

Thickening of Poly(vinyl Alcohol) by Borate

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Synopsis

Viscosity and pH of aqueous borate-poly(vinyl alcohol) mixtures were determined under different conditions toward a clarification of the thickening mechanism. Boric acid has little effect on dilute poly(vinyl alcohol) (PVOH), but sodium borate causes sharp viscosity increases which are temperature sensitive and apparently stem from labile exothermic crosslinking of PVOH by borate ions. The pH data indicate that the complexing of borate with simple polyols such as mannitol and glycerol is a different process from borate crosslinking of PVOH. The PVOH thickening and gelling effect probably arises from the replacement of labile waters of hydration on borate ion by OH groups of PVOH rather than from borospiroane formation.

INTRODUCTION

The mechanism by which small amounts of alkali borates produce remarkable increases in viscosity of aqueous poly(vinyl alcohol) solutions cannot be regarded as settled.

Marvel and Denoon¹ observed that poly(vinyl alcohol) (PVOH) and boric acid form a precipitate which becomes gelatinous on being treated with NaOH and suggested that random crosslinking occurs since neither precipitate nor gelatinous product seemed to be a definite compound.

Deuel and co-workers^{2,3} noted that dilute aqueous solutions of several high molecular weight polysaccharides are gelled by borax, that the gels are liquified by certain simple polyols such as mannitol and glycerol, and that gelation does not occur under acidic conditions, i.e., with H_3BO_3 . The suggestion was made that PVOH and the polysaccharides form complexes of the monodiol (1:1) type with H_3BO_3 and of the didiol or borospiroane (2:1) type with borax, the latter providing the crosslinks responsible for thickening and gelation. Beardwood and Czerwin⁴ also suggested that borax thickens PVOH by forming didiol complexes, while H_3BO_3 yields nonthickening monodiams.

Okada and Sakurada⁵ stated that H_3BO_3 in excess of 3% causes PVOH to precipitate, the precipitated material after orientation giving an amorphous x-ray pattern rather than the characteristic crystalline diagram of PVOH. They concluded that PVOH and H_3BO_3 form a didiol complex in which the crosslinks inhibit crystallization. Borax produced only gelation of PVOH, and compound formation was said to occur in this case.

The PVOH-borate diol structures mentioned above are identical to those proposed by Böeseken and co-workers⁶⁻⁸ for complexes of H_3BO_3 or alkali borate with simple polyols. Typical neutral polyols which exhibit strong complexing activity have a pair of *cis*-1, 2-OH groups. For example, glycerol and especially mannitol sharply increase the acidity of aqueous H_3BO_3 and are said to form monodiol and didiol complexes, the latter being strong acids. However, a mass of evidence now indicates that these simple polyols form only 1:1 borate complexes.⁹ A few compounds with 1,3-OH groups, e.g., pentaerythritol, also exhibit complexing activity but of a lower order.

These references clearly show that different roles have been assigned to H_3BO_3 and borax in crosslinking, that didiol or spirane crosslinks are not possible if borate and polyols form only 1:1 complexes, and that, having 1,3-OH groups and being atactic, PVOH would in any case possess little simple polyol-type of complexing activity. The present investigation was undertaken, therefore, to clarify the nature of the PVOH-borate interaction.

EXPERIMENTAL

A low-viscosity, fully hydrolyzed PVOH type (Gelvitol Resin, Grade 1-30, Monsanto Co.) which could be used at relatively high ultimate concentrations was made into a 0.1 g/ml stock solution. Preliminary tests had indicated that alkaline solutions of partially hydrolyzed PVOH undergo a downward pH drift, probably from saponification.

Standard solutions of 1*N* NaOH, 0.6*M* H_3BO_3 , and 0.15*M* $Na_2B_4O_7 \cdot 10H_2O$ were made from reagent-grade materials. Mannitol (NF grade, Atlas Chem. Ind.) and glycerol (USP) were made as neutral stock solutions containing 0.2 and 1.0 g/ml, respectively.

Solution viscosities were determined by Brookfield (Model LVF), and pH was measured by glass electrode, pH 7.0 buffer. For test solutions, the required volume of stock PVOH was diluted with the water needed for a prescribed final concentration; standard H_3BO_3 , borax, and NaOH in proper amounts were added as a surface layer and mixed simultaneously. These mixtures were then incubated at 50°C for 1 hr, shaken gently, and held at 24°C overnight prior to pH and viscosity tests.

RESULTS

PVOH and H_3BO_3

Mixtures of varied H_3BO_3 -constant PVOH and varied PVOH-constant H_3BO_3 are described in Table I. Note that precipitate formation appears to depend solely upon concentration of H_3BO_3 . The solutions in all cases were fairly thin liquids, with viscosities perceptibly higher at 0° than at 50°C.

The pH and viscosity of aqueous PVOH and H_3BO_3 solutions are given in Table II. At relatively high concentrations, H_3BO_3 causes a slight increase

TABLE I
Appearance of H_3BO_3 -Poly(vinyl Alcohol) Mixtures at 26°C^a

H_3BO_3 , mmoles	PVOH		
	1.5	2.0	2.5
0	C	C	C
3.0	C	C	C
7.2	C	C	C
9.6	H	H	H
12.0	P	P	P
16.0	P	P	P

^a Volume of mixtures 40 ml throughout; C = clear; H = milky haze; P = precipitate.

TABLE II
Viscosity and pH of Solutions of
Boric Acid, Poly(vinyl Alcohol) and Mixtures

0.6M Boric Acid, ml	10% PVOH, ml	Dist. H ₂ O, ml	pH	Viscosity cps ^a
50	50	—	5.40	30
50	—	50	4.68	ca. 1.0
—	50	50	6.70	20
10	90	—	5.82	40
10	—	90	5.45	ca. 1.0
—	90	10	6.72	40

^a #3 Spindle at 6 rpm.

in viscosity of PVOH, but in no case does PVOH depress the pH of H_3BO_3 solution.

Effect of pH on PVOH-Borate Viscosity

Stock PVOH was combined with appropriate volumes of water and standard H_3BO_3 , borax, and NaOH to give solutions having PVOH constant at 0.04 g/ml, B concentration constant at prescribed levels, and with pH varying upward from 6.5. For B concentrations of 0.05, 0.025, 0.012, and 0.0045 millimoles/ml and pH values, respectively, of 6.5, 7.3, 7.8, and 8.1, apparent solution viscosities were about 10 cps but rose steeply to near 100,000 cps at pH values of 8.8, 9.3, 9.8, and 11.1. Thus borate salt is far more active in crosslinking than is virtually undissociated H_3BO_3 .

Effect of Temperature on Viscosity of PVOH-Borate

Four high pH solutions from the preceding experiment, each having 0.04 g PVOH/ml but different borate concentrations, were heated to 60°C, at which temperature they were thin liquids. Apparent viscosities were then measured periodically as the solutions were cooled in a water bath. Apparent viscosity-temperature data, plotted in Figure 1, indicate the crosslinks to be thermolabile.

pH of Polyol-Borate Solutions

The effects of PVOH, glycerol, and mannitol on the pH of borax solution were determined under comparable conditions. Stock solutions of PVOH and the simple polyols were combined with water and standard borax to

TABLE III
pH Values of Polyol-Borax Solutions

Polyol, g/l.	Poly(vinyl alcohol)	Glycerol	Mannitol
Concentration of Borax = 0.025 <i>M</i>			
0	9.20	9.20	9.20
30	8.84	8.23	6.53
40	8.78 (gel)	8.05	6.13
50	8.63 (gel)	7.90	5.85
Concentration of Borax = 0.05 <i>M</i>			
0	9.20	9.20	9.20
20	9.05	8.60	8.12
30	8.98	8.38	7.45
40	8.82 (gel)	8.15	6.77

yield final mixtures of uniform borate content but varying polyol concentration. The pH values for these mixtures at two levels of borax are given in Table III. Gelation of PVOH is observed at a relatively high pH, while glycerol and especially mannitol cause solution pH to drop sharply.

Effect of Simple Polyols on Viscosity of PVOH-Borate

The viscosity reduction caused by mannitol in PVOH-borax systems might possibly stem from a pH lowering. Accordingly, viscosity measurements were made on PVOH-borax and PVOH-borax-polyol solutions with and without pH adjustment. The data in Table IV show that mannitol and glycerol destroy the gelling activity of borate regardless of pH.

TABLE IV
pH and Apparent Viscosity of PVOH with Borax and Simple Polyols^a

Solution composition	pH	Apparent viscosity, cps
PVOH only	6.8	20
PVOH-0.05 <i>M</i> borax	8.8	gel, >100,000
PVOH-borax-0.28 <i>M</i> mannitol	6.1	50
PVOH-borax-mannitol-NaOH	9.3	20
PVOH-borax-1.4 <i>M</i> glycerol	7.4	80
PVOH-borax-glycerol-NaOH	9.6	1840

^a Concentration of PVOH 0.04 g/ml in each case; other substances in moles/l.

DISCUSSION

While H_3BO_3 causes minor thickening and at higher concentrations, precipitation of PVOH, the sharp increase in viscosity as pH of the system rises above 7 indicates that borate ion is the effective crosslinking agent. The appreciable thickening of PVOH by low borate concentrations at high pH is consistent with this view, since higher pH would maintain borate ion concentration against hydrolysis. Borate ion would also explain the effects of H_3BO_3 on PVOH, since above $0.03M$, H_3BO_3 forms homocomplexes which are relatively strong acids.¹⁰⁻¹² Thus, polyborate ions are present in H_3BO_3 solutions where thickening and precipitation are observed.

The variation of PVOH-borax solution viscosity with temperature (Fig. 1) suggests crosslinking to be an exothermic process. Similarly, Schultz^{13,14} recently noted that rising temperature inhibits PVOH-borate crosslinking and gave estimates of 5.0 and 5.8 kcal/mole for energy to break these bonds. In effect, thickening and gelation of PVOH appears to be a reversible exothermic process which involves borate ions.

The available evidence indicates the crosslinking of PVOH and polysaccharides by borate to be a different process from the complexing of

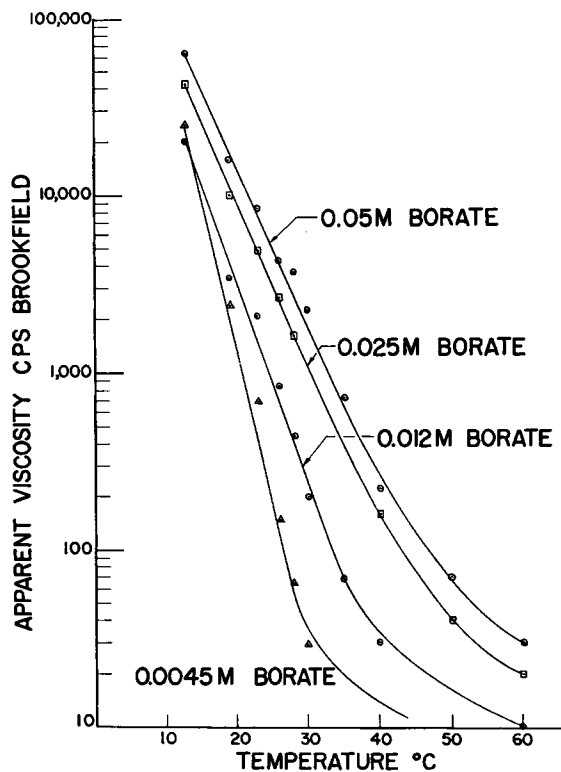


Fig. 1. Effect of cooling from 60° on the apparent viscosities of 4% PVOH solutions containing the indicated borate concentrations.

H_3BO_3 and alkali borates with simple polyols. Firstly, mannitol and glycerol are typical neutral polyols that sharply lower the pH of aqueous H_3BO_3 by forming appreciable quantities of strongly acidic polyol- H_3BO_3 complexes. Neutral PVOH, however, does not depress the pH of H_3BO_3 solutions but rather causes slight rises (Table II). Secondly, the gelation of PVOH by borax takes place with little pH change (Table III), while mannitol and glycerol cause substantial pH reductions under the same conditions, undoubtedly by complexing with H_3BO_3 from borax, a half-salt. Finally, the thickening and gelling activity of borax is destroyed by mannitol and glycerol even where pH is kept above 9 (Table IV). That is, mannitol- and glycerol-borate complexes form preferentially under conditions that otherwise favor crosslinking of PVOH by borate ions.

It is well established that at about 59.5°C borax ($Na_2B_4O_7 \cdot 10H_2O$) dissolves in its water of hydration and on careful drying loses up to 5 moles H_2O . Sodium metaborate ($NaBO_2$) holds up to 8 moles H_2O of hydration and dissolves in its water of crystallization at about 53.5°C. Both tetraborate and metaborate salts thus appear to have labile water of hydration. H_3BO_3 does not form a crystalline hydrate.

A reasonable explanation of the thickening and gelling of PVOH is that labile H_2O molecules on borate ion are replaced by OH groups of PVOH. Since several sites for such replacement exist on polynuclear borate ions, the result is a crosslinking. Being of the H-bond type, such crosslinks would be thermolabile as observed. The low viscosity of PVOH-borate systems in the temperature region where borate salts release water of hydration supports this mechanism.

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Received August 4, 1970