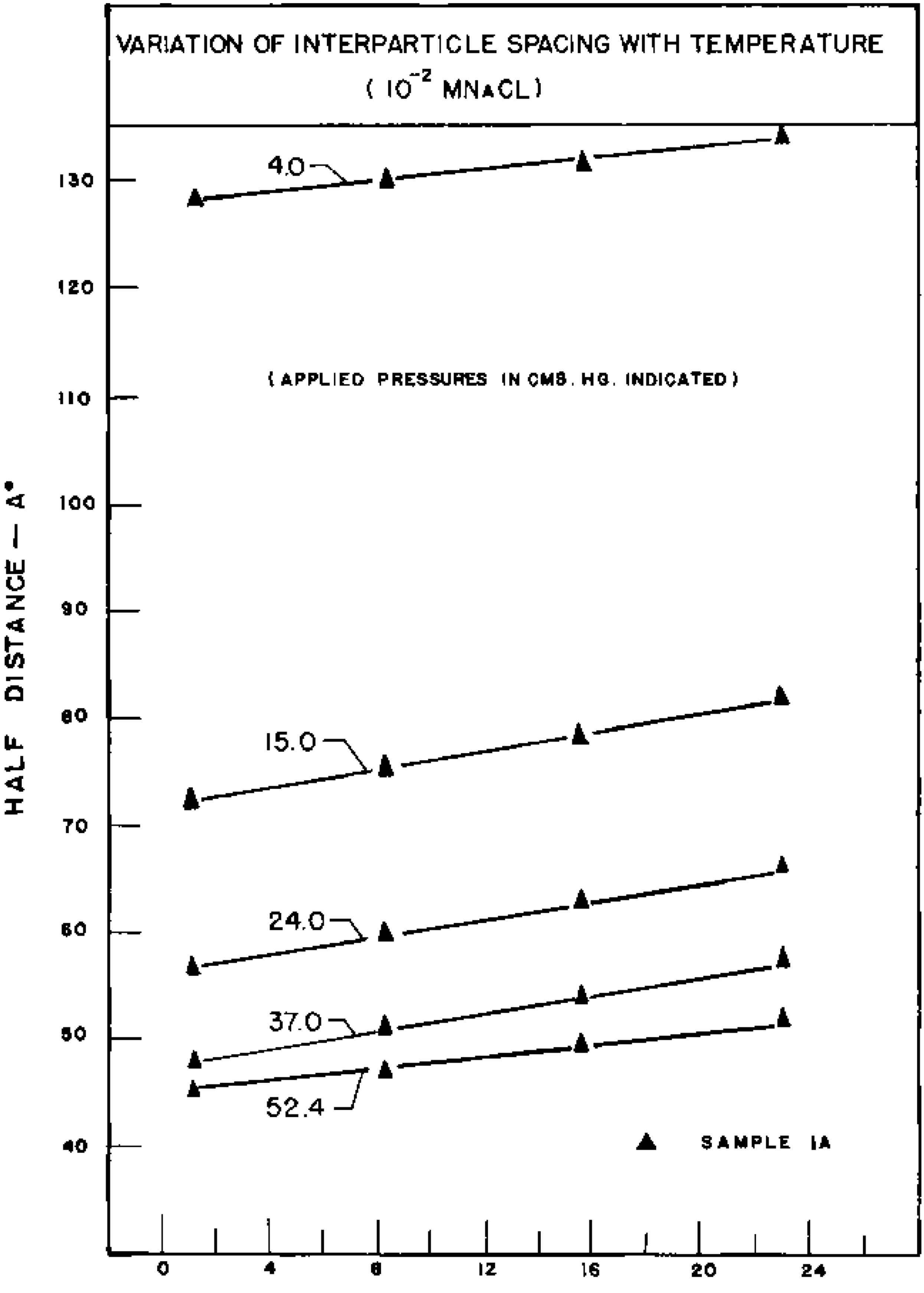

Figure 5 - VARIATION OF INTERPARTICLE SPACING WITH TEMPERATURE

(HIGH SALT CONCENTRATION)

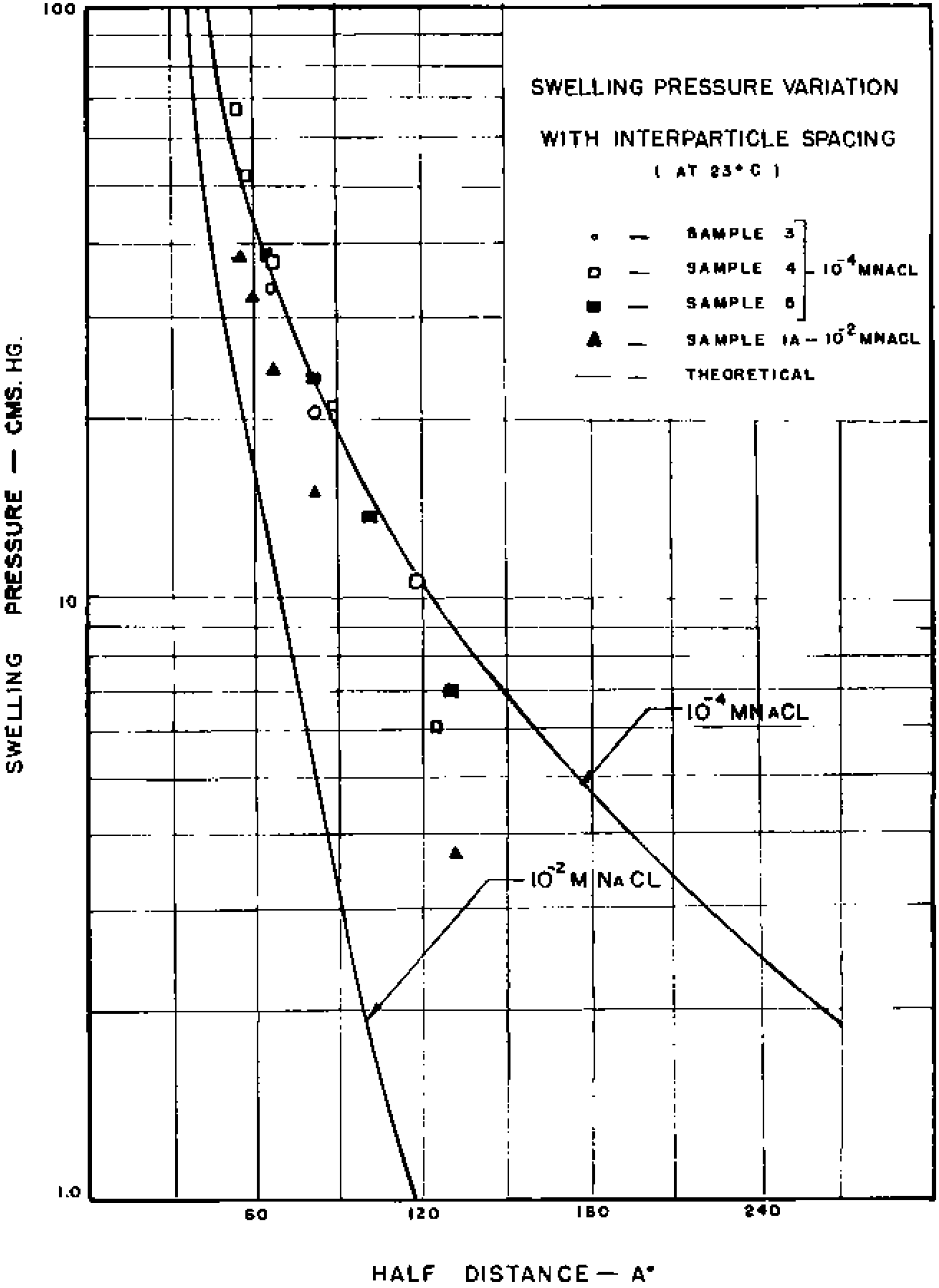

Figure 6 - SWELLING PRESSURE VARIATION

WITH INTERPARTICLE SPACING

(AT 23°C)

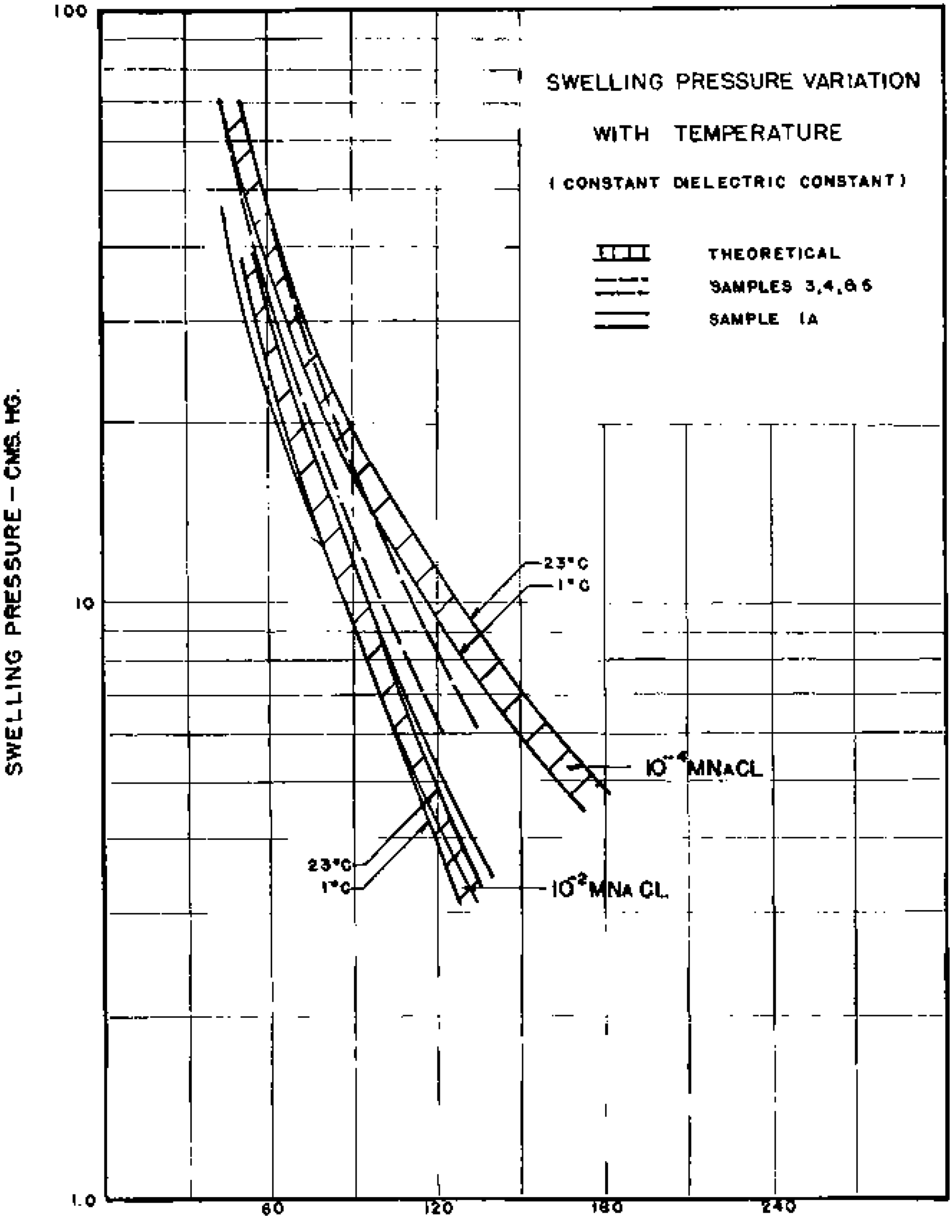

Figure 7 - SWELLING PRESSURE VARIATION

WITH TEMPERATURE

(Constant Dielectric Constant)

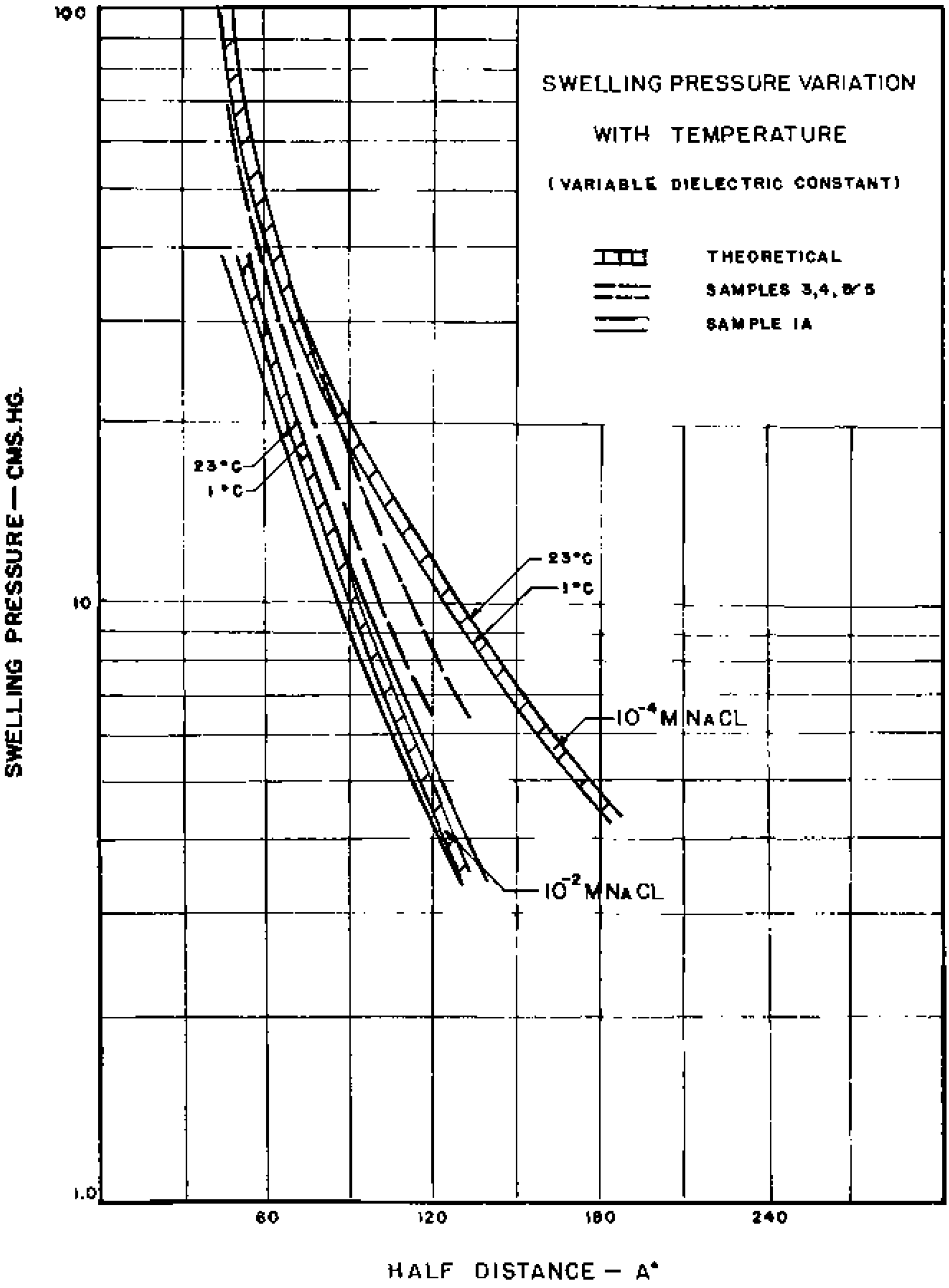

Figure 8 - SWELLING PRESSURE VARIATION

WITH TEMPERATURE

(Variable Dielectric Constant)