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Phase Transitions of Adsorbates

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ANALYZED

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LA TRANSFORMATION DES PHASES DES PRODUITS D'ADSORPTION.
V. SOLUTIONS AQUEUSES DE CHLORURE DE SODIUM ADSORBÉES
EN DU VERRE DE QUARTZ POREUX

par

G. G. Litvan

(NRCC 13437)

SOMMAIRE

Les isothermes d'adsorption de l'eau sur du verre de quartz poreux contenant divers montants de NaCl, déterminés à la température ambiante, peuvent être superposés si l'on suppose l'exclusion de sel dans la première couche monomoléculaire et des valeurs de pression relatives basées sur la concentration de sel existante. Les changements de dimensions et de teneur en chaleur des mêmes échantillons de verre complètement saturés d'eau sont déterminés à des cycles de température de non-équilibre entre +5 et -80°C. Les résultats s'expliquent par l'hypothèse que les particularités proviennent de la différence entre la pression de vapeur du produit adsorbé semblable à un liquide et celle du solide ambiant. Aucune séparation de phase n'est observée dans les pores occupés à l'équilibre. La distribution de la phase liquide dans les pores se produit à la fois dans les systèmes en vrac et dans les systèmes en : congélation sont en : deux aspects de la dé : l'expansion lors du : des vitesses rapide : atôt qu'une contra : pression de vapeur : pores plus larges : is avec des solution

Phase Transitions of Adsorbates

V. Aqueous Sodium Chloride Solutions Adsorbed of Porous Silica Glass¹

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Adsorption isotherms for water on porous silica glass containing various amounts of NaCl, determined at room temperature, can be superimposed if salt exclusion in the first monolayer and relative pressure values based on existing salt concentration are assumed. The changes in dimensions and heat content of the same glass specimens fully saturated with water were determined in nonequilibrium temperature cycles between +5 and -80°C. The results are explicable by the hypothesis that peculiarities result from the difference between the vapor pressure of the liquid-like adsorbate and that of the solid in the surroundings. No phase separation in the originally occupied pores was detected, but solidification of the solution after redistribution proceeded in a way similar to that of bulk two-component systems. Observations following first freezing were in full harmony with those for the salt-free system. Two aspects of the second freezing, however, were unlike the previously studied case: the magnitude of expansion on cooling was larger at slow rates than at rapid rates and expansion instead of contraction occurred on warming. Low vapor pressure, high viscosity and the presence of some ice in the larger pores are assumed to be the source of these anomalies. Results obtained with aqueous glycerine solutions as adsorbate appear to support this view.

The low-temperature behavior of porous bodies containing adsorbed water has been described (1) and the processes leading to their destruction have been discussed (2). The observations appear to be explicable by a single theory containing no assumptions specific to a particular system and are therefore expected to be of general validity. Indeed, it is possible to interpret the results obtained with different solids and adsorbates without introducing new assumptions.

Inclusion of aqueous solutions as adsorbate seems to be a logical extension of the investiga-

tions. Besides corroborating the proposed theory for consistency under these conditions, the merit of such a study lies in potential clarification of the phase relations in adsorbates. There are several areas where an understanding of the freezing phenomenon of solutions in the adsorbed state would be useful: frost action in porous building materials in the presence of de-icing salts, cryopreservation of biological materials and foodstuffs, desalination using porous membranes, impregnation of catalyst.

The present paper deals with the study of the porous glass-aqueous NaCl system; application of the results to practical problems will be the subject of forthcoming publications.

EXPERIMENTAL

Porous 96% silica glass (Corning 7930) specimens, 30 by 8 by 5 mm and having a BET

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nitrogen surface area of 100.1 m²/g, were used. Specimens were heated in an oven at 150°C to constant weight, then placed in individual glass cells and pumped down to 10⁻² Torr pressure. NaCl solution of known concentration was injected into the cell by means of a hypodermic syringe through a rubber septum, thus maintaining vacuum integrity. The amount of solution added to each cell was determined from weight increase ($\pm 4 \times 10^{-4}$ g).

Although separate experiments showed that there is no detectable change in the amount of salt contained in the glass after 6 hr, the specimens were immersed in the solutions for at least a month. Prior to the run each specimen was removed from the cell and again heated in an oven to 150°C until constant weight was attained. Salt deposit was not observed on the outer surface. The concentration of the NaCl solutions was determined by titration, using 0.01 M AgNO₃ solutions according to Mohr's method. Saturation with glycerol solutions was carried out in a similar fashion, omitting heating after saturation. A 60% stock solution was prepared gravimetrically from reagent grade glycerol, and individual solutions were prepared by volumetric dilution. Changes in dimensions and thermal properties of the samples during programmed temperature cycles were determined simultaneously (1).

Adsorption isotherms of water on porous glass containing various amounts of NaCl

were obtained by the desiccator method. Weighing dishes containing impregnated glass samples were placed in a desiccator over saturated solutions of various salts, and to shorten equilibration time the desiccator was de-aerated. It was necessary to stir the salt solutions with a magnetic stirrer and to use a thermostat to provide the required constancy of the relative pressure in the vessel. The specimens were conditioned over each solution until the weight change in 24 hr was less than 2 mg/g or 1% of the adsorbate weight. At least one week was required to achieve this state.

SALT REJECTION OF POROUS GLASS

Using the total pore volume and amount of salt contained in the pores, it is possible to calculate the concentration difference, if any, between adsorbed and impregnating liquid. (Pore volume was assessed from the water adsorption isotherm and salt content from the weight increase due to impregnation determined after drying to constant weight at 105°C. The estimated error is between 3.0 and 0.08% pending on the concentration.) The results for the six samples listed in Table I indicate that the concentration in the pores (Column 4) is less by approximately 10% (Column 5) than that of the penetrating liquid (Column 1).

Salt rejection in adsorbed layers has been reported for various systems such as porous

TABLE I
ESTIMATE OF SALT CONCENTRATION OF THE LIQUID ADSORBED IN SATURATED SPECIMENS
WITH AND WITHOUT ASSUMING THE EXISTENCE OF A SALT-FREE LAYER^a

1 Concentration of impregnating solution, %	2 Salt content of impregnated glass, g/g	3 Maximum water uptake, g/g	4 Adsorbate Concentration, % no salt-free layer	5 Difference Columns 4-1, %	6 Adsorbate Concentration, % one salt-free layer	7 Difference Columns 6-1, %
1.19	0.0028	0.2353	1.17	- 1.68	1.34	+12.6
4.98	0.0099	0.2320	4.09	-17.87	4.65	- 6.6
9.98	0.0218	0.2265	8.78	-12.02	9.94	- 0.4
13.84	0.0308	0.2224	12.16	-12.14	13.74	- 0.7
17.65	0.0402	0.2180	15.57	-11.78	17.54	- 0.6
25.38	0.0630	0.2075	23.29	- 8.23	26.09	+ 2.7

^a Total pore volume 0.2366 ml/g, ρ salt = 2.163 g/ml (3). ρ_{water} = 1.000 g/ml, monolayer capacity 0.0290 g/g, BET area 100.1 m²/g, area of water molecule 10.3 Å².

glass (4-8) and haemoglobin (9, 10). The phenomenon has been explained by ion exchange and Donnan potential (4, 5), but it has also been suggested that the water on the surface is structured and therefore unavailable to the solute (8, 11, 12). To test the validity of this hypothesis the concentration of the adsorbed liquid was calculated by assuming that one monomolecular layer is completely free of salt (Column 6, Table I). The values in Column 7 (Table I) indicate that the concentration of adsorbate, with the exception of the first layer, is essentially the same as that of the impregnating solution. This agreement supports the concept of solute exclusion in layers of bound water (13).

ISOTHERMS

Plotting water uptake of the various impregnated specimens against relative pressure of water results in a family of curves not unexpectedly different from the isotherm of untreated glass (Fig. 1). From among the possible causes of distortion of the isotherms, the

factors affecting relative pressure will be considered first.

The amount of salt in the specimen is fixed in the course of the adsorption process, and the concentration of adsorbate varies as shown in Fig. 2. Three phases may be differentiated:

(1) at low relative pressures the amount of water is insufficient to dissolve all the salt and both undissolved salt and saturated solution are present;

(2) all salt is dissolved and further uptake of water results in dilution of the solution; and

(3) when the available pore volume is completely filled, concentration of the impregnating solution is achieved (disregarding salt rejection in the monolayer).

Because state (3) is achieved at relative pressure less than unity (due to the lowering effect of dissolved salt on vapor pressure) further increase in relative humidity results in surface condensation and dilution. The following example may serve to illustrate this point: at 22°C the vapor pressure of a saturated NaCl solution is 14.9 Torr, that of water

FIG. 1. Adsorption isotherms for water on porous glass impregnated with NaCl solutions of various concentrations. Relative pressure is based on the saturation pressure of pure water.

FIG. 2. Concentration of salt solution in the pores as a function of amount of water adsorbed.

19.83 Torr. In a 100% relative humidity environment the system containing salt is exposed to a relative humidity of 133% $[(19.83/14.9) \times 100]$. It may be noted also that at any given relative humidity a porous body containing a soluble substance always has a higher degree of saturation than one containing only water. This fact is most important from the frost damage point of view.

Clearly, the water uptake of a salt-impregnated solid is not governed by relative pressure expressed in terms of pure water but rather in terms of the vapor pressure of a bulk solution having concentration identical to that of the pore liquid at the actual water content. Because the concentration of the liquid held in the capillaries varies during adsorption, relative

pressure has to be expressed in terms of appropriately changing saturation pressure values. Accordingly, the results of Fig. 1 were recalculated: the concentration of adsorbed liquid was estimated from the amount of salt and adsorbed water present; the capacity of the monolayer, 0.0290 g/g, was subtracted from the total water so that complete salt rejection in the first monolayer was assumed; the appropriate saturation pressure p° for the given concentration was found by interpolating published data (14) and the relative pressure computed. The replotted isotherms are shown in Fig. 3.

The isotherms are very similar in shape but cannot be superimposed for two reasons: as salt concentration increases, (1) the horizontal

Fig. 3. Adsorption isotherm for water on porous glass impregnated with NaCl solutions of various concentrations. Values of Fig. 1 replotted.

section of the curves at high relative pressures shifts to lower water content values and (2) the hysteresis loop occurs at lower relative pressures. The reduced pore volume resulting from the presence of salt may be the cause of the first effect. Table II shows the computed values of the volumes of the salt solutions plus the salt-free monolayer (Column 4). No trend is apparent and the estimated volumes closely approach the total pore volume obtained from the water isotherm.

The second effect, which changes the shape and position of the hysteresis loop, may be attributed to alterations of the morphology of the porous system by the undissolved salt. It is not unreasonable to assume that pore diameters are decreased by salt deposits and that increased surface tension of the brine may also affect the hysteresis mechanism.

In conclusion, it may be stated that the adsorbed salt solution located outside the first salt-free monolayer has properties—vapor pressure, density, solubility—that appear to be similar to those in the bulk state. Unusual features of the isotherms can be explained by the physical presence of salt. The great

similarity of the isotherms (Fig. 3) makes it improbable that the porous structure under the described conditions has been significantly altered by the presence of salt, a phenomenon reported in the literature (6, 7, 15).

HEAT EFFECTS AND DIMENSIONAL CHANGES IN NON-EQUILIBRIUM TEMPERATURE CYCLES

Summary of Previous Results

When water that has been adsorbed in a porous solid is cooled to below 0°C , it remains in a liquid-like state and has a vapor pressure similar to that of undercooled water unless rearrangement of the adsorbate occurs (16). Because the vapor pressure of undercooled water exceeds that of ice and because the experimentally realizable pressure is limited to that of ice, a fully saturated sample is subjected, on cooling, to relative pressures less than unity. A fraction of the adsorbate thus becomes unstable, leaves the pore system, and freezes on the outside surface, giving rise to the phenomenon referred to as “freezing at high temperatures” or “first freezing” (1).

The ice so formed is in the bulk state and, accordingly, melts at 0°C.

Although constant cooling rate produces a uniform decrease of relative pressure, the rate of desorption may vary between zero and infinity depending on the shape of the isotherm. With porous silica glass, water is liberated in such large quantities when the vertical section of the isotherm is traversed that it is unable to leave the pore system because of high viscosity and the low permeability of the adsorbent (decreased by the previously formed ice crystals). This phenomenon is called "freezing at low temperatures" or "second freezing."

Freezing at High Temperatures

The extension diagrams (Fig. 4a) and differential thermograms (Fig. 4b) of porous glass samples fully saturated with salt solutions of various concentrations show, (1) on cooling, anomalies 2 to 5 deg below the bulk freezing point of the respective solutions, and (2) on heating, anomalies at a temperature closely approaching the bulk freezing point (Fig. 5).

These results are consistent with the proposed model: on cooling, desorption takes place prompted by the appearance of ice in the cell, followed by freezing on the surface; on warming, melting occurs at the bulk freezing point. The double peaks in the thermograms for high salt concentration (18 and 22% and marked A and B in Fig. 4b) are caused by formation of ice in the undercooled liquid and the eutectic solid, respectively. Exothermic effect between the peaks is indication of continuous freezing, as expected. Significantly, if the impregnating solution is saturated NaCl only a single peak occurs.

The length change diagram of the glass-water system lends further support to the suggested mechanism, according to which contraction following the length anomaly is due to desorption. If one considers the temperature region 0 to -11°C, in which the maximum realizable vapor pressure decreases from unity

TABLE II
ESTIMATE OF VOLUME OF LIQUIDS ADSORBED IN
VARIOUS FULLY SATURATED SPECIMENS

Salt content of glass g/g	Weight of max water uptake g/g	Volume of adsorbed brine ml/g	Volume of adsorbed brine and salt-free monolayer ml/g
0.0000	0.2360	0.0000	0.2360
0.0028	0.2360	0.2208	0.2498
0.0099	0.2360	0.2101	0.2391
0.0218	0.2300	0.2079	0.2369
0.0308	0.2260	0.2074	0.2364
0.0402	0.2180	0.2030	0.2320
0.0630	0.2050	0.1992	0.2282

to 0.9 [Ref. (1), see Fig. 4], the expected loss of water is 4×10^{-3} g/g [Ref. (1), see Fig. 6] with a concomitant shrinkage of $\Delta l/l = 40 \times 10^{-5}$ [Ref. (1), see Fig. 9]. This is in excellent agreement with the extrapolated length change in this region (Fig. 4a).

The only novel feature of the length change curves is the small expansion that occurs when samples are cooled with 10, 18 and 20% solutions (Figs. 4a and 6). Because, according to the model, some of the liquid must leave the pores when the temperature is lowered, enclosure of the sample in an ice envelope results in expansion [Ref. (1), see Fig. 3]. The observed increase in length is attributed to inability of the liquid to flow at a sufficiently high rate. Thus, the exuded liquid solidifies, perhaps at the mouth of the pores, restricting the flow of further amounts of liquid desorbed at lower temperatures. The rate dependence of the phenomenon may be explained by this hypothesis, assuming that sufficient time is available for solid formation at a cooling rate of 0.0417°C/min (Figs. 6c, 6d) but not at 0.33°C/min. The increased viscosity at these low temperatures also hinders flow. Porous glass samples saturated with aqueous glycerine solutions often expand on first freezing (Fig. 7), an observation that has never been made with pure water as adsorbate under similar conditions and, very probably, due to the high viscosity of the fluid.

Freezing at Low Temperatures

1. In the temperature range -19 to -40°C anomalies were obtained in the dimensional changes and heat content of the water-saturated sample (Fig. 4). These are manifestations of second freezing (1) and are assumed to result from the following circumstances:

Maximum relative pressure (based on vapor pressure of undercooled water), on cooling, decreases continuously until at -10°C it reaches a value of 0.8 [Ref. (1), see Fig. 4], the inception point of the steep, descending section of the desorption branch of the isotherm [Ref. (1), see Fig. 6]. At constant rate of cooling the rate of desorption increases greatly in this region because, as the relative pressure changes

from 0.8 to 0.68, the equilibrium water content is reduced from 0.24 to 0.08 g/g, the difference being equal to 65% of the ultimate uptake and 92% of the capillary-held water. The transfer of such an amount of water causes significant disturbance even under equilibrium conditions, conditions seldom established owing to the inadequate migration rate.

The dynamic character of the phenomenon was demonstrated by very much reduced expansion at slow cooling rates compared with that observed at higher rates [Ref. (1), see Figs. 5 and 8]. In another experiment (Fig. 8) water-saturated glass was cooled at a rate of $0.33^{\circ}\text{C}/\text{min}$ until after the commencement of freezing at -18°C , when (apart from a drift of approximately 1°C) constant temperature

FIG. 4. Porous glass samples saturated with NaCl solutions of various concentrations during temperature cycle ($0.33^{\circ}\text{C}/\text{min}$). (a) Dimensional changes. (b) Differential thermograms.

was maintained for 17 hr. In this period, following an initial 53×10^{-5} relative unit expansion, the original dimensions were re-established. On resumption of cooling at a rate of $0.33^{\circ}\text{C}/\text{min}$ an overall expansion of 70×10^{-5} was obtained, a value very similar to that found at a rate of cooling of $0.0417^{\circ}\text{C}/\text{min}$ [Ref. (1), see Fig. 8]; this is in contrast with $\Delta l/l = 400 \times 10^{-5}$ expansion usually occurring at the higher rate of $0.33^{\circ}\text{C}/\text{min}$ (Fig. 4a). These results indicate that expansion is associated with nonequilibrium conditions

caused by too-rapid cooling for a given permeability and diffusion rate.

2. If, instead of water, NaCl solution is used as adsorbate, ice crystals appear in the cell at a lower temperature and the depression of the second freezing temperature is proportional to the salt concentration (Figs. 4 and 5).

3. With formation of ice crystals in the cell, a vapor-pressure difference is created between the solid outside and the undercooled liquid inside the porous system. Whereas in pure liquids equilibrium condition can be restored

Fig. 5. Freezing and melting points of salt solutions of various concentrations adsorbed in porous glass.

only by desorption, in solutions the possibility exists, at least theoretically, that the vapor pressure difference can be eliminated by increasing the concentration of the solution through ice formation, with no need to leave the originally occupied capillaries.

Exothermic heat effect and expansion, indicating second freezing, were found to occur approximately 20°C below the bulk freezing point of the solutions (Fig. 5), in good agreement with the value obtained for water (19°C deg). The melting points of the adsorbed solutions shifted to approximately 13°C deg below the corresponding bulk value, also in agreement

with the value obtained for water. The great similarity between the behavior of water and solution adsorbates suggests that the mechanism is the same in all cases. Phase separation, however, takes place in neither water nor salt solutions while held in the originally occupied capillaries. Thus, the mechanism described in the previous paragraph is a mere possibility and not a reality.

4. Having concluded that adsorbate is unable to solidify, even partially, in the original pores and that it migrates out of them, the question arises whether its free energy can be lowered by solidification in the larger pores or

it has to leave the porous system before it can freeze. The results of the present study suggest the former alternative.

The endothermic heat effect at -34°C , indicated by the differential thermogram in cases of concentrations above 14%, may be assumed to result from melting of the capillary-held eutectic mixture. This is suggested by the value and the invariance of the temperature at which the anomaly occurs and that it is concentration dependent. The peak occurs exactly 21 C deg below the melting point of capillary-held ice (-13°C), and this temperature difference is equal to the freezing point lowering of the eutectic mixture.

5. The behavior of systems containing salt differs in at least two respects from that of systems containing pure water as adsorbate: (1) the magnitude of expansion on low temperature freezing is greater on slow cooling than on rapid cooling (Figs. 6a and 6b), in direct contrast with the one-component case; and (2) instead of maintaining constant length or contracting, there is substantial expansion (-45°C) at low temperatures during warming of systems containing salt solutions of high concentration, the completely saturated solution (Fig. 4) being an exception.

The observations related to these phenomena may be summarized as follows:

1. Expansion occurs at temperatures below the second melting point and reaches its maximum just prior to the maximum endothermic heat effect. The minimum length, on warming, is attained during the endothermic heat effect.

2. Expansion on warming is obtained, regardless of heating rate, if the cooling rate is $0.33^{\circ}\text{C}/\text{min}$. The corollary of this statement was also true; regardless of heating rate, no expansion took place if the cooling rate was $0.0417^{\circ}\text{C}/\text{min}$ (Fig. 6).

3. The magnitude of expansion on warming is inversely proportional to that of expansion on second freezing (Fig. 9). The difference in length between the minimum on cooling and the maximum on warming, before second thawing, was the same at both cooling rates if

TABLE III

DIFFERENCE IN LENGTH BETWEEN MINIMUM ON COOLING AFTER FIRST FREEZING AND MAXIMUM BEFORE LOW TEMPERATURE THAWING OF A POROUS GLASS SAMPLE SATURATED WITH 20% NaCl SOLUTION $\Delta l/l \times 10^5$

Cooling rate, $^{\circ}\text{C}/\text{min}$	Warming rate, $^{\circ}\text{C}/\text{min}$	
	0.0417	0.33
0.0417	425	325
0.33	425	300

the warming rate was $0.0417^{\circ}\text{C}/\text{min}$, but the overall expansion was less at the higher warming rate of $0.33^{\circ}\text{C}/\text{min}$.

Phenomenologically, it may be interpreted that at a cooling rate of $0.33^{\circ}\text{C}/\text{min}$ expansion at low temperatures cannot be completed, becomes "frozen in," and that the system will continue to expand after the same temperature region has been attained on warming. The values shown in Table III indicate that overall expansion was reduced by the combination of rapid cooling and rapid warming, presumably because the shorter time period available on warming was less than that required for completion of the expansion prematurely terminated on cooling.

Although the information available is insufficient to identify the physical causes of the phenomena, certain factors regarding the behavior of salt solution are potentially significant:

1. The vapor pressure of the adsorbed salt solution is very low owing to low temperatures and the effect of the solute. Redistribution through transfer in the vapor phase is expected to be negligible.

2. The viscosity of the salt solutions is very high, again due to low temperatures but also to the presence of small ice crystals following phase separation in the larger voids. This effect may retard or even inhibit flow of liquid.

3. The formation of a solid phase in the pores probably leads mechanical strength and rigidity to the pore structure.

FIG. 6. Changes in dimensions and heat content of porous silica glass saturated with 20% NaCl solution during temperature cycle. (a) Cooling and heating rates, 0.33°C/min. (b) Cooling rate 0.33°C/min, heating rate 0.0417°C/min (c) Cooling rate, 0.0417°C/min, heating rate 0.33°C/min. (d) Cooling and heating rates 0.0417°C/min.

FIG. 8. Changes in dimensions and heat content of porous silica glass saturated with water during temperature cycle: cooling rate $0.33^{\circ}\text{C}/\text{min}$ between 0 and -18°C ; $0.12^{\circ}\text{C}/\text{min}$ between -18 and 21°C ; arrest for 17 hr at -21°C ; $0.33^{\circ}\text{C}/\text{min}$ rate in remainder of the cycle.

There is little doubt about the existence and relevance of the listed effects, but further work is required before a detailed mechanism can be suggested. The findings of the experiments with aqueous glycerine solutions (Fig. 7) may be accepted as evidence of the effect of the high viscosity of the solutions. Particularly instructive is the case of the 20% solution where, presumably because of the high viscosity after the appearance of ice in the system, no desorption took place and the locked-in liquid caused a very large expansion on first freezing. With the pore system sealed, the second freezing also resulted in a very large expansion ($\Delta l/l = 1700 \times 10^{-5}$). Expansion was obtained also on warming. The absence of significant changes in the dimensions of the higher concentrations may be attributed to their glass-forming capability on solidification, in which case no difference exists in the vapor pressure of the bulk solid and undercooled liquid. The cryo-

protective action of glycerine in biological systems has been explained by this mechanism (17).

MECHANICAL FAILURE

Frost action, i.e., the impairment of mechanical strength, is the most important practical aspect of the low temperature behavior of porous systems. As this subject will be discussed in a forthcoming publication on the study of cement paste containing NaCl solution as adsorbate, only a few comments will be made.

It appears that the system suffers mechanical damage in a temperature cycle if the redistribution of adsorbate cannot take place at an adequate rate. In this respect certain conditions specific to two-component systems are significant. The gradual freezing of such solutions and the widening of the temperature range of the phase change are beneficial.

FIG. 7. Porous glass samples saturated with aqueous glycerine solutions of various concentrations during temperature cycle ($0.33^{\circ}\text{C}/\text{min}$). (a) Dimensional changes. (b) Differential thermograms.

FIG. 9. Parameters of the extension curves of Fig. 4a as a function of salt concentration.

Figure 10 shows the amount of ice formed in bulk NaCl solutions of various concentrations per Centigrade degree. It may be seen that at intermediate concentrations the rate of ice formation is least nonuniform and that, accordingly, length changes of the system with 10 and 19% solutions are comparatively small.

The other factor assumed to have bearing on the behavior of the system is low temperature and its consequences, i.e., high viscosity, low vapor pressure, etc. One of the most significant observations of the present experiment is the fact that the temperature cycle destroyed every sample containing glycerine solution of less than 60% concentration, whereas with

pure water as adsorbate under similar circumstances this never happened.

CONCLUSIONS

It is the major conclusion of the present work that the low temperature behavior of the porous glass-water system in the presence of NaCl is, *mutatis mutandis*, similar to that in its absence. It is suggested that the primary cause of peculiarities is the vapor pressure difference between the bulk solid without and the undercooled liquid-like adsorbate within the pores. Confirmation of this hypothesis has been obtained regarding the phenomenon referred to as first freezing. With regard to the

FIG. 10. Amount of ice, expressed in weight per cent, formed in NaCl solutions of various concentrations per degree Celsius.

second freezing phenomenon, the modifying effect of very low temperatures, high viscosity, low vapor pressure and the freezing mechanism of two-component solutions is tentatively assumed to be responsible for the divergence in some of the features of the two systems.

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