Binding of borax to poly(vinyl alcohol) in aqueous solution

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The thickening and gelling of aqueous poly(vinyl alcohol) (PVA) solution upon addition of boric acid or its sodium salt (borax) have long been known, and many studies have been carried out to elucidate the thickening and gelling mechanisms. Deuel *et al.*[1] suggested that PVA forms complexes of the monodiol type with boric acid and the didiol type with borax, referring to the structures for complexes between simple polyols and borates proposed by Boeseken[2]. Another suggestion made was that some weak hydrogen bonding type of interactions are responsible for the complex formation[3,4]. However, most studies have been concerned with the rheological properties of solutions with comparatively concentrated ranges of borax and PVA, or with solid film[4–8]. The detailed binding characteristics of borates for PVA in dilute conditions have received little attention[9,10].

Measurement of the extent of binding of borates to PVA is important for clarifying interactions between PVA and borates. At a dilute concentration of PVA, where only a thickening of solution can be observed but gelling does not develop, the solution properties would be dependent on the extent of binding. Knowledge of the detailed binding characteristics of PVA with borax under dilute conditions were required for interpretation of ultracentrifuge and viscometric studies for aqueous PVA–borax systems[11]. In the present study, the binding isotherms of borax to PVA were determined from membrane equilibrium measurements for aqueous PVA–borax solutions, and conclusions drawn about the complexing mode between PVA and borate ion.

Experimental

Materials. PVA (99.9 mol % saponified) was fractionated into ten fractions using an n-propanol–water system. Each fraction was dialysed fully against water to remove any lower molecular weight species, and recovered by reprecipitation with acetone. It was dried at 50°C under reduced pressure until a constant weight was attained. In this investigation, two fractions ($\bar{M}_w = 5.99 \times 10^4$ and 8.33×10^4) were employed. The isotacticity of both samples was estimated to be about 48% in diad from their i.r. spectra, according to the equation of Fujii[12]. Sodium tetraborate (borax), $Na_2B_4O_7$, was used in anhydrous form. Distilled, deionized water was used as the solvent.

Methods. Equilibrium dialysis experiments were carried out to determine the concentration of free borax, $[B]_{free}$, in equilibrium with the PVA–borax complex at 25°C and hence the amount of borax bound to PVA. The usual procedure was applied in this case[13]. A Visking dialysis bag, which contained 20 ml aliquots of the PVA solution (c 0.5 g dl^{-1}) was immersed in a glass-stoppered flask which contained a fivefold volume of the borax solution at appropriate concentration, and equilibrated after slow shaking of the flask for one week. The control run, with water only inside the dialysis bag, was carried out to make whatever corrections were necessary for binding of borax to the bag. Equilibrium borax concentrations $[B]_{free}$, were determined by the standard titration method with hydrochloric acid. No leakage of PVA molecules through the bag was detected. The amount of borax bound to PVA was expressed as the average binding extent, X, in mol borax bound per monomol of PVA.

Results and Discussion

The binding isotherms at 25°C expressed as X are illustrated in *Figure 1* as a function of the free borax concentration, $[B]_{free}$, for two samples with different molecular weights. The values of X increased steeply in the lower range of $[B]_{free}$, but slowly increased in the higher range, indicating that a binding saturation will be attained at higher borax concentrations and that the binding behaviour is of the Langmuir type. This trend in X is very similar to the dependence of the intrinsic viscosity on the borax concentration studied previously[11], where the viscosity increase was almost saturated upon addition of borax up to ~0.05 M. Furthermore, no recognizable difference in the binding isotherms of two samples was observed over the whole range of the borax concentration considered. This means that the binding capability of PVA for borax is practically independent of the molecular weight of the polymer.

Generally, macromolecules such as PVA with many functional groups on the chain will bind many ligand molecules and their binding isotherms can be represented in terms of a series of equilibria. However, it is very difficult to analyse these in detail, because the equilibrium constants for each binding site cannot be measured experimentally. However, if all the binding sites on the polymer are identical and completely independent, the equilibrium can be treated as if only a single type of site were present[14]:

$$\text{Free site} + \text{Ligand} = \text{Combined site} \qquad (1)$$

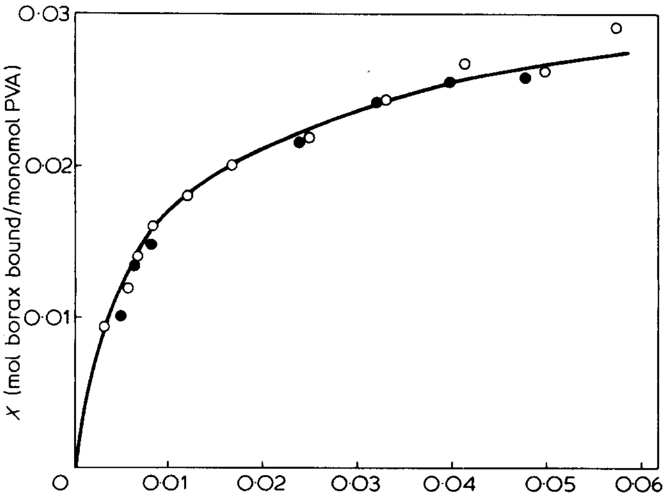

Figure 1 Binding isotherms of borax to PVA at 25°C. ●, $M_w = 5.99 \times 10^4$; ○, $M_w = 8.33 \times 10^4$

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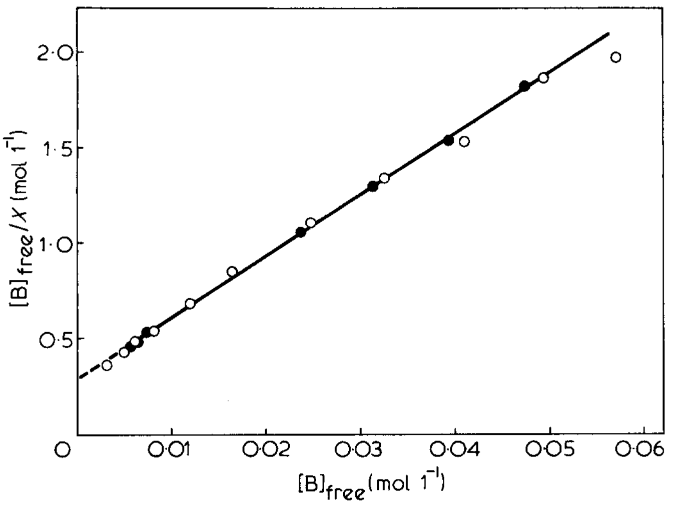

Figure 2 $[B]_{free}/X$ vs. $[B]_{free}$ plots for binding isotherms of the PVA–borax system. ●, $M_w = 5.99 \times 10^4$; ○, 8.33×10^4

Because the present binding isotherm is very simple (*Figure 1*) the situation above may be applicable to the present PVA–borax system. Here, the borate ion, $B(OH)_4^-$, was taken as the ligand in equation (1) rather than the borax molecule; thus, we are taking into account the general agreement that, in complexation between simple polyols and borax, the complexing species is the borate ion and not borax itself[15,16]. Then, the relation between the binding extent X and the free borax concentration $[B]_{free}$ may be expressed by a simple equation:

$$\frac{[B]_{free}}{X} = \frac{1}{nk} + \frac{4[B]_{free}}{n} \tag{2}$$

where k is the equilibrium constant referring to equation (1). n is the maximum number of borate ions bound to a monomeric unit of PVA when binding is saturated, according to the definition of X used here. Multiplication of $[B]_{free}$ by 4 shows that one borax molecule corresponds to four borate ions.

Figure 2 shows such plots as $[B]_{free}/X$ *versus* $[B]_{free}$ for the present PVA–borax systems. The plots are substantially linear in the whole range of borax concentration covered. This suggests that all the sites are identical to each other and have the same inherent tendency for borate ion binding. The values of k and n were determined to be 27.3 M^{-1} and 0.127 (mol borate ion bound/monomol PVA), respectively, from a least-squares fit of the experimental data.

The value of $k = 27.3$ M^{-1} obtained here is about thirty times larger than that of 0.85 M^{-1} determined from the dialysis study for the boric acid–PVA system[9]. The difference in values of k between the borax and boric acid systems may be ascribed to the different binding abilities of borate ion to PVA in basic and acidic conditions, i.e. the binding of borate ion to PVA occurs more readily in basic conditions. The similar effects of borate ion in basic and acidic conditions have been observed in the viscosity measurements of aqueous PVA solutions, where the viscosity increase is greater upon addition of borax than boric acid[3].

In view of the definition of n in equation (2), the value of $n = 0.127$ implies that one binding site for a borate ion is provided about every 8 (=1/0.127) monomeric units of PVA. If all the –OH groups of PVA do participate stoichiometrically in binding with borate ions to form such complexes of monodiol or didiol types as suggested by Deuel *et al.*, and the sites are saturated completely, the corresponding ratios of the complexed monomeric units of PVA per borate ion ($1/n$) should be 2 or 4, respectively. In fact, Saito *et al.* obtained a value of 2 in the aqueous PVA–boric acid system and they conclude that this implies the formation of the monodiol type of complex between PVA and borate ion in acidic conditions. However, the sequence of 8 monomeric units is much larger, and suggests that there are 4 or 6 –OH groups within this sequence which do not participate in the binding with borate ion even when the latter are in large excess, i.e. with regard to the –OH groups of PVA, a certain selective binding occurs in basic conditions.

By comprehensive studies on complexation between simple polyols and borate ion[2,17,18], it is known that the borate ion in basic conditions favourably forms the didiol type of complex, reacting with the two pairs of –OH groups of *cis* 1,2- or 1,3-diol structures, and that the valence angle of the tetravalent boron is tetrahedral. The PVA chain can be regarded as a polyol with successive 1,3-diol structures. Furthermore, the stereoregularity of the PVA chain may offer some information about the preferred conformations of the adjacent –OH groups in the borate ion bindings. In fact, it has been reported that Cu^{2+} ion binding to PVA[19] and to poly(methacrylic acid)[20], and ester hydrolysis of the side chain[21] occur preferentially in the portion of isotactic configuration. Therefore, by taking into account the isotacticity of our samples of about 48% in diad, it may be reasonable to suggest that two pairs of isotactic configuration (four –OH groups) among eight monomeric units of PVA chain may, on average, be available for complex formation with borate ion. Consequently, it may be concluded that in the present PVA–borax system the didiol type of complex is formed preferentially between one borate ion and stereo regularly selected four –OH groups with isotactic configuration. However, many problems remain unsolved concerning steric hindrance and electrostatic interaction upon complexation with borate ion and the average sequence-length of isotactic configuration of the PVA chain.

References

1 Deuel, H. and Neukom, H. *Makromol. Chem.* 1949, **3**, 13
2 Boeseken, J. 'Advances in Carbohydrate Chemistry' Vol 4, pp 189–210, W. W. Pigman and M. L. Wolfram, Eds, Academic Press, New York 1949
3 Volewski K. and Rychly, R. *Kolloid. Z. Z. Polym.* 1968, **288**, 48
4 Nickerson, R. F. *J. Appl. Polym. Sci.* 1971, **15**, 111
5 Okada, N. and Sakurada, I. *Kobunshi Kagaku* 1958, **15**, 491 and 497
6 Thiele, H. and Lamp, H. *Kolloid Z.* 1960, **173**, 63
7 Shultz, R. K. and Myers, R. R. *Macromolecules* 1969, **2**, 281
8 Ochiai, H., Fukushima, S., Fujikawa, M. and Yamamura, H. *Polym. J.* 1975, **8**, 131
9 Saito, S., Okuyama, H., Kishimoto, H. and Fujiyama, Y. *Kolloid Z.* 1955, **144**, 41
10 Vasudevan, T., Balakrishnan, T., Kothandraman, H. and Santappa, M. *J. Polym. Sci. (Polym. Chem. Edn)* 1976, **14**, 2319
11 Ochiai, H., Fujino, Y., Tadokoro, Y. and Murakami, I. *Polymer Preprints, Japan,* 1978, **27** (No. 6) 987, details will be published in *Eur. Polym. J.*
12 Fujii, K., Mochizuki, T., Imoto, S., Ukida, H. and Matsumoto, M. *J. Polym. Sci. (A)* 1964, **2**, 2327
13 Nakagaki, M. and Shimabayashi, S. *Nippon Kagaku Kaishi* 1972, 1496
14 Tanford, C. 'Physical Chemistry of Macromolecules' Wiley, New York, 1961, Ch. 8

15 Roy, G. L., Laferriere, A. L. and Edwards, J. O. *J. Inorg. Nucl. Chem.* 1957, **4**, 106

16 Conner, J. M. and Bulgrin, V. C. *J. Inorg. Nucl. Chem.* 1967, **29**, 1953

17 Hermans, P. H. *Z. Anorg. Chem.* 1925, **142**, 83

18 Isbell, H. S., Brewster, F. J., Holt, N. B. and Frush, H. L. *J. Res. Nat. Bur. Stand.* 1948, **40**, 129

19 Hojo, N., Shirai, H., Sakata, K. and Fukada, M. *Kogyo Kagaku Zasshi* 1970, **73**, 130

20 Costantino, L., Crescenzi, V., Quadrifoglio, F. and Vilagliano, V. *J. Polym. Sci. (A-2)* 1967, **5**, 771

21 Morawetz, H. 'Macromolecules in Solution' 2nd Edn., Wiley–Intersceince, 1975, Ch. 1X