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Complex formation between poly(vinyl alcohol) and borate ion

Hiroshi Ochiai, Sanae Shimizu, Yuji Tadokoro* and Ichiro Murakami

Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Naka-ku, Hiroshima 730, *Japan*

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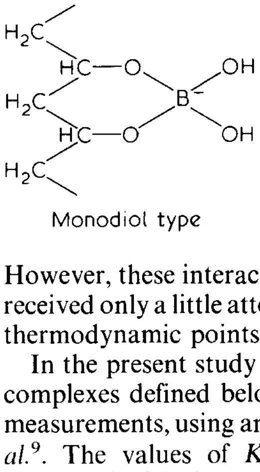
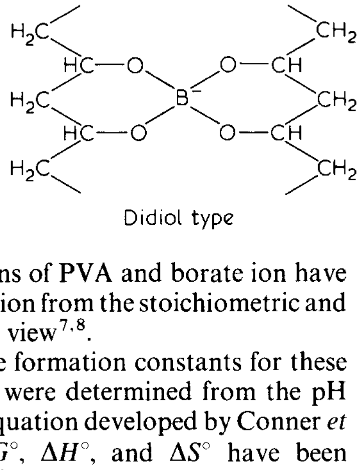
Introduction

Numerous studies have been carried out on the aqueous poly(vinyl alcohol) (PVA)–borate systems to interpret their thickening and gelling phenomena[1]. It is generally believed that these phenomena result from the complex formation of monodiol or didiol types between the OH groups of PVA and borate ion, similar to those in the simple low-molecular-weight polyol–borate systems[2–6].



Monodiol type



Didiol type

However, these interactions of PVA and borate ion have received only a little attention from the stoichiometric and thermodynamic points of view[7,8].

In the present study the formation constants for these complexes defined below were determined from the pH measurements, using an equation developed by Conner *et al.*[9]. The values of $K\Delta G^\circ$, ΔH°, and ΔS° have been compared with those of the analogues.

$$B^- + P = BP^-, \qquad K_1 = [BP^-]/[B^-][P] \qquad (1)$$

$$B^- + 2P = BP_2^-, \qquad K_2 = [BP_2^-]/[B^-][P]^2 \qquad (2)$$

where B^- is the borate ion, and P is PVA expressed in 2 monomer units. BP^- and BP_2^- are monodiol and didiol types of complexes, respectively. [ ] denotes the concentration expressed in mols per litre.

Experimental

The sample PVA (fully hydrolysed grade) was crudely fractionated into three fractions with n-propanol–water systems. The middle fraction, which was used as the sample in the present study, was treated with aqueous sodium hydroxide to complete saponification, and was purified by dialysis. Thus obtained, the material did not show any characteristic absorption band corresponding to a residual acetyl group in its i.r. spectrum. The degree of polymerization estimated from viscosity measurements was about 500. Anhydrous borax (sodium tetraborate) ($Na_2B_4O_7$) was used after heat-treatment (Suprapur, Merck). CO_2-free conductivity water was always used. All the reaction mixtures were prepared by a procedure previously described[9,10], and allowed to set in a nitrogen atmosphere for at least 1 day to attain the complexing equilibrium prior to pH measurements.

Measurements of pH were made with a TOA model HM-18E pH-meter, using a GST-155C combination electrode. All measurements were carried out in a nitrogen atmosphere to prevent CO_2-contamination, using a conventional water bath to give a temperature control of $\pm 0.05^\circ$ at 10°, 25°, and 35°C. The meter was standardized separately at each working temperature with standard buffers. A correction for the medium was not made since the PVA concentration was not high.

Results and Discussion

The results of pH measurements at three temperatures are presented in *Figure 1* as a function of PVA concentration expressed on the basis of mols of 2 monomer units per litre. A set of curves indicates the increasing acidity of boric acid with increasing PVA concentration, and this trend is greater at lower temperatures.

An equation developed by Conner *et al.* for the simple polyol–borate complexes may be useful in measuring the complexing ability between PVA and borate ion. The theory behind the derivation of the equation is that the complexation increases the acidity of boric acid and this increase is dependent on the complexant (PVA) concentration. Furthermore, it is assumed that the amount of unionized boric acid [HB] does not significantly change with PVA concentration and remains

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* Chemistry Laboratory, Faculty of Integrated Arts and Sciences

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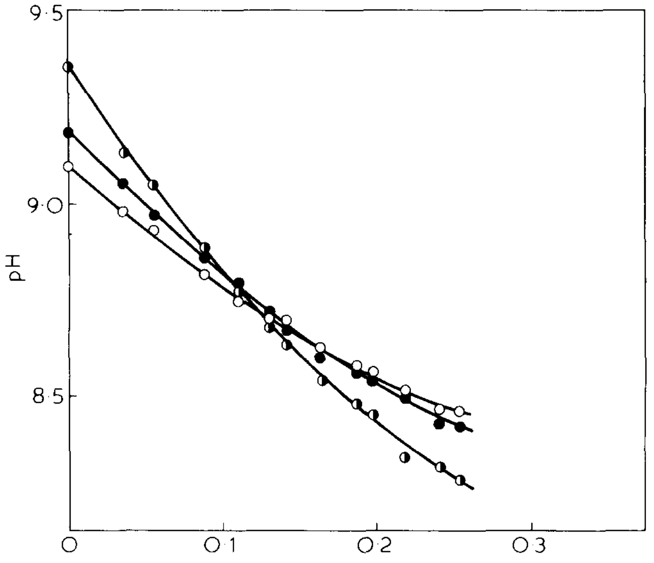

Figure 1 Dependence of pH on PVA concentration at various temperatures. ◑, 10°C; ●, 25°C; ○, 35°C. $[B^-]_0 = 5.25 \times 10^{-3}$ (mol l^{-1})

equal to the initial value $[HB]_0$.

$$\left(\frac{[H^+]}{K_a}-1\right)\frac{1}{[P]}=K'=K_1+K_2[P] \qquad (3)$$

where K_a is the first ionization constant of boric acid, $K_a = [H^+][B^-]/[HB]$, which was estimated from the pH-value of borax solution without PVA, since borax has a chemical composition such that its aqueous solution is a half-neutralized solution of boric acid. [P] is the concentration of uncomplexed free PVA and given as follows,

$$[P]=\frac{[P]_T-2[B^-]_0+2K_a[B^-]_0/[H^+]}{1-K_1K_a[B^-]_0/[H^+]} \qquad (4)$$

where subscripts zero and T imply the initial and total concentrations, respectively. Although in this equation [P] and K_1 were unknown, [P] was determined by a successive approximation method until a self-consistency was attained, using an initial value of K_1 estimated as a first approximation that $[P]=[P]_T$ in equation (3)[9].

The plots of K' vs. [P] result in straight lines with positive slopes and intercepts, which are best explained on the basis of the formation of two different borate complexes, i.e., monodiol and didiol types. The formation constants derived from respective slopes and intercepts are listed in *Table 1* (see *Figure 2*). At all temperatures K_2 has a greater value than K_1, suggesting primarily the formation of didiol type of complex. Both K_1 and K_2 have negative temperature dependence, especially K_2 which decreases rapidly with increasing temperature. The formation constant values obtained here for the PVA–borate complexes are compatible with our previous results obtained from an equilibrium dialysis study[8], and are slightly larger than the reported values for the simple aliphatic 1,2- or 1,3-diol-borate complexes[9-10]. But, they are very small in comparison with the complexes with mannitol, where K_1 and K_2 have an order of 10^3 and 10^5, respectively. This high complexing ability of mannitol is generally ascribed to its *cis*-hydroxyls favourable to react with tetrahedral borate ion[9-10].

The standard free energy change ΔF°, enthalpy change ΔH°, and entropy change ΔS° corresponding to each complex formation at 25°C were calculated from the familiar thermodynamic relations (see *Table 2*). As expected, the enthalpy changes of both complex formations are negative, where ΔH_2 for the didiol type is more exothermic than ΔH_1° for the monodiol type. These values and the trend of the present enthalpy changes are fairly consistent with those for the other polyol borate complexes[9-11]. The entropy changes are also negative for both complexes. This indicates that any entropy gain from the liberation of the solvated and/or ordered water molecules on PVA and borate ion, and/or around their moieties does not exceed the entropy loss realized by the complex formations themselves and the chain

Table 1 Formation constants for PVA–borate complexes

	10°C	25°C	35°C
$K_1 = [BP^-]/[B^-][P]$	13.4	9.7	9.3
$K_2 = [BP_2^-]/[B^-][P]^2$	128	39.9	18.7

at $[B^-]_0 = 5.25 \times 10^{-3}$ (mol l^{-1})

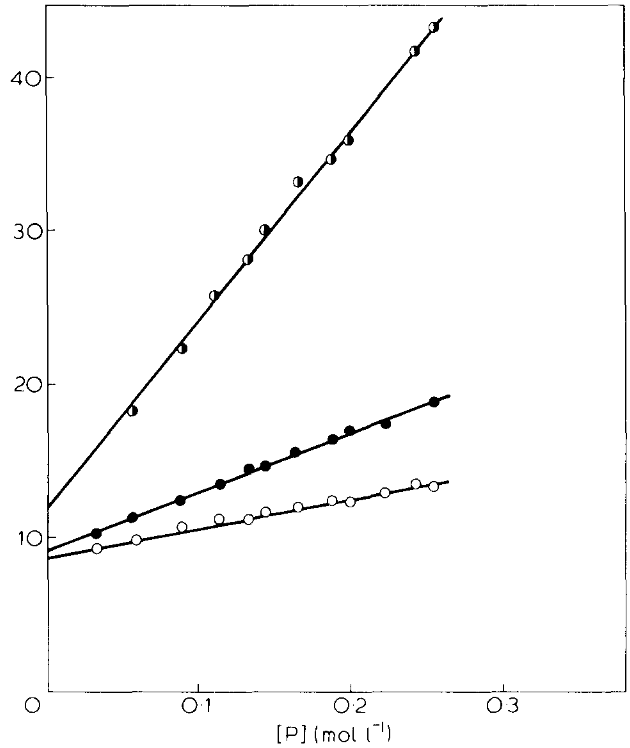

Figure 2 Plots of pseudo equilibrium constant K' vs. free PVA [P] at various temperatures. ◑, 10°C; ●, 25°C; ○, 35°C. $[B^-]_0 = 5.25 \times 10^{-3}$ (mol l^{-1})

Table 2 Thermodynamic functions for PVA–borate complexes at 25°C

	$-\Delta G^\circ$ kJ mol^{-1}	$-\Delta H^\circ$ kJ mol^{-1}	$-\Delta S^\circ$ kJ mol^{-1} deg^{-1}
$B^- + P = BP^-$	5.63	11.2	18.9
$B^- + 2P = BP_2^-$	9.13	52.3	145

contraction. The extreme entropy loss in the didiol type complex formation can be ascirbed to the fact that the present ligands are the OH groups on the polymeric PVA chain: the PVA chain must take a special conformation favourable to react with the tetrahedral borate ion, i.e., two sets of adjacent OH groups of PVA must be in a *cis*-conformation[9–16]. Furthermore, crosslinking might be expected to cause considerable reduction in the conformational entropy of the PVA chain. Thus, it appears that here, as in the other polyol–borate systems, the main contribution to the complex stabilities for the present PVA–borate complexes are the favourable enthalpy changes, in contrast to most metal complexes where the complexing ability results mainly from the entropy contribution[17].

Finally, since the present PVA–borate complexes are both polyelectrolytes, the effect of ionic strength must be taken into consideration and the values are not always definitive. But, the present results are felt to be valid as a first stoichiometric approach for the thickening and gelling phenomena of aqueous PVA–borax system.

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A commentary on 'Free radicals and new end groups resulting from chain scission: 1. γ-Irradiation of polyethylene'

Malcolm Dole
Department of Chemistry, Baylor University, Waco, Texas 76798, *USA*

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Introduction

Under the above title DeVries, Smith and Fanconi[1] (DSF) recently published a paper in which they have attempted to relate the concentration of free radicals produced in the γ-irradiation of polyethylene (PE) to 'the resultant concentration of new chemical groups'. However, their estimates of free radical yields differ from commonly accepted values by an order of magnitude. Furthermore as explained below they overlooked what is probably the most important mechanism for the formation of *t*-vinylene double bonds. Let us consider the free radical yield problem first.

Free radical yields. Using a linear polyethylene DSF irradiated a sample *in vacuo* at 77K to a dose of 50 Mrad and measured the free radical yield by the e.s.r. method at $-160°$C. From the data of their *Figure 3* and of *Tables 2* and *3* it is possible to calculate $G(\mathrm{R}\cdot)$ or the number of free radicals produced per 100 e.V. of absorbed radiation from the equation

$$G(\mathrm{R}\cdot)=\frac{[\mathrm{R}\cdot]100}{r} \qquad (1)$$

where r is the dose in e.V. g^{-1} that produced a concentration $[\mathrm{R}\cdot]$ of free radicals per gram. Since[2] 1 rad equals 6.25×10^{13} e.V., 50 Mrad is 31.25×10^{20} e.V. and since $[\mathrm{R}\cdot]$ was found by DSF to be 4.8×10^{18} radicals per gram for their irradiation in vacuum, $G(\mathrm{R}\cdot)$ can be calculated to be only 0.15. For their 3 Mrad irradiation *in vacuo*, $G(\mathrm{R}\cdot)$ is calculated to be 0.21. Dole[3] has summarized $G(\mathrm{R}\cdot)$ values obtained by a number of workers; for Marlex-6002 irradiated to 20 Mrad at 77K values range from 3.6 for films to 4.2 for single crystals. More recently[4] for a 7 Mrad dose at 77K Gvozdic and Dole found $G(\mathrm{R}\cdot)$ equal to 2.96 (average of 4 samples) for annealed Marlex-6002 (PE) and 3.59 (average of 6 samples) for the quenched samples. Waterman and Dole[5] showed that for radiations in vacuum (they used electron beam irradiation) at 77K the alkyl free radical yield was constant with dose up to 70 Mrad. Their $G(\mathrm{R}\cdot)$ value was 3.3 ± 0.5 which demonstrates no essential difference between γ-ray and electron beam irradiation of the 10 mil thick Marlex-6002 film used by them. DSF's yield of free radicals was also constant with dose for their vacuum irradiations.

All of the above mentioned $G(\mathrm{R}\cdot)$ values are an order of magnitude greater than those calculated from DSF's data. The exact cause of this discrepancy is unknown at the present time. DSF did not describe how they calibrated the dose of γ-rays absorbed by their samples. They used 1.25 mW power in their e.s.r. measurements whereas we[4] have found that alkyl radicals saturate at a power of 0.063 mW.

Double bond yields. DSF give 5.4 ± 3.5 and 2.3 ± 1 for their yields of *t*-vinylene double bonds per free radical for doses of 3 and 50 Mrad *in vacuo* at 77K respectively. Multiplying these numbers by the $G(\mathrm{R}\cdot)$ values calculated

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