

Differential Scanning Calorimetry of Aqueous Polymer Solutions and Gels

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Synopsis

The melting phenomena of aqueous polymer solutions and gels have been investigated by differential scanning calorimetry (DSC). The polymers used were synthetic polyacrylamide and poly(vinyl alcohol) samples as well as guar and xanthan gums. By using an empirical relation, the energy measured from the area under the melting peak yielded heats of mixing and sorption, when fitted by an association factor computed from the data. This factor (independent of the concentration) is a measure of the water fraction associated with the polymer and has a definite and characteristic value for a given polymer in water. When a crosslinking agent (potassium pyroantimoniate or chromic nitrate) was added to the water-polymer system, the association factor varied with the polymer concentration; the macromolecular chains thus become less accessible to penetrating water. If a branched gel was obtained owing to the formation of chemical crosslinks, a hump appeared on the melting peak.

INTRODUCTION

Water gel explosives have enjoyed successful industrial application in the last ten years. The main ingredients of slurry explosives are suspended in a chemically crosslinked aqueous medium to form a rubbery and stable water resistant gel. Much development effort was expended in the investigation of the chemistry and structure of gels in order to improve the physical properties of slurry explosives. The state of the art in this field is completely empirical, and thus differential scanning calorimetry (DSC) as a more scientific approach was thought to be a good technique for a systematic study of the properties of gels.

Direct thermal analysis techniques have been employed for investigation of the thermodynamic behavior of macromolecular solutions. Recently, some studies on polymer solutions, using thermoanalytical methods such as DSC, have been reported in the literature.

Rai and Miller¹ used DSC to investigate the thermal behavior of the system poly(benzyl glutamate)-dimethyl formamide. In their case, thermograms for pure solvent and for pure solid polymer showed no evidence of thermal transition, whereas the thermograms of polymer solutions in the same temperature range yielded heats of polymer-solvent mixing. Van Emmerik and Smolders² using DSC studied the phase separation phenomena of solutions of poly(2,6-dimethyl-1,4-phenylene oxide) in

toluene. By measuring the melting point depression of the polymer in solution, they obtained the heat of fusion of the polymer-solvent crystals. Frommer and co-workers³ determined by DSC the relative amounts of freezing and nonfreezing water in cellulose acetate membranes.

A study using DSC has been performed at the Defence Research Establishment Valcartier (DREV) during 1972-73 on the melting of aqueous polymer solutions and gels and on the effect of a crosslinker and its concentration on these water-polymer mixtures. Guar and xanthan gums and synthetic polymers [polyacrylamide, poly(vinyl alcohol)] were used as polymers; potassium pyroantimoniate and chromic nitrate were employed as crosslinking agents.

EXPERIMENTAL

Materials

PVA. Completely hydrolyzed poly(vinyl alcohol) sample (Elvanol 85-60) from du Pont. At room temperature, the dissolution rate is slow but increases as the temperature is raised.

P₂₇. Hallmark Polyhall 27 from Stein-Hall Ltd. A nonionic polyacrylamide with a rapid dissolution rate in cold water.

P₂₉₅. Hallmark Polyhall 295 from Stein-Hall Ltd. A slightly anionic high molecular weight polyacrylamide which hydrates extremely rapidly to form viscous solutions.

Xanthan. Biopolymer XB-23 xanthan gum from General Mills Chemicals. Lot (OF 1421) and Lot (B 2135-1) were used and gave similar results. Xanthan is an anionic heteropolysaccharide produced by the fermentation of a carbohydrate by the bacterium *Xanthomonas campestris*. The chain is made up of many mannose, glucose and glucuronic acid units linked together. The functional groups of the molecule are hydroxyl and carboxyl with the carboxyl group actually being the sodium or potassium salt.

Guar. Jaguar 170 gum from Stein-Hall Ltd. A high molecular weight nonionic polysaccharide. The guar molecule is essentially a galactomannan: a straight-chain mannan branched at quite regular intervals with single-membered galactose units on alternate mannose units.

Chromic nitrate, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at (pH 10-11), and potassium pyroantimoniate, $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ (at pH 4-5), were used as crosslinking agents. Both crosslinkers used were from Fisher Scientific Company.

Instrument

A Perkin-Elmer Model DSC-1B differential scanning calorimeter was used for all the melting measurements. Samples were prepared with concentrations between 2 and 20 wt-% polymer. The crosslinker concentration varied between 2.5 and 25 wt-% relative to polymer. Mixtures were prepared and studied in less than 24 hr to prevent bacterial attack. The DSC was calibrated by using indium, benzene, *n*-octane, and water as

standards. About 7–21 mg mixture was transferred to the Al sample pan (normally used for liquids). The pan was then hermetically sealed to prevent solvent loss. The sample was cooled down to -80°C by using liquid nitrogen and then heated slowly at a scanning rate of $10^{\circ}\text{C}/\text{min}$ up to 50°C . The area under the melting peak was measured with a mechanical planimeter.

THEORY

Definition of Terms

Solutions and Gels. The synthetic polymers (PVA, P_{27} , and P_{295}), when dissolved in water, give solutions with a viscosity dependent on the solute and its concentration. The gums (guar and xanthan), when hydrated in cold water, form viscous, colloidal dispersions or smooth, opaque sols. A gel is obtained from the transformation of the water–polymer mixture into a coherent liquid-rich system. This process may take from a few minutes to 1 hour (this is usually the time of hydration). In this report, the term “gel” designates any water–polymer solution or suspension. The addition of a crosslinker to this type of system can either have no visible effect or it may give a cohesive water-resistant material. In the first case, the term “gel” will still be used, and the expression “branched gel” will apply to the second case owing to the existence of chemical crosslinks. The formation and strength of these rubbery structural gels depend on the pH, temperature, time, and concentration of reactants. This conversion to a crosslinked gel could be instantaneous but may also last from a few hours to a day. Whether there is a branching or not, the gels formed, although they are not fluid, can be regarded thermodynamically as solutions. In this report, the word “solution” will apply to any water–polymer mixture and also to the combination (water–polymer–crosslinker).

Polymer Molar Concentration. The polymer concentration in solution was expressed as moles of monomeric units. The molecular weight of the monomer (M_2) was used in the evaluation of the number of moles of the following polymers in solution:

PVA. A value of 44 was used for M_2 , which is the molecular weight of acetaldehyde. (Vinyl alcohol, which is the monomer of PVA, cannot be isolated.)

P_{27} and P_{295} . No information was available about the monomer of these commercial polyacrylamides. A value of 80 was chosen for M_2 , which corresponds to the average of $\text{CH}_2=\text{CH}-\text{CONH}_2$ ($M_2 = 71$), $\text{CH}_2=\text{C}(\text{CH}_3)\text{CONH}_2$ ($M_2 = 85$) and $\text{CH}_3-\text{CH}=\text{CH}-\text{CONH}_2$ ($M_2 = 85$).

Guar and Xanthan. The guar chain is made up of mannose ($M_2 = 180$) and galactose ($M_2 = 180$) units. The xanthan chain is made up of mannose, glucose ($M_2 = 180$), and glucuronic acid ($M_2 = 194$) units. Although for guar and xanthan gums, a monomeric unit does not have the same significance as in an ordinary polymer, a value of 180 was chosen for M_2 for practical purposes.

Polymer Volume Fraction. Assuming that the volume contraction on mixing is negligible, ϕ_2 (polymer volume fraction) was calculated by means of the expression

$$\phi_2 = \frac{d_1 P_2}{d_2 P_1 + d_1 P_2}$$

where d_1 and d_2 are the densities of the water and polymer, respectively; and P_1 and P_2 are the weight fraction of water and polymer, respectively. Since the temperature dependence of the volume fraction of each component can be ignored, the values at 25°C were employed for the densities. PVA, P₂₉₅, and P₂₇ had respectively a density of 1.268, 1.308, and 1.605 g/ml, whereas guar and xanthan had a density of 1.561 g/ml. These values were determined from the volume of mercury displaced by weighed, compressed tablets (1.27 cm diameter) of solid polymer obtained under 4500 kg in a Carver press.

Calculations

Two main pieces of information can be obtained from the melting thermogram of a polymer solution: the melting temperature (position of the peak) and the transition energy involved (area under the peak).

Melting point depression of relatively concentrated polymer solutions provide information on thermodynamic properties such as the heat of fusion and the activity. If the polymer melting point depression is investigated, the heat of fusion of the polymer can be obtained. If, however, the solvent freezing point depression is measured, then the solvent activity, which yields information on the polymer-solvent interactions, can be determined. In the present experiments, water freezing point depression was observed for all polymer solutions.

The energy involved at the melting of a polymer solution proved to yield much more information. In fact, the difference between the observed heat (area under the peak) and the expected heat of fusion ($Q_f P_1$) could yield information on the solvation and interactions in the solution. This heat difference can be expressed in different forms:

$$B = \frac{(Q_{\text{obs}} - Q_f P_1)}{P_2} \quad \text{cal/g polymer} \quad (1)$$

or

$$C = \frac{B P_2}{(n_1 + n_2)} \quad \text{cal/mole solution} \quad (2)$$

where Q_{obs} is the observed heat in cal/g solution, Q_f is the heat of fusion of ice (80 cal/g), n_1 is the number of moles of water in 1 g of solution, and n_2 is the number of moles in polymer in 1 g of solution.

The difference between the fraction of freezing water Q_{obs}/Q_f and the total fraction of water P_1 present in the mixture can also yield information

on the water-polymer association (or sorption) that occurs in the solution. It is possible to define an association factor f such that

$$(1 - f) = \frac{n_{1a}}{n_{1a} + n_2} \quad (3)$$

n_{1a} is the number of moles of water associated with n_2 moles of polymer during the melting of 1 g of solution:

$$n_{1a} = \frac{\left(P_1 - \frac{Q_{\text{obs}}}{Q_f}\right)}{18} \quad (4)$$

An empirical relation can be derived where C is expressed as a sum of two terms:

$$C = Q_a + Q_m.$$

The first term (Q_a) corresponds to the heat of association (or sorption) of water to the polymer during the melting of the solution. This term should depend on n_{1a} and is consequently related to C by the proportionality factor $(1 - f)$:

$$Q_a = C(1 - f) \text{ cal/mole solution.}$$

Q_a may be expressed in kcal/mole polymer by the relation

$$Q_a = \frac{BM_2}{1000} (1 - f). \quad (5)$$

The second term (Q_m) corresponds to the heat of mixing of polymer with water and is related to C by the expression

$$Q_m = Cf \text{ cal/mole solution.} \quad (6)$$

Q_m is given by the interaction of chain units (segments) with solvent molecules and may be represented by a Van Laar mixing expression:

$$Q_m = \chi RT (1 - x_2)\phi_2 \text{ cal/mole solution} \quad (7)$$

where χ is the polymer-solvent interaction parameter, R is the gas constant, T is the absolute temperature, and x_2 mole fraction of polymer in solution.

RESULTS AND DISCUSSION

Thermograms obtained for all pure solid polymers from -80°C to 50°C showed no evidence of thermal transition. Thermograms for solutions from room temperature to 50°C gave no indication of heat release or absorption. The thermograms between -80°C and 50°C showed an absorption of heat corresponding to the melting of the solution. The position of the peak obtained and the area under the curve were reproducible.

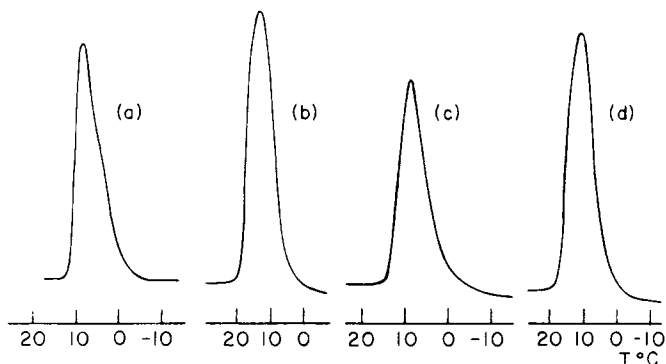


Fig. 1. Typical DSC melting thermograms: (a) H_2O - P_{27} (18%); (b) H_2O -guar (9%); (c) H_2O (78%)-PVA (20%)-chromic nitrate (2%); (d) H_2O (89.5%)-xanthan (10%)-chromic nitrate (0.5%).

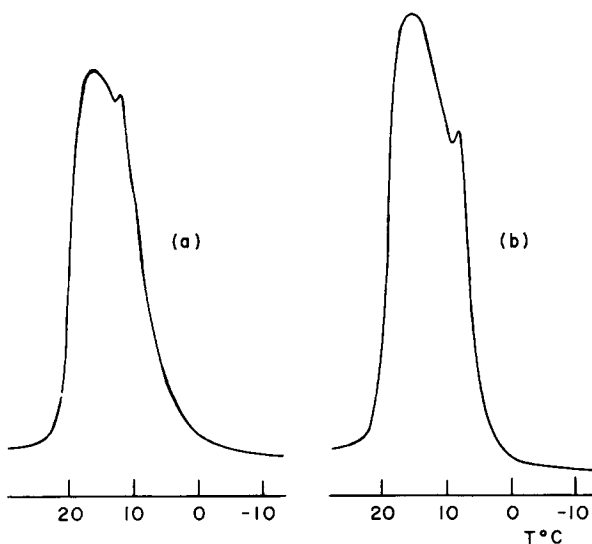


Fig. 2. DSC melting thermograms of branched gels: (a) H_2O (91.2%)- P_{295} (8%)-chromic nitrate (0.8%); (b) H_2O (95.05%) -Guar (4.5%)-potassium pyroantimoniate (0.45%).

Typical thermograms are shown in Figures 1a and 1b for water-polymer solutions. If the addition of a crosslinking agent to the solution does not form a branched gel, then a typical peak is again observed, as is shown in Figures 1c and 1d. On the other hand, if branching occurs, then a hump appears on the peak, as is shown in Figure 2.

The presence of this hump on the melting thermogram of all branched gels confirms the existence of two freezing points. The origin of this hump could be explained if, in the freezing process, the branched gel is separated into two distinct phases. The first one is outside the surface of the gel

and corresponds to ice crystals, whereas the second phase is inside the gel and includes the partly freeze-dried gel system.

Water-Polymer Solutions (Tables I and II)

The temperature of fusion listed for polymer solutions decreases with the solute concentration as expected. The temperature of fusion corresponds to the temperature at which the first evidence of the change appears (the point of first observable deflection from the baseline).

The exothermic values of B and C were determined respectively from relations (1) and (2). The heat values in cal/mole solution reported for C (which is proportional to the heat of mixing) are a function of the polymer concentration, as expected. B , expressed in cal/g polymer, seems to vary first very rapidly with polymer concentration, then reach a maximum and constant value as P_2 increases. As the precision was not good for lower polymer concentrations, this variation of B with lower P_2 values could not be clearly distinguished. However, an average value of B was computed (for $P_2 > 6\%$) which is sufficiently definite for each of the polymers studied. The error on this average value of B was calculated by the "best linear unbiased estimator" statistical method.

The f values were calculated from relations (3) and (4). No variation of f with P_2 was detected, and an average value of f was computed for each polymer. Guar and xanthan gums as well as the synthetic polyacrylamides (P_{27} and P_{295}) all have a similar value of f (0.14 ± 0.02), which is about half the value listed for PVA ($f = 0.35 \pm 0.02$). This means that there is less water-polymer association (or sorption) in the case of PVA compared to the other polymers.

The Q_a values (in kcal/mole polymer) were determined using relation (5). As the heat of sorption is proportional to B , an average value of Q_a was also computed for each polymer ($P_2 > 6\%$). Here again, PVA has a lower value of Q_a (-1.7 ± 0.1 kcal/mole polymer) compared to the values listed for the other polymers, which vary from -5.0 to -10 kcal/mole polymer. This was, of course, predictable from eq. (5), where Q_a is directly proportional to $(1 - f)$.

The χ values estimated in this report from relations (6) and (7) represent the enthalpy contribution to the interaction parameter (which is divided into entropy and enthalpy terms). All the χ values listed were calculated at a temperature of 273°K . Here again, no appreciable variation of the interaction parameter with P_2 was noticed, and an average value of χ was computed for each polymer (for $P_2 > 6\%$).

Guar and xanthan gums gave an average value of -0.38 ± 0.08 for χ ; the synthetic polyacrylamides (P_{27} and P_{295}) had a χ value of -0.73 ± 0.06 , whereas that of PVA was -1.0 ± 0.03 . Amaya and Fujishiro⁴ reported measurements of the heats of dilution of PVA in water for polymer concentration between 5% and 15%. The χ value calculated from their data was -0.07 at 30°C . This value has the same sign as that of the present experiment, but its magnitude is remarkably lower even if the

TABLE I
DSC Results for PVA, P₂₇, and P₂₉₅

Polymer	P ₂ , %	Q _{obs} ± 1, cal/g solution	-B ₂ , cal/g polymer	-C ± 18, cal/mole solution	-Q _a , kcal/mole polymer	-x̄	f	T _{fusion} , °C
PVA	3	75.7	63 ± 30	35	1.8 ± 0.8	0.95 ± 0.47	0.33	0
	6	71.8	57 ± 15	63	1.6 ± 0.4	0.88 ± 0.26	0.32	0
	9	67	64 ± 10	110	1.8 ± 0.3	1.01 ± 0.17	0.33	-2
	12	62.8	63 ± 8	149	1.8 ± 0.2	1.05 ± 0.14	0.33	-5
	15	59	60 ± 6	177	1.7 ± 0.2	0.98 ± 0.11	0.36	-5
	18	55.6	56 ± 5	202	1.6 ± 0.1	0.91 ± 0.09	0.38	-7
	21	51.5	56 ± 5	240	1.6 ± 0.1	0.95 ± 0.03	0.37	-7
P ₂₇	3	75	87 ± 30	48	5.8 ± 2	-x̄ = 1.0 ± 0.03	f̄ = 0.35 ± 0.02	0
	6	69.7	92 ± 15	104	6.2 ± 1	0.74 ± 0.28	0.17	0
	9	64.8	89 ± 11	155	6.0 ± 0.7	0.81 ± 0.14	0.13	0
	12	60.9	79 ± 8	188	5.3 ± 0.5	0.80 ± 0.10	0.14	-3
	15	56.5	77 ± 7	234	5.2 ± 0.4	0.69 ± 0.07	0.16	-5
	18	52.1	75 ± 5	282	5.0 ± 0.3	0.69 ± 0.06	0.18	-5
			-B̄ = 82 ± 5		-Q _a = 5.4 ± 0.3	0.74 ± 0.05	0.19	-5
P ₂₉₅	2.2	76.2	91 ± 45	37	6.3 ± 3.1	-x̄ = 0.73 ± 0.05	f̄ = 0.16 ± 0.02	-2
	2.5	74.5	140 ± 40	64	9.6 ± 2.8	0.56 ± 0.28	0.17	-2
	3.2	72.9	141 ± 30	83	9.7 ± 2.1	0.85 ± 0.24	0.12	-2
	5	70	120 ± 20	112	8.2 ± 1.4	0.87 ± 0.19	0.11	-2
	6.2	68	114 ± 16	132	7.8 ± 1.1	0.76 ± 0.12	0.15	-5
	8	65.1	106 ± 12	163	7.3 ± 0.8	0.71 ± 0.10	0.13	-10
	9	62.8	111 ± 11	194	7.6 ± 0.7	0.69 ± 0.68	0.14	-20
	10.5	60.1	110 ± 10	225	7.6 ± 0.7	0.73 ± 0.07	0.14	-20
	11	58.7	114 ± 9	246	7.6 ± 0.6	0.71 ± 0.06	0.14	-20
	11.5	57.8	113 ± 8	257	6.8 ± 0.5	0.76 ± 0.06	0.14	-20
			-B̄ = 111 ± 8		-Q _a = 7.6 ± 0.5	0.76 ± 0.06	0.14	-20
				-x̄ = 0.73 ± 0.06	f̄ = 0.14 ± 0.02			

TABLE II
DSC Results for Guar and Xanthan Gums

Polymer	P ₂ , %	Q _{obs} ± 1, cal/g solution	-B, cal/g polymer	-C ± 18, cal/mole solution	-Q _s , kcal/mole polymer	-x̄	f	T _{fusion} , °C
Guar	2.5	76.9	44 ± 40	20	6.8 ± 6.2	6.8 ± 6.2	0.12	0
	3.2	75.7	53 ± 30	32	8.2 ± 4.6	0.39 ± 0.2	0.11	-2
	6.2	72.2	46 ± 15	53	7.1 ± 2.3	0.33 ± 0.1	0.12	-5
	9.0	68.3	50 ± 10	88	7.7 ± 1.5	0.38 ± 0.08	0.12	-5
	12.0	64.7	48 ± 8	115	7.4 ± 1.2	0.38 ± 0.06	0.12	-6
				-B̄ = 48 ± 8		-Q̄ _s = 7.4 ± 1.2	-x̄ = 0.36 ± 0.06	f̄ = 0.12 ± 0.02
Xanthan	2.2	77.2	46 ± 40	18	7.3 ± 6.3	0.30 ± 0.3	0.12	0
	2.5	76.5	60 ± 40	28	9.5 ± 6.3	0.37 ± 0.2	0.16	0
	3.2	75.4	63 ± 30	37	10.0 ± 4.8	0.38 ± 0.2	0.10	-2
	5.0	73	60 ± 20	57	9.5 ± 3.2	0.38 ± 0.1	0.11	-3
	6.2	71	65 ± 15	76	10.3 ± 2.4	0.40 ± 0.1	0.10	-5
	7.5	69	67 ± 12	96	10.6 ± 1.9	0.41 ± 0.09	0.10	-5
	9.0	67.3	61 ± 10	108	9.7 ± 1.5	0.40 ± 0.07	0.13	-7
	11.0	64.5	59 ± 8	130	9.3 ± 1.3	0.40 ± 0.06	0.10	-7
	15.0	58	67 ± 6	208	10.6 ± 1.0	0.46 ± 0.05	0.10	-8
				-B̄ = 64 ± 6		-Q̄ _s = 10.1 ± 1.0	-x̄ = 0.42 ± 0.05	f̄ = 0.12 ± 0.02

TABLE III
DSC Results for the System Water-PVA-Crosslinker

Crosslinker	Product obtained	P_3 , %	$\frac{P_3}{P_2}$, %	$Q_{\text{obs}} \pm 1$, cal/g solution	$\frac{B'}{\bar{B}} \pm 15\%$	$\frac{f'}{\bar{f}} \pm 0.1$	$\frac{Q_a'}{\bar{Q}_a} \pm 15\%$	$\frac{X'}{\bar{X}} \pm 15\%$	T_b , °C	T_b , °C
Chromic nitrate	gel	20	10	51.6	0.9	1.1	1.0	0.9	-12	
		20	15	48.4	1.1	1.2	1.0	1.0	-14	
		20	20	46.4	1.2	1.2	0.9	1.4	-16	
		20	25	48.0	1.0	1.1	1.1	1.0	-23	
		11	5	59.6	1.7	0.7	1.9	1.2	-7	8
Potassium pyroantimonate	branched gel	11	10	59.7	1.6	0.6	2.1	1.0	-7	8
		11	15	58.0	1.8	0.7	2.1	1.0	-8	8
		11	20	58.2	1.7	0.8	2.1	0.9	-8	8
		14	5	57.3	1.3	0.8	1.5	1.1	-10	7
		14	10	55.1	1.5	0.8	1.7	1.0	-10	8
		14	15	55.3	1.4	0.8	1.7	1.1	-10	8
		14	20	54	1.5	0.7	1.7	0.8	-12	8
		17	5	52.4	1.3	0.9	1.3	0.9	-12	8
		17	10	50.7	1.4	1.0	1.4	1.0	-14	8
		17	15	52.2	1.2	1.1	1.4	1.0	-12	7
		17	20	50.4	1.3	0.9	1.3	1.0	-12	7
		20	20	46.4	1.2	1.1	1.0	1.1	-16	8

temperature effect on χ is taken into consideration. According to Meares,⁵ the χ value for a polymer solution should be about 80% of that of the corresponding monomer in solution. If ethanol is regarded as a monomeric unit of PVA, then the interaction parameter (-1.2) computed at 25°C using the data in the literature⁶ for ethanol-water solutions agrees very well with the value found in our experiment in the same concentration range.

The System "Water-Polymer-Crosslinker" (Tables III to VI)

T_1 and T_2 represent the two freezing points mentioned before in the case of branched gels. T_1 corresponds to the temperature at which the first deflection from the baseline appears. T_1 varies with the polymer and crosslinker concentration, while T_2 corresponds to the temperature of appearance of the hump in the melting peak and is equal to $10 \pm 2^\circ\text{C}$ in all cases.

The dash superscript designates the data obtained when a crosslinker is added to the water-polymer solution. The results obtained with a crosslinker were computed from the same relations used in the case of water-polymer solutions. \bar{B} , f , \bar{Q}_a , and $\bar{\chi}$ in the ratios B'/\bar{B} , f'/f , Q_a'/\bar{Q}_a , and $\chi'/\bar{\chi}$ respectively correspond to the average values reported in Table I and II for water-polymer solutions.

When a crosslinking agent is added to the water-polymer solution, whether a branched gel is formed or not, B' , Q_a' , and f' vary with P_2 for all the polymers studied, whereas χ' is not altered. B'/\bar{B} decreases with P_2 , as is shown in Figure 3, while f'/f increases with P_2 (Fig. 4). This means that as the polymer concentration is increased in a solution containing a crosslinker, less water is able to penetrate inside the surface of the gel and consequently less heat is released. In fact, by increasing the relative amount of polymer in the solution, the solute-solute interactions

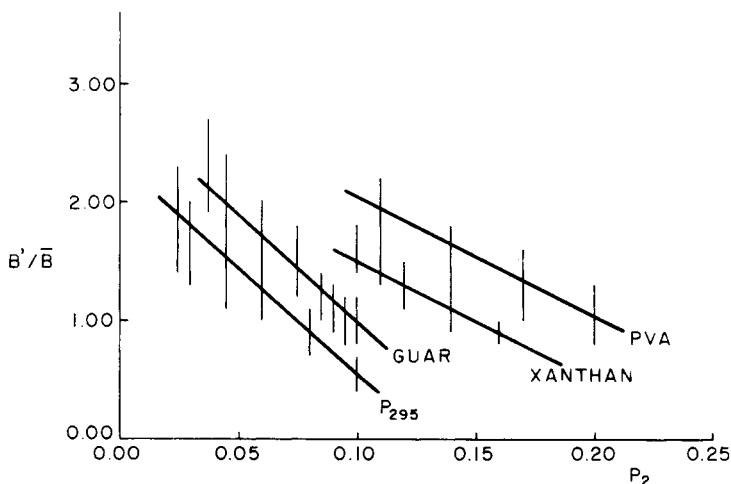


Fig. 3. Variation of B'/\bar{B} with P_2 .

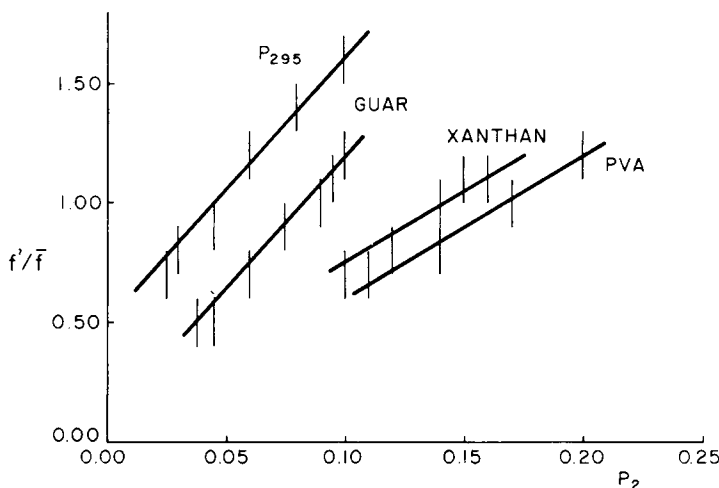


Fig. 4. Variation of f'/\bar{f} with P_2 .

are increased and the polymeric chains become less accessible to penetrating water. Guar and P_{295} have a similar rate of decrease of B'/\bar{B} with polymer concentration ($-dB'/\bar{B}/dP_2 = 18 \pm 5$), whereas this rate for PVA and xanthan has a value of 10 ± 3 . The rate of increase of f'/\bar{f} with P_2 is also the same for guar and P_{295} ($df'/\bar{f}/dP_2 = 11 \pm 3$), while it is equal to 6 ± 2 for PVA and xanthan. The slopes of the curves in Figures 3 and 4 in the range of concentration studied yielded these rates of variations of B'/\bar{B} and f'/\bar{f} with P_2 which are related together according to the empirical relation

$$\frac{\left(\frac{dB'/\bar{B}}{dP_2}\right)_{\text{guar, } P_{295}}}{\left(\frac{dB'/\bar{B}}{dP_2}\right)_{\text{PVA, xanthan}}} = \frac{\left(\frac{df'/\bar{f}}{dP_2}\right)_{\text{guar, } P_{295}}}{\left(\frac{df'/\bar{f}}{dP_2}\right)_{\text{PVA, xanthan}}} = 1.8$$

The crosslinker behavior with each of the polymers studied was the following:

Guar. The use of potassium pyroantimoniate (PP), even in small proportions, gave branched gels, whereas chromic nitrate gave branching only for solutions having $P_2 > 9\%$ and $P_3/P_2 > 5\%$, owing probably to the presence of some intramolecular H bonding. P_3 is the weight fraction of crosslinker in the solution.

Xanthan. No branching was formed when PP was added even in relatively high concentration. This is probably due to the interaction of PP with the carboxyl in preference to the hydroxyl groups on the xanthan chain. It is the presence of OH groups in the monosaccharide units that permits controllable crosslinking through a H bonding mechanism. The use of chromic nitrate gave branched gels only for solutions having $P_3 > 1.4\%$, likely because of some intramolecular H bonding as in guar.

TABLE IV
DSC Results for the System Water-P₂₀₃-Crosslinker

Crosslinker	P ₂ , %	P ₃ / P ₂ , %	Q _{obs} ± 1, cal/g solution	B' B̄	f' ± 0.1 f̄	Q _a ' Q̄ _a	X' ± 20% X̄	T ₂ , °C	T ₁ , °C
Potassium pryaoanti- moniate	8	5	64	1.0 ± 0.1	1.3	1.0 ± 0.1	1.1		-10
	8	10	63.7	1.0 ± 0.1	1.4	0.9 ± 0.1	1.1		-10
	8	15	61.4	1.2 ± 0.1	1.3	1.0 ± 0.1	1.0		-12
	8	20	62.1	1.1 ± 0.1	1.4	1.1 ± 0.1	1.2		-10
Chromic nitrate	2.5	15	72.5	1.8 ± 0.4	0.7	2.0 ± 0.4	1.0	9	-3
	2.5	20	72.1	1.9 ± 0.4	0.6	1.9 ± 0.4	1.1	12	-3
	3	10	71.5	1.7 ± 0.3	0.8	1.7 ± 0.3	1.1	9	-5
	3	15	71.6	1.6 ± 0.3	0.8	1.8 ± 0.3	1.2	11	-5
	3	20	71.1	1.7 ± 0.3	0.7	1.8 ± 0.3	1.2	12	-5
	4.5	10	69.2	1.3 ± 0.2	0.9	1.5 ± 0.2	1.1	10	-7
	4.5	15	68.1	1.5 ± 0.2	0.8	1.5 ± 0.2	1.1	9	-7
	4.5	20	67.9	1.5 ± 0.2	0.9	1.4 ± 0.2	1.1	8	-7
	6	10	65.6	1.3 ± 0.2	1.1	1.3 ± 0.2	1.0	12	-12
	6	15	66.1	1.2 ± 0.2	1.1	1.2 ± 0.2	1.1	8	-7
	6	20	65.1	1.3 ± 0.2	1.2	1.3 ± 0.2	1.0	8	-9
	8	10	64.6	0.9 ± 0.1	1.4	1.0 ± 0.1	1.1	12	-15
	8	15	63.3	1.0 ± 0.1	1.3	1.0 ± 0.1	1.0	8	-16
	8	20	64.9	0.8 ± 0.1	1.4	1.0 ± 0.1	1.0	8	-15
	10	10	65.4	0.5 ± 0.1	1.6	0.5 ± 0.1	0.9	12	-8
	10	15	63.8	0.6 ± 0.1	1.7	0.4 ± 0.1	0.9	8	-15
10	20	63.4	0.6 ± 0.1	1.6	0.5 ± 0.1	1.0	8	-20	

TABLE V
DSC Results for the System Water-Guar-Crosslinker

Crosslinker	Product obtained	$P_1, \%$	$\frac{P_3}{P_2}, \%$	$Q_{\text{obs}} \pm 1, \text{ cal/g solution}$	$\frac{B'}{\bar{B}} \pm 20\%$	$\frac{f'}{\bar{f}} \bullet 0.1$	$\frac{Q_{e'}}{\bar{Q}_e} \pm 20\%$	$\frac{X'}{\bar{X}} \pm 20\%$	$T_2, \text{ }^\circ\text{C}$	$T_1, \text{ }^\circ\text{C}$
Chromic nitrate	gel	3.8	25	72.0	2.3	0.4	2.2	1.1		-4
		4.5	5	71.8	2.0	0.6	2.1	1.0		-2
		4.5	10	71.4	2.1	0.5	2.0	1.1		-2
		4.5	20	71.0	2.0	0.6	2.2	0.9		-2
		6	5	70.1	1.7	0.7	1.9	1.1		-5
		6	10	69.5	1.8	0.7	1.8	1.0		-5
		6	15	70.2	1.8	0.6	1.8	1.0		-8
		7.5	5	68.3	1.5	0.9	1.5	1.0		-7
		7.5	10	68.0	1.5	0.9	1.5	1.1		-5
		8.5	10	67.2	1.3	1.0	1.3	0.9		-8
9.0	2.5	67.6	1.1	1.1	1.1	1.0		-8		
	branched gel	9.0	5	67.9	1.2	1.1	1.2	1.1	8	-7
		9.5	5	67.7	1.1	1.0	1.1	1.1	10	-7
		9.5	10	67.1	1.1	1.1	1.2	1.0	9	-8
		9.5	15	67.1	1.0	1.1	1.1	0.9	8	-9
		9.5	20	66.8	1.1	1.0	1.1	1.0	10	-10
		10	5	66.8	1.0	1.2	1.0	1.1	8	-8
		4.5	5	71.6	2.1	0.6	2.2	1.1	8	-1
		4.5	10	71.6	2.0	0.5	2.2	1.0	8	-3
		6	5	69.8	1.8	0.7	1.8	1.1	10	-5
		6	10	69.8	1.7	0.7	1.8	0.9	8	-5
Potassium pyroantimoniate	branched gel	7.5	2.5	69.3	1.5	1.0	1.5	1.2	8	-6
		7.5	5	68.4	1.5	0.9	1.5	1.0	10	-6
		7.5	10	68.3	1.6	0.8	1.6	1.1	8	-8
		7.5	15	68.0	1.5	0.9	1.6	0.9	12	-6
		7.5	20	67.7	1.4	0.9	1.5	1.1	12	-5
		7.5	25	67.4	1.5	0.9	1.5	1.0	9	-6
		8.5	5	67.5	1.3	1.0	1.3	1.1	8	-7
		8.5	10	67.2	1.3	0.9	1.3	0.9	8	-8
		10	5	66.3	1.1	1.2	1.1	1.0	8	-8

TABLE VI
DSC Results for the System Water-Xanthan-Crosslinker

Crosslinker	Product obtained	P_2 , %	$\frac{P_3}{P_2}$, %	$Q_{\text{obs}} \pm 1$, cal/g solution	$\frac{B'}{B} \pm 15\%$	$\frac{f'}{f} \pm 0.1$	$\frac{Q_a'}{Q_a} \pm 15\%$	$\frac{X'}{X} \pm 20\%$	T_2 , °C	T_1 , °C
Potassium pyroantimoniate	gel	14	10	57.6	1.2	1.0	1.3	0.9		-10
		14	15	57.0	1.2	0.9	1.2	1.2		-10
		14	20	56.4	1.2	0.9	1.1	1.1		-10
Chromic nitrate	gel	14	25	55.8	1.3	0.9	1.2	0.9		-10
		10	5	62.6	1.5	0.7	1.6	1.0		-10
		10	10	62.2	1.6	0.7	1.6	1.1		-10
		12	10	59.3	1.4	0.8	1.4	0.9		-14
		14	8.5	57.7	1.2	0.9	1.2	1.1		-12
Potassium pyroantimoniate	branched gel	14	9.5	57.6	1.2	1.0	1.3	0.9		-12
		15	5	58.5	1.0	1.1	1.0	1.2		-12
		15	8	58	1.1	1.1	1.1	1.1		-12
		10	15	61.8	1.5	0.7	1.6	1.1		8
		10	20	61.4	1.5	0.6	1.5	1.0		8
		10	25	61.0	1.6	0.6	1.6	1.0		8
		12	15	59.1	1.4	0.9	1.5	1.0		8
		12	20	58.4	1.4	0.8	1.4	1.2		8
		12	25	58.0	1.4	0.8	1.4	1.0		8
		14	10	57.6	1.2	1.0	1.2	1.0		12
		14	15	57.0	1.3	0.9	1.3	1.2		12
Chromic nitrate	gel	14	20	56.5	1.2	1.0	1.2	1.0		-18
		14	25	56.0	1.1	1.0	1.1	1.2		-18
		16	10	58.2	0.8	1.1	0.8	1.0		-20
		16	15	57.6	0.9	1.1	0.8	0.9		-22
		16	20	56.9	0.8	1.2	0.9	0.9		-20
16	25	56.3	0.9	1.1	0.8	0.9		-20		

PVA. Branched gels were formed when PP was used, whereas chromic nitrate gave no branching even when added in relatively high concentration. This may be explained if we consider that PVA displays more extensive intramolecular H bonding than in the case of guar and xanthan gums.

P₂₉₅. Chromic nitrate formed branched gels, whereas the use of PP gave no branching at all, probably because of its interaction with the carbonyl and carboxyl groups present in the polymer. P₂₉₅ is a commercial polyacrylamide and contains likely some COOH groups because of partial hydrolysis introduced to achieve optimum solubility and solution performance.

CONCLUSIONS

An association factor can be computed from the area under the melting peak obtained by DSC for polymer solutions. This factor is a measure of the water fraction associated (or sorbed) to the polymer and is independent of the polymer concentration in solution. The f factor has a definite and characteristic value for a given polymer in water. PVA has an f value of 0.35 ± 0.02 compared to the value of 0.14 ± 0.02 measured for the gums (guar, xanthan) and polyacrylamides (P_{27} , P_{295}).

By fitting the association factor into the energy involved at the melting of the polymer solution, an empirical relation may be derived which yields the heats of mixing and sorption. The polymer-solvent interaction parameter χ (measured from the heat of mixing) has the values of -0.38 , -0.73 , and -1.0 , respectively, for gums, polyacrylamides, and PVA. The heat of sorption, expressed in kcal/mole polymer, is independent of the polymer concentration ($>6\%$) and has a value of -1.7 ± 0.1 for PVA and varies from -5.0 to -10 for the other polymers.

When a crosslinker is added to the water-polymer solution, whether a branched gel is formed or not, the association factor and the heat of sorption, in kcal/mole polymer, vary with the polymer concentration while the interaction parameter remains constant.

It is the type of crosslinker used and its concentration that determine whether branching will occur or not with such or such a polymer. If a branched gel is formed, then a hump appears on the melting peak obtained by DSC.

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