

progress on the effect of structure of the base and of the cation on cation-base interaction in aprotic solvents of low dielectric constant.

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## The Polyacrolein-Bisulfite Equilibrium

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To gain a better understanding of the structure and properties of polyacrolein in aqueous  $\text{HSO}_3^-$  solution the effect of the extent of reaction on the polyacrolein-bisulfite equilibrium has been investigated. Since the rate of dissociation of the polyacrolein-bisulfite adduct in cold aqueous solution is very slow, the extent of reaction of  $\text{HSO}_3^-$  with polyacrolein at equilibrium can be measured directly by iodine titration of the free  $\text{HSO}_3^-$ . The observed equilibrium constant for bisulfite addition decreases as the extent of the reaction of  $\text{HSO}_3^-$  with polyacrolein increases from 40 to 85 mole %, but in all cases rates of addition and dissociation and the observed equilibrium constant are smaller than those for monomeric aldehydes. It is suggested that these phenomena result primarily from changes in the relative concentrations of the various structures of the potential aldehyde and hydroxysulfonate groups in the polymer with the extent of reaction.

### Introduction

The structure of polyacrolein prepared by free-radical polymerization processes is a distribution of cyclic intracetal-like groups, aldehyde groups, and interacetal-like crosslinks.<sup>1,2</sup> The polymers are intractable and insoluble in nonreactive solvents. Kern, Schulz, and co-workers have discussed the structure of polyacrolein and demonstrated the reaction of the polymer with many typical aldehyde reagents.<sup>3-6</sup> These reactions are believed to result in the simultaneous breaking of the interacetal-like crosslinks, since soluble reaction products are usually obtained.<sup>1,6</sup>

Polyacrolein reacts with  $\text{HSO}_3^-$  to form a high molecular weight, water-soluble polyelectrolyte. This reaction involves an equilibrium between the polyacrolein,  $\text{HSO}_3^-$ , and polyacrolein-bisulfite adduct.<sup>1,3,7</sup> The reaction is of particular interest because the structure of the polymer is complex and because an equilibrium occurs between negatively charged ions and a polymer chain containing negative charges. To the authors' knowledge no description has been given of the extent of the reaction of  $\text{HSO}_3^-$  with polyacrolein or of the magnitude of the equilibrium constant. To understand the structure of the polyacrolein-bisulfite adduct in aqueous solution and, likewise, to interpret its solution behavior, a quantitative description of the equilibrium properties is required. It is the purpose of this paper to describe some of the properties of the reaction.

### Experimental

**Preparation of Polyacrolein.**—The polyacrolein samples used in this study were prepared by modifications of a previously described suspension polymerization.<sup>8</sup> To a glass-lined, 5-gal. autoclave fitted with a three-blade stirrer was added under an atmosphere of nitrogen 7.90 kg. of heptane, a solution of 6.6 g. of disodium N-tallow- $\beta$ -iminodipropionate (Deriphat 154, a product

of General Mills Co.) in 1.31 kg. of deionized water that had been adjusted to pH 4.5 with 2.8 g. of 85%  $\text{H}_3\text{PO}_4$ , and 2.63 kg. of freshly distilled acrolein (commercial grade product of Union Carbide Corp., Chemicals Division). The temperature was adjusted to 20°, and then 13 g. of  $\text{K}_2\text{S}_2\text{O}_8$  and 2.6 g. of  $\text{AgNO}_3$  were added as 10% aqueous solutions. After 19-hr. reaction time, the resultant slurry was filtered and the solid product was washed thoroughly with water to remove unreacted acrolein and catalyst residues. It was then washed once with 12 l. of acetone containing 23 g. of phenothiazine and dried *in vacuo* at 65° for 24 hr. The product, 1.87 kg., was obtained as a fine, white powder having a reduced viscosity of 4.2 dl.-g.<sup>-1</sup> at 0.2% concentration in water saturated with  $\text{SO}_2$  at 30°. The intrinsic viscosity of the sodium bisulfite adduct at 30° in 0.5 M aqueous NaCl solution was 2.0 dl.-g.<sup>-1</sup>.

Although the theoretical carbon content of polyacrolein is 64.3%, the carbon contents of the polyacrolein samples used in this study were only 58.8 to 60.4%. The samples were found to contain about 1-3% physically absorbed water, based on Karl Fisher analysis. The remaining 4-6% of the polymer was assumed to be chemically bound water, present in the form of aldehyde hydrate and hemiacetal-like structures. The polymers were somewhat hygroscopic. Total water contents as high as 22% were obtained after exposure to 100% relative humidity at room temperature. By rigorous drying, over  $\text{P}_2\text{O}_5$  at 56° (1 mm.) for 24 hr., the carbon content increased to 62.8%; that is, almost 98% of the theoretical value. In general, the more thoroughly the polyacrolein is dried, the less hygroscopic it is and the slower its rate of reaction with aldehyde reagents.

Two methods of analysis were employed to determine total carbonyl in the polyacrolein. In the first method<sup>4</sup> the reaction of polyacrolein with hydroxylamine hydrochloride in the presence of pyridine at ambient temperature for 64 hr. was followed by titration of the liberated HCl. After correction for the total water contained in the polyacrolein, this method indicated an increase in the mole % aldehyde reacted from 74 to 80% over the time interval of 16-64 hr. Some difference has been observed in the rate with which polyacrolein reacts with the reagent.<sup>4</sup> Differences in the degrees of hydration, ring formation, and even particle size and porosity could contribute to this. It is, therefore, quite difficult to choose a final value for the extent of reaction because the reaction is slow at room temperature, particularly at high extents of reaction. Our results obtained by this method are in the same range found by Schulz, *et al.*,<sup>4,9</sup> for various polyacrolein samples including polymers prepared by oxidation-reduction catalysts in water and the spontaneous polymer, disacryl.

It has been reported that polyacrolein, prepared in a liquid medium with a free-radical-yielding catalyst at a temperature below 30° and in the presence of a material having an OH group, contains over 95% of theoretical aldehyde function as determined

- (1) R. C. Schulz, *Kunststoffe*, **47**, 303 (1957).
- (2) M. V. Chistyakova, *Russ. Chem. Rev.*, **31**, 224 (1962).
- (3) R. C. Schulz and W. Kern, *Makromol. Chem.*, **18/19**, 4 (1956).
- (4) R. C. Schulz, H. Fauth, and W. Kern, *ibid.*, **20**, 161 (1956).
- (5) R. C. Schulz, H. Fauth, and W. Kern, *ibid.*, **21**, 227 (1956).
- (6) R. C. Schulz, *Kunststoffe-Plastics*, **6**, 32 (1959).
- (7) R. C. Schulz, I. Löflund, and W. Kern, *Makromol. Chem.*, **32**, 209 (1959).
- (8) F. J. Welch, U. S. Patent 3,089,389 (1962).

- (9) R. C. Schulz, H. Cherdron, and W. Kern, *Makromol. Chem.*, **24**, 141 (1957).

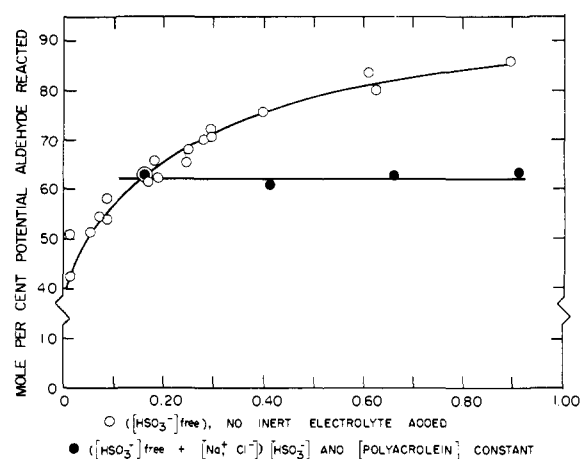


Fig. 1.—Effect of free  $\text{HSO}_3^-$  concentration relative to inert salt concentration on the extent with which  $\text{HSO}_3^-$  reacts with polyacrolein; polyacrolein concentrations are 0.28 to 3.4 weight % in water.

by addition of hydroxylamine hydrochloride and titrating the liberated water with Karl Fisher reagent, with allowance being made for the water already present in the polymer.<sup>10</sup> In the second method<sup>11</sup> the liberated water was titrated with Karl Fisher reagent to an electrometric end point after a reaction time of 2 hr. at 98°. Under these conditions about 110% theoretical aldehyde was found in the same polyacrolein sample as the one analyzed by the first method, but no attempt was made to refine the procedure further.

We conclude, therefore, that polyacrolein prepared by our procedure has essentially the same per cent of the theoretical aldehyde function as that described by the other workers,<sup>4,9,10</sup> and that the differences which have been reported are a result of different methods of analysis rather than actual appreciable differences in polymer structure.

**Other Materials.**—Mallinckrodt Chemical Works  $\text{NaHSO}_3$  (minimum of 58.5%  $\text{SO}_2$ ), Mallinckrodt Chemical Works  $\text{K}_2\text{S}_2\text{O}_8$  (minimum of 95%  $\text{K}_2\text{S}_2\text{O}_8$ ), J. T. Baker Chemical Co.  $\text{NH}_4\text{HSO}_3$  (47% aqueous solution), and Merck and Co.  $\text{NaCl}$  (minimum of 99.8%  $\text{NaCl}$ ) were employed without further purification. The water employed as the solvent was freshly distilled and then freed of  $\text{O}_2$  and  $\text{CO}_2$  by boiling and cooling the water while passing  $\text{N}_2$  through it with a fritted-glass gas inlet tube. Standard iodine solutions, 0.0998–0.0999 *N*, were employed for all titrations.

**Preparation of Solutions.**—The salts were first dissolved in the purified water. The resulting solutions, 250 ml., and a measured weight of polyacrolein were added under  $\text{N}_2$  to 350-ml. Pyrex bottles, which were then capped with polyethylene-lined caps and rotated in a constant temperature bath at 30°. The polyacrolein dissolved completely to form clear, homogeneous solutions. Control solutions, containing all additives other than polyacrolein, were prepared and treated identically with the polymer solutions.

**pH Values of Solutions.**—The pH values of the polyacrolein- $\text{NaHSO}_3$  solutions varied from about 5.2 to 5.4, the slightly higher than theoretical pH values being due to the presence of  $\text{SO}_3^{2-}$ . Since the intrinsic system is most amenable to study and acts itself as a buffer, no extraneous control of pH was attempted. Solutions prepared from  $\text{K}_2\text{S}_2\text{O}_8$  were slightly lower in pH value due to the lower concentrations of  $\text{SO}_3^{2-}$ . The  $\text{NH}_4\text{HSO}_3$  solution had a pH value of only 2.7. In a comparison of  $\text{NaHSO}_3$ ,  $\text{KHSO}_3$ , and  $\text{NH}_4\text{HSO}_3$  it was necessary to adjust the two lower pH values up to that of the  $\text{NaHSO}_3$  by the addition of appropriate quantities of  $\text{KOH}$  and  $\text{NH}_4\text{OH}$ , respectively.

**Analysis of Solutions.**—After the reaction had reached equilibrium at 30°, 20-ml. duplicate samples of both the control and the polymer solution were cooled rapidly to near 0° under  $\text{N}_2$  in an ice bath. The free bisulfite was then titrated with standard iodine solution. Under these conditions the adduct is quite stable, whereas the sulfite is oxidized rapidly and smoothly to sulfate. The average per cent error on duplicate titrations of polymer solutions and of control solutions was less than one.

**Molecular Weight of Polyacrolein.**—Although no absolute measurements of molecular weight were attempted, the reduced viscosities of all polyacrolein samples were measured at 0.2% polyacrolein concentration in aqueous solutions saturated with  $\text{SO}_2$ . The reduced viscosities of the polyacrolein samples measured by this technique ranged from 1.3 to 8.5 dl.-g.<sup>-1</sup>. The reduced viscosities obtained in saturated aqueous  $\text{SO}_2$  correspond to intrinsic viscosities in solutions of high  $\text{Na}^+$  concentration of about 0.5 to 3.5 dl.-g.<sup>-1</sup>. The relationship between the intrinsic viscosity of the polyelectrolyte in salt solutions and the molecular weight has not yet been determined. However, Schulz<sup>1</sup> has measured osmotic molecular weights of thiophenol mercaptals of polyacrolein and compared them to viscosities of polyacrolein obtained in aqueous  $\text{SO}_2$ - $\text{NaCl}$  solutions. Based on this correlation, the molecular weights of the polyacroleins employed in the polyacrolein-bisulfite equilibrium experiments are probably in the range of 50,000 to 500,000 or greater.

## Results

**Equilibrium Constant.**—The degrees of addition of  $\text{HSO}_3^-$  to polyacrolein were measured over greater than tenfold ranges of both  $\text{HSO}_3^-$  and polyacrolein concentrations. A steady increase in extent of reaction with increasing free  $\text{HSO}_3^-$  concentration (Fig. 1) is evidence that a measurable equilibrium exists in solution. The data in Fig. 1 illustrate further that for a given free  $\text{HSO}_3^-$  concentration the mole % potential aldehyde groups reacted are essentially independent of the polyacrolein concentration. For a given extent of reaction the polyacrolein-bisulfite adduct and free potential aldehyde concentrations are, therefore, of the same kinetic order in the rate expression. The straight line in the middle of Fig. 1 illustrates that the increase in the extent of reaction is not due to the corresponding increase in the cation concentration which accompanies the increase in the  $\text{HSO}_3^-$  concentration. In these experiments the  $\text{NaHSO}_3$  and polyacrolein concentrations were held constant while increasing the  $\text{NaCl}$  concentration.

At the lowest total  $\text{HSO}_3^-$  to potential aldehyde mole ratio, 0.52, illustrated by the lowest point on Fig. 1, a measurable amount of free  $\text{HSO}_3^-$  remained in solution at equilibrium. The free  $\text{HSO}_3^-$  concentration in this solution remained constant over a 4-day interval, illustrating that equilibrium had been obtained. Mole ratios of total  $\text{HSO}_3^-$  to potential aldehyde below 0.5 also produce water-soluble derivatives, but higher total concentrations, higher temperatures, and/or longer reaction times are required. Under these more strenuous conditions water-soluble products are produced at total  $\text{HSO}_3^-$  to potential aldehyde mole ratios of about 0.3. Bisulfite derivatives from high molecular weight polyacroleins which were completely soluble in water could not be produced at total  $\text{HSO}_3^-$  to potential aldehyde mole ratios below 0.25.

Having established that equilibrium exists at various  $\text{HSO}_3^-$  and polyacrolein concentrations, an attempt was made to calculate the equilibrium constant for bisulfite addition. The order of the reaction was assumed to be the same as the molecularity. This order has been observed previously for monomeric aldehydes.<sup>12,13</sup> The equilibrium constants calculated from the equation,  $K = [\text{hydroxysulfonate}]/([\text{free sulfite}][\text{free potential aldehyde}])$ , are given in units of l.-mole<sup>-1</sup>.

(10) R. F. Fischer, U. S. Patent 3,079,357 (1963).

(11) J. Mitchell, Jr., D. M. Smith, and W. M. D. Bryant, *J. Am. Chem. Soc.*, **63**, 573 (1941).

(12) J. A. Sousa and J. D. Margerum, *ibid.*, **82**, 3013 (1960).

(13) P. Salomaa, *Acta Chem. Scand.*, **10**, 306 (1956).

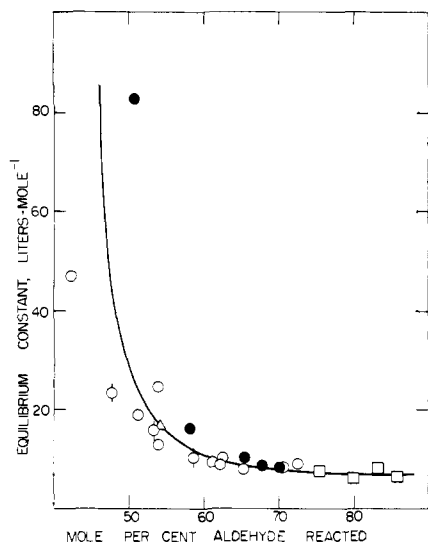


Fig. 2.—Dependence of the polyacrolein-bisulfite equilibrium constant on the mole % of the theoretical potential aldehyde groups reacted with  $\text{HSO}_3^-$ :  $\circ$ ,  $\bullet$ ,  $\text{Na}^+$ ;  $\square$ ,  $\text{K}^+$ ;  $\triangle$ ,  $\text{NH}_4^+$ ;  $\bullet$ , 0.28 to 3.4 weight % polyacrolein, 0.32 total g. ion  $\text{HSO}_3^-$  1. l.<sup>-1</sup>;  $\circ$ ,  $\triangle$ ,  $\square$ , approximately 1 weight % polyacrolein, 0.08 to 1.04 total g. ion  $\text{HSO}_3^-$  1. l.<sup>-1</sup>;  $\phi$ , 1 weight % polyacrolein, 0.24 total g. ion  $\text{HSO}_3^-$  1. l.<sup>-1</sup> and dilutions to 50 and 25% of the original concentration.

The equilibrium constants which were calculated by this method for various  $\text{HSO}_3^-$  and polyacrolein concentrations are illustrated with Fig. 2. Two of the points in Fig. 2 were obtained after dilution and equilibration of a solution of known equilibrium concentration. The equilibrium was, therefore, approached from both sides and yielded similar values. In those experiments using  $\text{NH}_4\text{HSO}_3$  and  $\text{K}_2\text{S}_2\text{O}_5$ , the pH values of the polymer solutions after dissolution were adjusted to that of the  $\text{NaHSO}_3$ -polyacrolein solution. Equilibrium constants obtained from these data fitted the curve nicely, illustrating that the various cations do not alter the equilibrium appreciably. These data are also included in Fig. 2.

Higher values of the equilibrium constant were obtained for more concentrated solutions of the adduct at the lower extents of reaction. The highest point in Fig. 2 is for a solution containing about 6–7% adduct. For solutions containing about 10% adduct at about 50 mole % reaction, values of the equilibrium constant of the order of several hundred were observed, indicating an even greater slope for the curve illustrated in Fig. 2. Considerably more scatter in the data is observed in the region representing low extents of reaction, primarily because of the large variations in the value of the equilibrium constant for only small variations in the mole % of potential aldehyde groups reacted.

It was also of interest to examine the effect of reduced viscosity of the polyacrolein on the extent of the reaction and the equilibrium constant. The results of this experiment are illustrated in Fig. 3. Only a slight decrease in the mole % potential aldehyde reacted and in the value of the equilibrium constant was observed over this range of reduced viscosity at 60–65 mole % potential aldehyde reacted, illustrating that the results reported in this paper are applicable to a broad range of polyacrolein molecular weights.

In a typical system, having about 62 mole % of potential aldehyde reacted at equilibrium, the degree

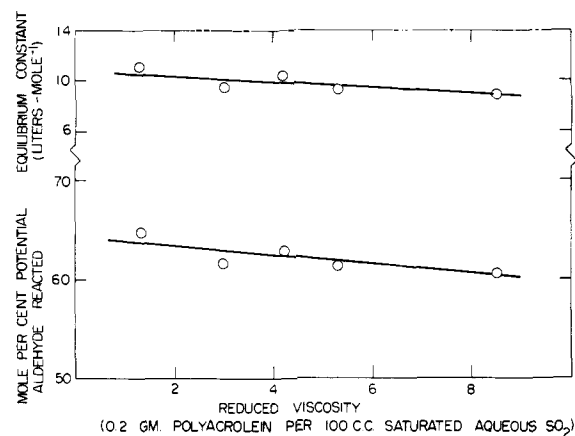


Fig. 3.—Effect of the reduced viscosity of polyacrolein on the extent of the reaction of  $\text{HSO}_3^-$  with polyacrolein and its effect on the equilibrium constant.

of addition of  $\text{HSO}_3^-$  to polyacrolein remained essentially constant over a period of 21 to 147 hr. These results are illustrated in Table I. Reaction times of 16–70 hr. were employed for solutions containing large excesses of  $\text{HSO}_3^-$  concentration. Other solutions were allowed to react for 40–300 hr. One point at 54 mole % reaction obtained after a reaction time of 35 days still fitted the curve in Fig. 2 nicely, indicating that equilibrium was obtained in several hours.

TABLE I  
EFFECT OF TIME ON THE EXTENT OF THE REACTION OF BISULFITE ION WITH POLYACROLEIN AND ITS EFFECT ON THE EQUILIBRIUM CONSTANT (TEMPERATURE, 30°)

Time, hr.	Free		Adduct, g. ion/l.	Mole % adduct	K, l./mole
	sulfite, g. ion/l.	potential aldehyde, mole/l.			
21	0.163	0.066	0.111	62.8	10.3
64	0.167	0.061	0.095	60.9	9.3
76	0.160	0.062	0.101	62.0	10.2
88	0.165	0.062	0.103	62.5	10.1
147	0.157	0.065	0.098	60.1	9.6

For those data listed in Table I only about 40 mole % of the available  $\text{HSO}_3^-$  and 60 mole % of the theoretical aldehyde groups had reacted at equilibrium. The equilibrium constant for the polyacrolein-bisulfite reaction, as expressed in l.-mole<sup>-1</sup>, is, therefore, relatively low as compared to those of monomeric aldehydes. Slightly higher end points were obtained for titrations performed at room temperatures, illustrating that a measurable degree of dissociation occurs at ambient temperatures, even at the low pH value which is reached at the end point of the titration. The question of whether dissociation occurs during the titration is, therefore, pertinent.

**Rate of Dissociation of Adduct.**—If a significant amount of dissociation occurs during the titration, the observed equilibrium constant will be lower than its actual value. This was pointed out recently by Sousa and Margerum,<sup>12</sup> who found that the rate constant of dissociation of the benzaldehyde-bisulfite compound is 0.017 sec.<sup>-1</sup> at 13°. To examine this aspect more closely, the rates of dissociation of the polyacrolein-bisulfite compound were measured at 30° in a buffered solution of sodium acetate and acetic acid of pH 4.7 and in a solution of pH value equal approximately to that reached at the end point of the titration, pH 1–2.

TABLE II  
RATE OF DISSOCIATION OF POLYACROLEIN-BISULFITE ADDUCT  
AT VARIOUS EXTENTS OF REACTION (TEMPERATURE, 30°)

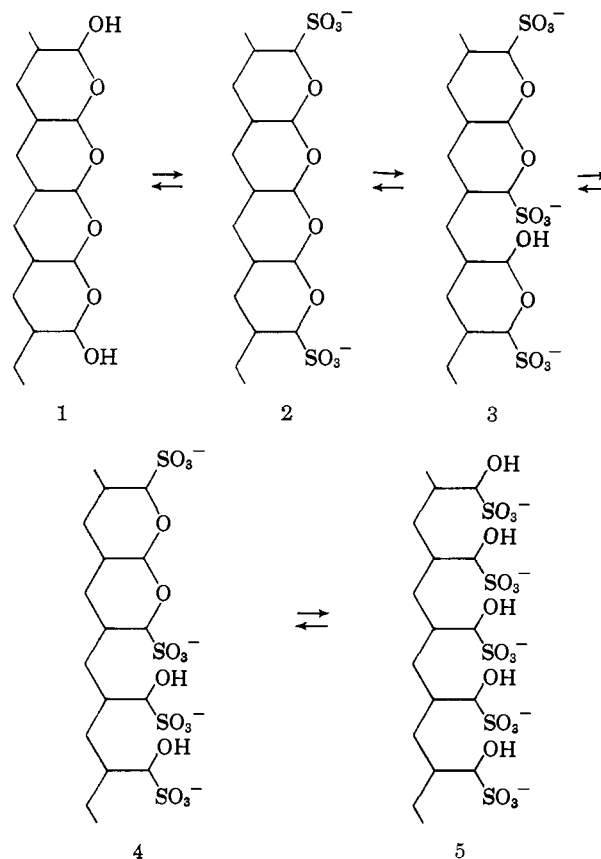
Adduct, g. ion/l.	Mole per cent adduct	$k \times 10^4, \text{sec.}^{-1}$	
		pH 4.5-4.7	pH 1-2
0.017	69	12.8	10.7
0.015	63	6.3	5.6
0.013	55	2.4	2.3
0.011	49	1.2	1.1

The solutions were first titrated to the end points with iodine. Excess iodine solution (1 ml.) was then added and the time required to consume the excess iodine was measured. This procedure was then repeated several times with successive 1-ml. portions of iodine solution. The calculated first-order rate constants were of the order of  $10^{-4}$  to  $10^{-5}$   $\text{sec.}^{-1}$  at extents of reaction representing approximately 50-70 mole % reaction (Table II). Only a small effect of pH was observed. Of significance is the fact that the rate of dissociation of polyacrolein-bisulfite at 30° is 100-1000 times slower than that observed by Sousa and Margerum for benzaldehyde-bisulfite at 13°. At 5-10° the rate of dissociation of the polyacrolein-bisulfite adduct was observed to be about 20-30 times slower than it is at 30°. For further proof that no appreciable dissociation due to dilution occurred during the cold titrations, portions of a sample were diluted threefold and tenfold with water at less than 10° and the resulting solutions were then titrated immediately with iodine solution. The initial solution and the resulting solutions analyzed for 61.7, 61.3, and 62.4 mole % potential aldehyde combined with  $\text{HSO}_3^-$ , respectively, illustrating that dissociation did not occur under the conditions imposed by the titration. The slow rates of dissociation in conjunction with the low temperature at which the titrations were performed illustrate, therefore, that reasonably accurate measurements of the equilibrium concentrations can be obtained by this method.

### Discussion

The observed value of the equilibrium constant decreases sharply over the range of 45 to 65 mole % potential aldehyde reacted, and then decreases only slightly thereafter (Fig. 2). Based on these values of  $K$  alone, the decrease in  $K$  with increasing extent of reaction could be interpreted as being due to corresponding decreases in the rate constant for the forward reaction as a result of increased electrostatic repulsion and increased steric interference, and increases in the rate constant for the dissociation reaction due to increased electrostatic repulsion. This simple interpretation is not, however, consistent with all of the experimental results. An increase in the neutral salt concentration does not affect the equilibrium appreciably at 60-62 mole % reaction (Fig. 1), indicating that electrostatic factors do not play an important role. Further, the observed rate constant for the dissociation reaction increases more rapidly than  $K$  decreases, illustrating that the corresponding calculated rate constant for the forward reaction actually increases as the extent of reaction increases over the range of 50-70 mole %. The observed rate constant for the dissociation reaction is also much smaller than those observed for monomeric aldehydes.

While different stereochemical configurations are known to influence the reactivity of groups on polymers,<sup>14,15</sup> the complex structure of polyacrolein would likely exert a more pronounced effect. Potential aldehyde groups in polyacrolein existing as aldehyde, hydrated aldehyde, and tetrahydropyran-like rings have been discussed previously in some detail.<sup>1,2</sup> Based on the amount of bound water in the polyacrolein samples of this study, calculated from comparisons of per cent carbon and Karl Fisher analyses, the average number of fused tetrahydropyran rings per sequence is about four. Considering then that the basic unit in the polymer is one containing an average of four fused rings per sequence, the following schematic diagram is given to illustrate some of the changes in the structure of the polymer which probably occur during its reaction with  $\text{HSO}_3^-$ . This is not to imply



that reactions 2-3 and 4-5 necessarily proceed by direct attack of  $\text{HSO}_3^-$  on the acetal linkage, but is meant only to represent types of structures which probably are present at different extents of reaction and to indicate that all are in equilibrium. Actual reactions may proceed through hydrolysis of acetals to hemiacetals which then react with  $\text{HSO}_3^-$ . Schulz and co-workers<sup>16,17</sup> have recently studied the reactions of low-molecular-weight model compounds of polyacrolein. The reactions were divided into two groups, one leading to the tetrahydropyran derivatives and the other to the acyclic aldehyde derivatives. Relative reactivities of the different groups would be expected to increase

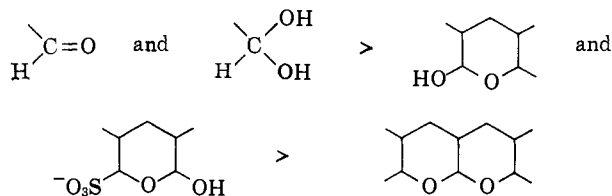
(14) H. Morawetz and E. Gaetjens, *J. Polymer Sci.*, **32**, 526 (1958).

(15) G. Smets and W. De Loecker, *ibid.*, **45**, 461 (1960).

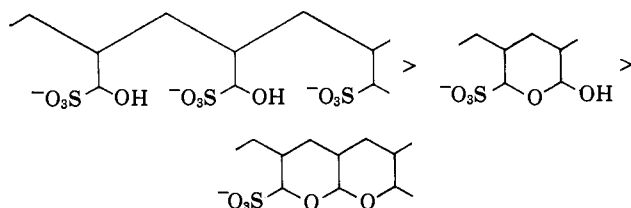
(16) R. C. Schulz, K. Meyersen, and W. Kern, *Makromol. Chem.*, **54**, 156 (1962).

(17) R. C. Schulz, K. Meyersen, and W. Kern, *ibid.*, **59**, 123 (1963).

as the groups become less tightly bound into the tetrahydropyran-type ring structures. Relative reactivities of potential aldehyde groups of the following order



and relative rates of dissociation of hydroxysulfonate groups of the following order



is predicted. As the extent of reaction increases above about 40 mole % the fraction of the more reactive sulfonate groups also increases, resulting in a corresponding increase in the observed first-order rate constant for dissociation. Likewise, the fraction of the more reactive aldehyde groups also increases due to the breaking of more rings, resulting in a corresponding increase in the observed second-order rate constant for the addition of  $\text{HSO}_3^-$  to polyacrolein. If  $\text{HSO}_3^-$  reacts only with aldehyde, hydrated aldehyde, and hemiacetal-type aldehyde structures, or possibly only aldehyde or hydrated aldehyde structures, the concentrations of the reactive species would then be governed by their respective rates of hydrolysis. The decrease in the value of the observed equilibrium constant as the extent of reaction increases demonstrates, however, that the observed rate constant for dissociation increases more rapidly than does the calculated second-order rate constant for addition.

Considerably more experimental data would be required to substantiate the above mechanism. A method for measuring the relative concentrations of the different structures at any given time would be required before the individual rate constants could be determined. Differences in the value of the equi-

librium constant might, for example, result from different original degrees of ring formation in the polymer, as a result of different extents to which the polymer is dried. Likewise, the rates of dissociation of the adduct at a given extent of reaction could vary depending on the extent to which the polymer was originally reacted with bisulfite. In general, the proposed mechanism predicts that any factor which would influence the relative amount of ring structure in the polymer at any given time would also influence both the forward and reverse reactions.

The values of the observed equilibrium constant for the polyacrolein-bisulfite equilibrium are smaller than those reported for monomeric aldehydes. Equilibrium constants for monomeric aldehydes range from about  $10^3 \text{ l. mole}^{-1}$  for benzaldehyde<sup>12,18</sup> to  $10^7 \text{ l. mole}^{-1}$  for formaldehyde.<sup>19</sup> A comparison of these values demonstrates that the potential aldehyde groups in polyacrolein do not function as normal free aldehyde groups. The rates of both the forward and reverse reactions are slower for the polymer reaction in the 50–70 mole % range than are those for the monomeric aldehydes. The lower value of the equilibrium constant for the polymer reaction reflects the over-all slower rate of addition relative to rate of dissociation for the polymer reaction compared to those of the monomeric reactions. The higher value of the equilibrium constant for formaldehyde-bisulfite, relative to that observed for polyacrolein-bisulfite, was demonstrated directly by adding formaldehyde to an aqueous solution of polyacrolein-bisulfite. After some time the polyacrolein precipitated from solution, illustrating that the formaldehyde removed the bisulfite from the polyacrolein *via* the equilibrium by virtue of its greater affinity for the  $\text{HSO}_3^-$ . The precipitated polyacrolein was then removed by filtration, washed, and redissolved in aqueous  $\text{NaHSO}_3$  solution. The structures in polyacrolein which are responsible for its insolubility in water were, therefore, re-formed in the absence of  $\text{HSO}_3^-$ .

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(18) M. A. Gubareva, *J. Gen. Chem. USSR*, **17**, 2259 (1947).

(19) A. E. Parkinson and E. C. Wagner, *Ind. Eng. Chem. (Anal. Ed.)*, **6**, 433 (1934).