

Melting of Hydrogels Containing Ammonium Nitrate

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Synopsis

The fusion of hydrogels containing ammonium nitrate (AN) has been investigated by differential scanning calorimetry (DSC). The polymers used were guar and xanthan gums as well as synthetic polyacrylamide polymers. Water in hydrogels could be classified into three types labeled as ordinary water (hump on the melting peak), intermediate water (broad component of the peak), and bound nonfreezing water (without any phase transition). The temperature of fusion of intermediate water was about 10° to 35°C lower than that of ordinary water. Intermediate and bound water was found in all the gels studied, whereas ordinary water existed mainly in mixtures with total water content higher than 62%. The presence, type, and concentration of a crosslinker had no effect on the amount of bound water in hydrogels containing AN. In such mixtures the amount of nonfreezing water increased with the polymer concentration as well with the AN proportion relative to water and represented in some cases up to 27% of the gel. Cold-crystallization was observed in all cases (except xanthan) and was probably initiated by AN or the crosslinking agent.

INTRODUCTION

Different techniques were employed to study the extent of water binding and the existence of structured water in the gels in order to understand the properties of water and its interaction with the polymers. Karmas and DiMarco¹ determined by differential scanning calorimetry (DSC) the water binding in proteins by measuring the heat of evaporation of water from various foodstuffs. Dehl² estimated the amount of unfrozen water in collagen fibers by using independent techniques such as DSC and nuclear magnetic resonance (NMR). Aizawa and Suzuki³ proposed that water in macromolecular gels be classified into three groups according to their dilatometric studies of agarose and crosslinked dextran gels.

Frommer and Lancet⁴ determined by DSC the relative amount of freezing and nonfreezing water in cellulose acetate membranes and found by NMR that the bound water is highly mobile compared with ice. Belfort and coworkers⁵ indicated by NMR studies that the occluded water in porous glass had about ten times the average viscosity of bulk water but was four orders of magnitude less viscous than ice. With regard to mobility, the water in the pores behaved more like liquid than ice but exhibited a degree of ordering quite different from that of conventional water.

Lee and coworkers⁶ suggested that three classes of water might exist in certain hydrogels according to their dilatometric, specific conductivity and DSC measurements of poly(hydroxyethyl methacrylate) gels. These classes of water were labeled as bulk, intermediate, and bound water. Taniguchi and Horigome⁷ proposed that water in cellulose acetate membranes be classified into four states according to their experimental observations from DSC. These states of water were those of completely free water, free water very weakly interacting with polymer, bound water which could contain salts, and bound water which rejected salts.

TABLE I
DSC Results for the System H₂O-P₂₇-CR

| $P_1, \%$ | $P_2, \%$ | $P_3, \%$ | $P_{12}, \%$ | $T_x, ^\circ\text{C}$ | $T_y, ^\circ\text{C}$ | $T_c, ^\circ\text{C}$ |
|-----------|-----------|-----------|--------------|-----------------------|-----------------------|-----------------------|
| 91.6 | 8 | 0.4 | 11.4 | -4 | -16 | -35 |
| 90.4 | | 1.6 | 11.6 | -7 | -15 | -31 |
| 89.6 | | 2.4 | 11.2 | -8 | -16 | -33 |
| 89.5 | 10 | 0.5 | 13.8 | -5 | -17 | -35 |
| 88 | | 2 | 13.3 | -7 | -16 | -34 |
| 87 | | 3 | 12.8 | -6 | -16 | -30 |
| 85.3 | 14 | 0.7 | 15.5 | -5 | -16 | -39 |
| 83.2 | | 2.8 | 13.7 | -7 | -16 | -37 |
| 81.8 | | 4.2 | 14.6 | -4 | -14 | -38 |
| 81.1 | 18 | 0.9 | 15.4 | -5 | -17 | -37 |
| 78.4 | | 3.6 | 14.7 | -4 | -18 | -39 |
| 76.6 | | 5.4 | 16.4 | -8 | -18 | -37 |
| 76.9 | 22 | 1.1 | 13.2 | -4 | -18 | -41 |
| 74.7 | | 3.3 | 14.3 | -4 | -16 | -39 |
| 73.6 | | 4.4 | 15.2 | -4 | -17 | -32 |

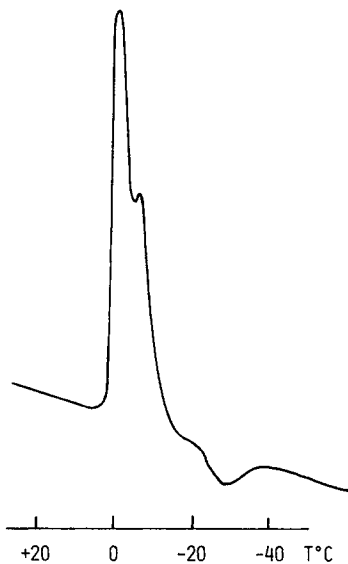


Fig. 1. DSC melting thermogram for the system H₂O (83.2%)-P₂₇(14%)-CR(2.8%).

In a previous DSC study by the author⁸ on the effect of a crosslinker and its concentration on aqueous polymer solutions and gels, it was found that a fraction of the water in these mixtures was associated to the polymer, and in some cases two distinct freezing points were observed. The objective of the present work is to study the effect of AN on the extent of water binding and on the relative proportion of nonfreezing water in different types of hydrogels. Guar and xanthan gums as well as synthetic polyacrylamide polymers were used in this study.

TABLE II
 DSC Results for the System H₂O-Guar-CR-AN

| $P_1, \%$ | $P_2, \%$ | $P_3, \%$ | $P_4, \%$ | $P_{12}, \%$ | $T_x, ^\circ\text{C}$ | $T_y, ^\circ\text{C}$ | $T_c, ^\circ\text{C}$ |
|-----------|-----------|-----------|-----------|--------------|-----------------------|-----------------------|-----------------------|
| 50.2 | 2 | 0.08 | 47.7 | 7 | | -23 | |
| 59.2 | | 0.24 | 38.6 | 6.7 | | -27 | |
| 65.1 | | 0.32 | 32.6 | 6.6 | -7 | -26 | |
| 78 | | 0.48 | 19.5 | 6.4 | -4 | -25 | |
| 84.7 | | 0.64 | 12.7 | 6.2 | -4 | -24 | |
| 48.6 | 5 | 0.20 | 46.2 | 11.5 | | -31 | |
| 57.2 | | 0.60 | 37.2 | 10.5 | | -29 | |
| 62.8 | | 0.80 | 31.4 | 10 | -6 | -26 | |
| 75 | | 1.20 | 18.8 | 9.3 | -7 | -28 | |
| 81.2 | | 1.60 | 12.2 | 9 | -7 | -31 | -62 |
| 47 | 8 | 0.32 | 44.6 | 14 | | -34 | |
| 60.5 | | 1.28 | 30.2 | 13 | | -25 | |
| 67 | | 1.60 | 23.4 | 12.5 | -7 | -26 | |
| 72.1 | | 1.92 | 18 | 11.5 | -8 | -34 | -60 |
| 77.8 | | 2.56 | 11.6 | 11 | -5 | -34 | -49 |
| 45.9 | 10 | 0.40 | 43.6 | 16 | | -28 | |
| 58.9 | | 1.60 | 29.5 | 15 | | -27 | |
| 65.2 | | 2.0 | 22.8 | 14 | -6 | -32 | -60 |
| 70.1 | | 2.4 | 17.5 | 13.6 | -6 | -34 | -55 |
| 75.5 | | 3.2 | 11.3 | 12.5 | -7 | -34 | -40 |

EXPERIMENTAL

Materials

Guar, a nonionic polysaccharide (jaguar 170 gum) from Stein-Hall Limited; Xanthan, an anionic heteropolysaccharide gum from General Mills Chemicals, Biopolymer XB-23 (Lot B2135-1); P₂₉₅, a slightly anionic polyacrylamide from Stein-Hall Ltd.; and P₂₇, a nonionic polyacrylamide from Stein-Hall Ltd., were used.

Chromic nitrate, Cr(NO₃)₃·9H₂O, at pH 10–11, and potassium pyroantimonate, K₂H₂Sb₂O₇·4H₂O, at pH 4–5, were used as crosslinking agents. Both crosslinkers as well as the ammonium nitrate, NH₄NO₃, were from Fisher Scientific Company.

Instrument

A Perkin-Elmer Model DSC-2 differential scanning calorimeter was used for all the melting measurements. Samples were prepared with concentrations between 2 and 22 wt-% polymer. The crosslinker concentration varied between 5 and 30 wt-% relative to polymer. The ammonium nitrate (AN) concentration varied between 15 and 95 wt-% relative to water. Gels were prepared and studied in less than 24 hr to prevent bacterial attack especially in the case of guar and xanthan gums. The DSC was calibrated by using benzene and water as standards. About 7–20 mg gel was transferred to the Al sample pan (normally used

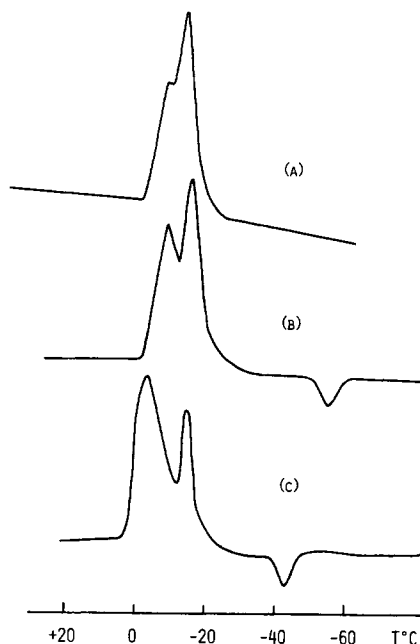


Fig. 2. DSC melting thermograms for guar hydrogels: (a) H₂O(67%)–guar(8%)–CR(1.6%)–AN(23.4%); (b) H₂O(72.1%)–guar(8%)–CR(1.92%)–AN(18%); (c) H₂O(77.8%)–guar(8%)–CR(2.56%)–AN(11.6%).

for liquids) which was then hermetically sealed to prevent evaporation. The sample was cooled down to -90°C by using liquid nitrogen and then heated slowly in a stream of nitrogen gas at a scanning rate of $10^{\circ}\text{C}/\text{min}$ up to 20°C . The area under the melting peak was measured with a mechanical planimeter.

RESULTS AND DISCUSSION

Hydrogels Without Ammonium Nitrate

A significant fraction of the water in the gels did not freeze at temperatures as low as -90°C . The freezing water content was determined from the area under the melting endotherm. The amount of bound (nonfreezing) water was taken as the difference between the total water content in the gel and the amount of freezing water:

$$P_{1z} = P_1 - \frac{Q_{\text{endo}}}{Q_f} \quad (1)$$

where P_{1z} and P_1 are the weight fraction of bound and total water in the gel, respectively; Q_{endo} is the observed endothermic heat, in cal/g gel; and Q_f is the heat of fusion of ice (80 cal/g). The heat of fusion for the freezing water in the gels was assumed to be identical to that of pure ice as has been shown² by independent DSC and NMR techniques.

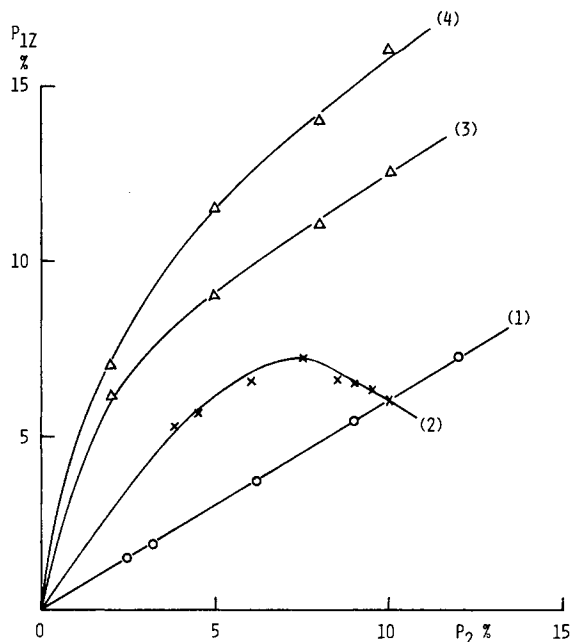


Fig. 3. Variation of P_{1z} with P_2 for different types of guar gels: (1) H₂O-guar; (2) H₂O-guar-crosslinker; (3) H₂O-guar-crosslinker-AN ($P_4/P_1 = 0.15$); (4) H₂O-guar-crosslinker-AN ($P_4/P_1 = 0.95$).

The data for gels of the type H₂O-polymer and H₂O-polymer-crosslinker were published in a previous paper.⁸ In the present work the results for the system H₂O-P₂₇-crosslinker, which were not available at that time, are reported. Chromic nitrate (CR) and potassium pyroantimoniate (PP) were used as crosslinking agents, and the results were similar in both cases. To avoid repetition, only the results of the system H₂O-P₂₇-CR are reported in Table I. P_2 and P_3 represent the weight fractions of the polymer and the crosslinker in the gel, respectively.

All the mixtures studied yielded humps (sharp components) on the endothermic peak and small exothermic peaks preceding the melting endotherm, as shown in Figure 1. The exothermic peak is due to the cold-crystallization, which occurs at temperatures far below the melting point. The T_c values ($-35 \pm 5^\circ\text{C}$) reported in Table I correspond to the temperature of appearance of the cold-crystallization exotherm. The presence of a hump on the melting thermogram confirms the existence of two types of freezing water: The first one, X type, is ordinary bulk water and corresponds to the hump or sharp component on the melting endotherm. The second one, Y type, is intermediate water which is represented by the broad component of the melting peak. On the other hand, bound water, Z type, exhibited no phase transitions over the range -90° – 20°C . The temperatures T_x ($-6 \pm 2^\circ\text{C}$) and T_y ($-16 \pm 2^\circ\text{C}$) reported in Table I represent the temperatures of fusion of ordinary and intermediate water, respectively. T_y corresponds to the temperature at which the first deflection from the baseline appears, and T_x corresponds to the temperature of the hump (sharp component) on the melting peak.

As is indicated in Table I, the amount of bound water (Z type) in the gel is not

TABLE III
DSC Results for Systems H₂O-Xanthan-PP-AN and H₂O-P₂₉₅-PP-AN

| P_1 , % | P_2 , % | P_3 , % | P_4 , % | H ₂ O-xanthan-PP-AN | | | H ₂ O-P ₂₉₅ -PP-AN | | | |
|--------------|--------------|--------------|--------------|--------------------------------|---------------|---------------|--|---------------|---------------|---------------|
| | | | | P_{1z} , % | T_x , °C | T_y , °C | P_{1z} , % | T_x , °C | T_y , °C | T_c , °C |
| 50.2 | 2 | 0.08 | 47.7 | 9 | | -25 | 9.4 | | -26 | |
| 59.2 | | 0.24 | 38.6 | 8 | | -25 | 8 | | -26 | |
| 65.1 | | 0.32 | 32.6 | 7.5 | -6 | -25 | 7.5 | -6 | -31 | |
| 78 | | 0.48 | 19.5 | 6.5 | -5 | -26 | 6.2 | -6 | -27 | |
| 84.7 | | 0.64 | 12.7 | 6 | -8 | -26 | 6.2 | -4 | -26 | |
| 49.1 | 4 | 0.16 | 46.6 | 10.8 | | -30 | 13.6 | | -27 | |
| 57.9 | | 0.48 | 37.6 | 9.5 | | -30 | 13.2 | | -27 | |
| 63.6 | | 0.64 | 31.8 | 9 | -6 | -30 | 12.4 | -7 | -28 | |
| 76 | | 0.96 | 19 | 8.5 | -6 | -28 | 8.8 | -7 | -31 | |
| 82.4 | | 1.28 | 12.4 | 8 | -6 | -28 | 8.8 | -4 | -30 | -61 |
| 48.6 | 6 | 0.24 | 45.7 | 12.6 | | -30 | 15.6 | | -29 | |
| 56.5 | | 0.72 | 36.8 | 12 | | -28 | 15 | | -29 | |
| 62 | | 0.96 | 31 | 11 | -8 | -30 | 13.8 | -8 | -31 | |
| 74 | | 1.44 | 18.6 | 10.5 | -7 | -30 | 10.2 | -8 | -32 | -60 |
| 80.1 | | 1.92 | 12 | 10.2 | -8 | -29 | 10.2 | -4 | -33 | -55 |
| 47 | 8 | 0.32 | 44.6 | 14.4 | | -35 | 17.6 | | -30 | |
| 60.5 | | 1.28 | 30.2 | 13.5 | | -35 | 16 | | -31 | |
| 67 | | 1.60 | 23.4 | 13 | -8 | -31 | 11.2 | -8 | -34 | -58 |
| 72.1 | | 1.92 | 18 | 12.5 | -7 | -32 | 11.2 | -7 | -33 | -56 |
| 77.8 | | 2.56 | 11.6 | 12 | -7 | -32 | 11.0 | -6 | -35 | -50 |
| 45.9 | 10 | 0.40 | 43.6 | 16 | | -36 | 19 | | -32 | |
| 53.8 | | 1.20 | 35 | 15 | | -36 | 18.1 | | -35 | -62 |
| 65.2 | | 2.0 | 22.8 | 15 | -8 | -36 | 12 | -8 | -36 | -56 |
| 70.1 | | 2.4 | 17.5 | 14 | -8 | -36 | 12 | -8 | -36 | -53 |
| 75.5 | | 3.2 | 11.3 | 14 | -8 | -33 | 12 | -4 | -34 | -48 |

a function of the crosslinker proportions in the mixture but varies slightly with the polymer concentration. This is in agreement with the results obtained in the previous study⁸ for the other polymers.

Hydrogels Containing Ammonium Nitrate

When AN is used in the gel composition, the observed endothermic heat (Q_{endo}) is in most cases higher than the expected heat of fusion ($Q_f P_1$) owing to the presence of the salt. For this reason, eq. (1) is not valid for the determination of the amount of bound water (Z type) in hydrogels containing AN. For such mixtures, P_{1z} is computed by comparing the results obtained when AN is added to the gel to those obtained for a (H₂O-AN) solution with the same AN concentration relative to water as in the gel:

$$P_{1z} = \frac{\Delta A}{Q_f} \quad (2)$$

and

$$A = Q_{\text{endo}} - Q_f P_1 \quad (3)$$

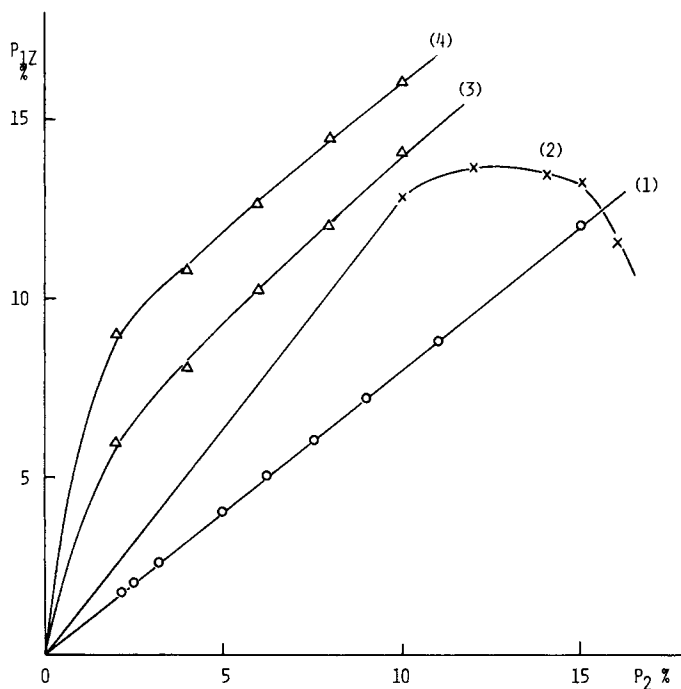


Fig. 4. Variation of P_{12} with P_2 for different types of xanthan gels: (1) H_2O -xanthan; (2) H_2O -xanthan-crosslinker; (3) H_2O -xanthan-crosslinker-AN ($P_4/P_1 = 0.15$); (4) H_2O -xanthan-crosslinker-AN ($P_4/P_1 = 0.95$).

The Δ sign represents the difference between the A value for a binary solution H_2O -AN and the A value for a gel of the type H_2O -polymer-AN or the type H_2O -polymer-crosslinker-AN and having the same ratio P_4/P_1 as the H_2O -AN solution (P_4 is the weight fraction of AN in the mixture).

The expression "bound water," when used in the case of gels containing AN, designates actually the nonfreezing water, which is not necessarily entirely bound to the polymer. As a matter of fact, a fraction of the nonfreezing water could well be associated or hydrated to the AN salt.

Guar Hydrogels

In the system H_2O -guar-AN, for each polymer concentration the ratio P_4/P_1 varied from 0.15 to 0.95.

In the system H_2O -guar-crosslinker-AN, three cases were studied. In the first case, for each polymer concentration the two ratios P_3/P_2 and P_4/P_1 varied simultaneously. In the second case, for each polymer concentration the ratio P_3/P_2 was kept constant at 0.30 while the ratio P_4/P_1 varied from 0.15 to 0.95. In the third case, for each polymer concentration P_4 was kept constant at 32% while the ratio P_3/P_2 varied from 0.05 to 0.30. In each one of these three cases, both CR and PP were used as crosslinkers.

From all these studies, the following facts were established: (1) The presence, type, and concentration of a crosslinker used in hydrogels containing AN have no effect on the results. Gels of the type H_2O -guar-AN and H_2O -guar-crosslinker-AN give similar results probably because the crosslinker effect is negli-

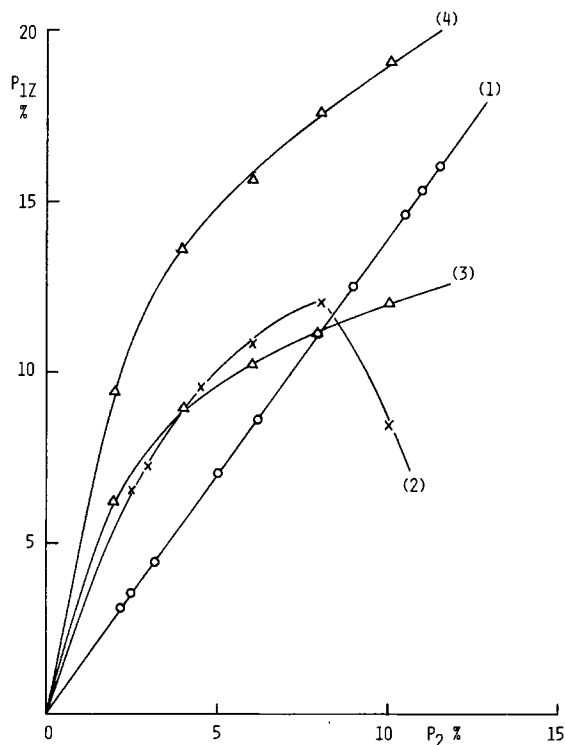


Fig. 5. Variation of P_{1z} with P_2 for different types of P_{295} gels: (1) H_2O - P_{295} ; (2) H_2O - P_{295} -crosslinker; (3) H_2O - P_{295} -crosslinker-AN ($P_4/P_1 = 0.15$); (4) H_2O - P_{295} -crosslinker-AN ($P_4/P_1 = 0.95$).

gible compared to the more important salt effect. (2) The amount of bound water depends mainly on P_2 and on the ratio P_4/P_1 in the gel.

In order to avoid repetition, only the results of the system H_2O -guar-CR-AN are reported in Table II. Conventional water (X type) has a freezing point $T_x = -6 \pm 2^\circ C$, whereas intermediate water (Y type) has a temperature of fusion $T_y = -29 \pm 5^\circ C$. Gels containing less than 62% water have only one freezing temperature, corresponding to intermediate water. On the other hand, gels with $P_1 > 62\%$ exhibit two freezing points, representing ordinary and intermediate water. Ordinary water exists mainly in high water-content gels, and its relative proportion increases gradually with the total amount of water in the mixture. This is clearly shown in Figure 2, where the hump on the melting endotherm that corresponds to ordinary water is becoming larger and expands as the total water content in the gel is increased. The cold-crystallization exotherms appear for gels with a ratio P_2/P_4 higher than 0.34, and the temperatures T_c for these mixtures increase from -62° to $-40^\circ C$ with the ratio P_2/P_4 . Cold-crystallization depends particularly on the structure of the polymeric material and is probably initiated by some substances such as AN or a crosslinking agent.

The graph of P_{1z} versus P_2 for different types of guar hydrogels is plotted in Figure 3. For the system H_2O -guar, P_{1z} increases linearly with P_2 (0.60 g bound water per g guar). In the system H_2O -guar-crosslinker, some branching occurs, and as the polymer concentration is gradually increased, less water is able to penetrate inside the surface of the gel. For this reason P_{1z} increases rapidly with

TABLE IV
 DSC Results for the System H₂O-P₂₇-AN

| P_1 , % | P_2 , % | P_4 , % | P_{1z} , % | T_x , °C | T_y , °C | T_c , °C |
|-----------|-----------|-----------|--------------|------------|------------|------------|
| 47.2 | 8 | 44.8 | 17.5 | | -36 | |
| 61.3 | | 30.7 | 14.6 | | -33 | |
| 68.1 | | 23.9 | 10 | -8 | -32 | -55 |
| 73.6 | | 18.4 | 7.8 | -7 | -31 | -52 |
| 80 | | 12 | 6.3 | -7 | -29 | -49 |
| 46.2 | 10 | 43.8 | 20.3 | | -39 | |
| 60 | | 30 | 17.4 | | -36 | -55 |
| 66.7 | | 23.3 | 13.1 | -7 | -35 | -52 |
| 75 | | 15 | 10.6 | -6 | -29 | -48 |
| 78.3 | | 11.7 | 9.4 | -6 | -29 | -47 (-74) |
| 45.1 | 12 | 42.9 | 22.3 | | -40 | |
| 58.7 | | 29.3 | 20.4 | | -38 | |
| 65.2 | | 22.8 | 16.5 | -9 | -35 | -49 |
| 73.3 | | 14.7 | 14 | -5 | -27 | -47 (-74) |
| 76.5 | | 11.5 | 12.8 | -6 | -27 | -47 (-60) |
| 44.1 | 14 | 41.9 | 24.8 | | -43 | |
| 57.3 | | 28.7 | 23.4 | | -41 | |
| 63.7 | | 22.3 | 19.6 | -10 | -40 | -47 |
| 68.8 | | 17.2 | 17.5 | -9 | -33 | -45 (-74) |
| 74.8 | | 11.2 | 15.6 | -10 | -29 | -45 (-56) |
| 43.1 | 16 | 40.9 | 27.2 | | -45 | |
| 56 | | 28 | 26.5 | | -41 | -49 |
| 62.2 | | 21.8 | 22.8 | -10 | -40 | -47 |
| 67.2 | | 16.8 | 20.6 | -7 | -33 | -46 (-65) |
| 73 | | 11 | 18.8 | -6 | -29 | -45 (-54) |

P_2 at lower polymer concentrations until it reaches a maximum value (7.2%), and then it starts to decrease at higher polymer concentrations. When AN is added to the hydrogel, P_{1z} increases furthermore with P_2 , and the higher the ratio P_4/P_1 , the higher the increase in the amount of bound water. However, one cannot affirm explicitly whether this increase in P_{1z} is due principally to the fact that more water is bound to the polymer or rather to an increase in the fraction of water associated (hydrated) to AN, or to a combination of both factors.

Xanthan and P₂₉₅ Hydrogels

The crosslinking agents PP and CR were used in xanthan gels, and the results were identical in both cases and similar to those obtained for the system H₂O-xanthan-AN. To avoid repetition, only the results of the system H₂O-xanthan-PP-AN are reported in Table III. P₂₉₅ hydrogels containing CR as a crosslinker were unstable when the water proportion in the mixture was higher than 62%. On the other hand, when PP was tested with P₂₉₅ gels, the results obtained (Table III) were reproducible and similar to those obtained for the system H₂O-P₂₉₅-AN.

Two freezing temperatures (for ordinary and intermediate water) were ob-

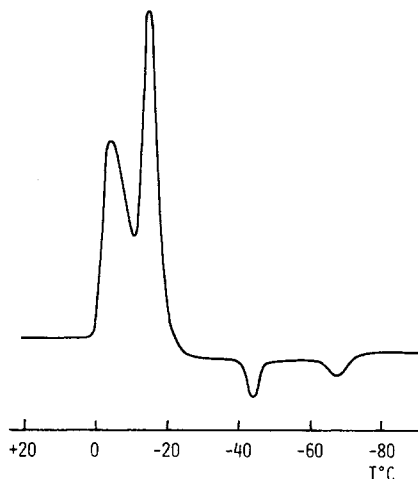


Fig. 6. DSC melting thermogram for the system $\text{H}_2\text{O}(73.3\%)\text{-P}_{27}(12\%)\text{-AN}(14.7\%)$.

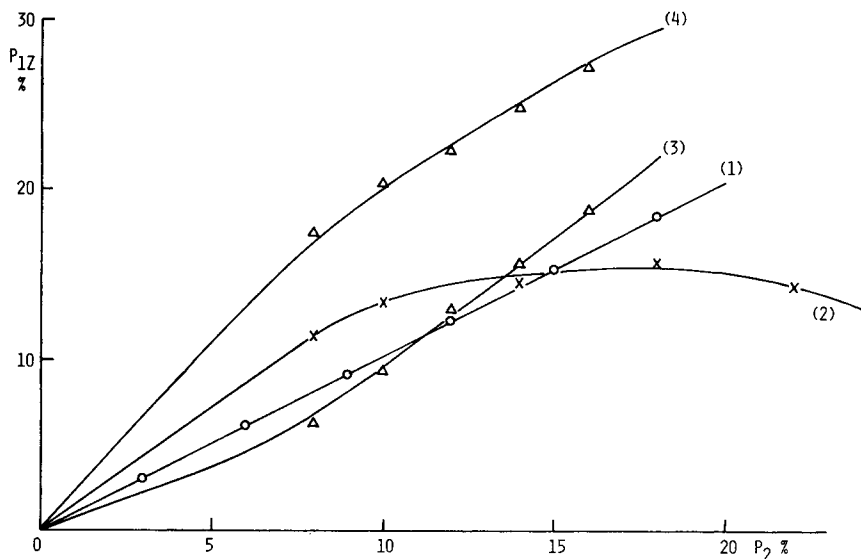


Fig. 7. Variation of P_{1z} with P_2 for different types of P_{27} gels: (1) $\text{H}_2\text{O}\text{-P}_{27}$; (2) $\text{H}_2\text{O}\text{-P}_{27}\text{-crosslinker}$; (3) $\text{H}_2\text{O}\text{-P}_{27}\text{-crosslinker-AN}$ ($P_4/P_1 = 0.15$); (4) $\text{H}_2\text{O}\text{-P}_{27}\text{-crosslinker-AN}$ ($P_4/P_1 = 0.95$).

served when $P_1 > 62\%$ for xanthan and P_{295} hydrogels. Conventional water (X type) had a freezing temperature $T_x = -6 \pm 2^\circ\text{C}$, and intermediate water (Y type) had a freezing temperature T_y which decreased slightly from -25° to -36°C with the ratio P_1/P_2 .

Cold-crystallization did not occur in the case of xanthan gels. On the other hand, cold-crystallization was observed for P_{295} hydrogels when $P_2/P_4 > 0.29$ and the temperature of appearance of the small exothermic peaks, T_c , varied from -62° to -48°C with the ratio P_2/P_4 .

The variation of P_{1z} with P_2 for different types of xanthan and P_{295} gels are plotted in Figures 4 and 5, respectively. The amount of bound water per gram polymer is constant and equal to 0.80 and 1.38 for the systems $\text{H}_2\text{O}\text{-xanthan}$ and

H₂O-P₂₉₅, respectively. For gels of the type H₂O-polymer-crosslinker, P_{1z} increases more rapidly with P_2 to a maximum value (13.7% for xanthan and 12% for P₂₉₅) and then decreases at higher polymer concentrations. In the case of gels containing AN, the amount of bound water (Z type) increases more rapidly with the polymer concentration, and the higher the ratio P_4/P_1 , the higher the increase of P_{1z} .

P₂₇ Hydrogels

The crosslinker PP was used with P₂₇ gels, and the results were identical to those obtained for the system H₂O-P₂₇-AN, which are presented in Table IV.

The temperature of fusion, T_y , of intermediate water decreased from -29° to -45°C with the ratio P_1/P_2 . Ordinary water existed mainly when $P_1 > 62\%$ and had a freezing temperature $T_x = -8 \pm 2^\circ\text{C}$.

Cold-crystallization occurred when $P_2/P_4 > 0.33$ (for P_2 lower than 12%) or when $P_2/P_4 > 0.53$ (for higher polymer concentrations). The cold-crystallization exotherm separated into two small peaks, as shown in Figure 6, when the ratio P_2/P_4 was higher than 0.81. Such a phenomenon was observed by Kimura et al.⁹ in the initial state of the recrystallization of amorphous cellulose with water by increasing the relative humidity. The T_c temperatures (values between brackets in Table IV) for the first exothermic peak varied from -74° to -54°C with the ratio P_2/P_4 , whereas the second exothermic peak had a T_c temperature of $-50 \pm 5^\circ\text{C}$.

The variation of P_{1z} with P_2 is presented in Figure 7 for different types of P₂₇ gels. In the system H₂O-P₂₇, P_{1z} varies linearly with the polymer concentration (1.0 g bound water per g P₂₇). In the system H₂O-P₂₇-crosslinker, the amount of bound water (Z type) increases with P_2 until it reaches a maximum value (15.7%) and then starts to decrease at higher polymer concentrations. When AN is present in the mixture, the increase in P_{1z} with P_2 is higher for gels containing higher proportions of AN relative to water. In such mixtures the amount of nonfreezing water represented in some cases up to 27% of the gel.

CONCLUSIONS

Three types of water could exist in hydrogels: ordinary normal water (X type), intermediate water (Y type), and bound nonfreezing water (Z type). The broad component of the melting endotherm corresponded to intermediate water, and the sharp component (hump) of the peak represented ordinary water. The freezing temperature of intermediate water was 10° to 35°C lower than that of ordinary water and depended on the polymer type and on the water proportion in the gel. Bound water exhibited no phase transitions over the range of -90° – -20°C . Intermediate and bound water were present in all the gels studied, whereas ordinary water existed mainly in mixtures containing more than 62% water.

The amount of bound water per gram polymer was constant for a given H₂O-polymer system. For gels of the type H₂O-polymer-crosslinker, the amount of bound water was independent of the type of crosslinker used and its proportion in the mixture but increased rather rapidly with polymer concentration to a maximum value (saturation point) and then decreased at higher

polymer concentrations. For gels containing AN, the use of a crosslinker did not affect the results probably because the AN effect was more important than the crosslinker effect. When AN was used, the amount of bound water increased with the polymer concentration as well as with the AN proportion relative to water and varied from 6% to 27% depending on the system studied. The increase in the amount of nonfreezing water with polymer concentration was generally higher in the case of gels containing AN than it was for gels without AN. This could be explained by an increase in the relative proportion of water bound to the polymer as well as by an increase in the fraction of water hydrated to AN or by a combination of both.

Cold-crystallization occurred in all the polymers studied, except xanthan. The temperature of appearance of the cold-crystallization exotherm varied slightly with the polymer proportion in gels containing AN.

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