The Partial Specific Volume and Preferential Interactions of Poly(vinyl alcohol) in Aqueous Borax Solutions

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ABSTRACT: Density measurements were carried out at 25°C for aqueous poly(vinyl alcohol) (PVA) solutions of various borax concentrations. The partial specific volume $\bar{v}_2^\circ$ of PVA increased slightly with increasing borax concentration, from 0.754 ml g^{-1} in water to 0.777 ml g^{-1} in 5×10^{-2} mol l^{-1} aqueous borax. From the density increments in the dialysed systems, the apparent volume ϕ' was found to decrease from 0.725 ml g^{-1} at 4.6×10^{-3} mol l^{-1} borax to 0.635 ml g^{-1} at 5.7×10^{-2} mol l^{-1} borax. The preferential interaction parameter ξ_3° (grams of borax bound per gram of PVA) was positive and became larger with increasing borax concentration. The net hydration ξ_1° (grams of water bound per gram of PVA) was negative and became less negative with an increase in borax concentration. The relationships between ξ_3° and ξ_1° and physical binding and exclusion of low-molecular-weight components are discussed in terms of a simple model proposed by Reisler et al. It was found that at a limit of infinite concentration of borax, about 0.085 g of borax is bound and 7.0 g of water is excluded per gram of PVA.
    KEY WORDS   Poly(vinyl alcohol) / Borax / Density Measurement / Constant Molality / Dialysis Equilibrium / Partial Specific Volume / Apparent Volume / Density Increment / Preferential Interaction / Net Hydration /

For a clear understanding of the thickening and gelling mechanisms of aqeuous PVA solutions on addition of small amounts of boric acid and alkali borates, it is important to obtain information on the interaction between PVA and borate ions. Many investigators have interpreted these thickening and gelling phenomena as a result of a three-dimensional network formation due to the complex formation[1–3] or weak hydrogen-bonding interaction,[4,5] between the OH groups of PVA and tetrafunctional borate ions. Of course, such interpretations based on interchain crosslinkings by borate ions may be adequate for moderately concentrated solutions of PVA. However, at a dilute concentration of PVA, where only a thickening of the solution can be observed but no gelling, even when borate ion is in large excess, the thickening would be dominated mainly by the intrachain interactions of PVA with borate ion and/or solvent water. Furthermore, these interactions would probably give rise a considerable change in basic solution properties, such as the extent of hydration of the PVA chain and water structures around the chain.

Generally, in multi-component systems, mutual interactions among solution components occur in a complicated fashion. The use of equations for a simple two-component system is, therefore, inadequate in these systems. Many theoretical and experimental efforts have been directed toward these problems.[6–11] For instance, the partial specific volumes and the density increments of the respective solution components can be derived from density measurements taken on well-defined solutions.

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These values provide much information on pre-ferential interactions in a solution and other thermodynamic quantities.[12–14] In this study, we carried out density measurements for a three-component system of water–PVA–borax under the conditions of constant molalities of borax and constant chemical potentials of diffusible components (at dialysis equilibrium). The density increment, partial specific volume, and apparent volume of PVA in borax solutions were determined. The preferencial interaction parameter of PVA is discussed in relation to further clarification of the mechanism for the thickening of aqueous PVA resulting from the addition of borax, and the solution properties.

Basic Equations

To understand the thermodynamic quantities which may be derived from density measurements for the three-component system composed of water (component 1), PVA (component 2), and borax (component 3), the basic equations derived by Casassa and Eisenberg have been used in the present study.[6,11] The preferential interactions are reflected in the values of the density increment $(\partial\rho/\partial c_2)_\mu^\circ$; in the present three-component system, the pre-ferencial interaction of the PVA chain with low-molecular-weight components may be due to the binding of water and/or borax, or the Donnan effect, if the electrostatic charges reside on the chain. To a good approximation under the conditions of low polymer concentration and negligibly small effect of osmotic pressure, the following equation was used:

$$(\partial\rho/\partial c_2)_\mu^\circ = (1-\bar{v}_2^\circ\rho^\circ) - \xi_3^\circ(1-\bar{v}_3\rho^\circ) \qquad (1)$$

where $\xi_3^\circ = (\partial w_3/\partial w_2)_\mu^\circ$, which denotes the pre-ferential interaction parameter, and means the change in weight molality w_3 (in unit of grams of borax per gram of water) with change in molality w_2, in order to maintain constancy of chemical potentials, μ_1 and μ_3; c_2 is the volume concentration of PVA in g ml^{-1}; $\bar{v}_2^\circ$ is the partial specific volume of PVA at its vanishing concentration, $\bar{v}_2^\circ = (\partial v/\partial w_2)_{w_3}^\circ$, whereas $\bar{v}_3$ corresponds to the finite concentration of borax, $\bar{v}_3 = (\partial v/\partial w_3)_{w_2=0}$; ρ and ρ° are the densities of the solution and the solvent mixture without polymer. The superscript zero refers to the vanishing PVA concentration and subscript μ signifies constancy of all chemical

potentials of components diffusible through a membrane. Since constant temperature and pressure are assumed throughout, the subscripts T and p are not indicated.

The density increment $(\partial\rho/\partial c_2)_\mu^\circ$ for the dialysed system is often expressed, as a simple two-component system, by introducing an apparent volume ϕ' defined by,[6]

$$(\partial\rho/\partial c_2)_\mu^\circ = 1 - \phi'\rho^\circ \qquad (2)$$

This quantity is usually used for estimating the buoyancy term in a sedimentation study.

The partial specific volume $\bar{v}_2^\circ$ at various borax concentrations can be determined by use of a simplified equation which is applicable at low polymer concentrations, where ρ is linear against c_2,

$$(\partial\rho/\partial c_2)_{w_3}^\circ = 1 - \bar{v}_2^\circ\rho^\circ \qquad (3)$$

EXPERIMENTAL

The PVA sample (99.9 mol% saponified) used here was a fraction characterized by $M_w = 9.45 \times 10^4$. Anhydrous sodium tetraborate, $Na_2B_4O_7$ (borax), was used. Both materials were completely dried under suitable conditions until a constant weight was attained. Water was deionized and distilled, and was fully degassed by boiling before use. In preparing the solutions, all weighed masses were corrected to vacuum. Since PVA is not soluble in cold water, a stock solution of PVA was prepared by dissolving the weighed mass of the dried PVA in a suitable amount of water at an elevated temperature of *ca.* 90°C, and after cooling to room temperature, the water content was determined by weight. Solutions for partial specific volume determinations were prepared by adding either appropriate (weighed) amounts of the stock solution of PVA (of known concentration) or degassed water to the weighed sample of borax. The amount of water was adjusted so as to provide the same molalities of borax as in the PVA-containing solutions. A similar procedure was used for estimating the partial specific volume of Deoxyribonucleic acid (DNA) in salt solutions.[12,13]

Solutions on which density-increment measure-ments were made at constant chemical potentials of diffusible components were obtained as follows. A dialysis bag, containing 20 ml aliquots of PVA stock solution (of known concentration), was immersed in

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a glass-stoppered flask which contained about a five-fold volume of borax solution of appropriate concentration, and equilibrated at 25°C for one week after slow shaking of the flask. The equilibrium borax concentration was determined by a standard titration method with hydrochloric acid. A small concentration change in PVA due to the redistribution of diffusible components during dialysis was corrected from the volume change of the inner solution. For a series of density measurements at a given borax concentration, 15—20 test solutions of various PVA concentrations up to 0.4 $g\,ml^{-1}$ were made by diluting with corresponding borax solutions and dialysates.

Density measurements were made with a digital precision densitometer SS-D-200 (Shibayama Co.) at 25°C with a temperature control of $\pm 1 - 2 \times 10^{-2}°C$. Experimental precision was limited to $5 \times 10^{-6}\, g\,ml^{-1}$ in density due to thermostat performance and small fluctuations in room temperature.

RESULTS AND DISCUSSION

The results of the density measurements are summarized in Table I for the systems at constant borax molalities and constant chemical potentials (dialysed). For all systems, density values were found to be linear with the PVA concentration c_2;

thus, the density increments could easily be determined as the respective slopes of ρ vs. c_2 plots.

The values for $(\partial \rho / \partial c_2)^\circ_{w_3}$ at constant molalities of borax decreased with increasing borax concentration, exhibiting a slightly slow decrease in a higher concentration range. The partial specific volumes $\bar{v}_2^\circ$ in these solutions calculated by eq 3 are listed in column 4 of Table I. It is seen that $\bar{v}_2^\circ$ increases very slightly with increasing borax concentration. The value of $0.754\ ml\,g^{-1}$ in water at 25°C is in close agreement with the literature value of $0.756\ ml\,g^{-1}$ at 30°C, determined by a flotation method for the sample of $M_w = 7.04 \times 10^4$.[15]

On the other hand, for the dialysed systems, the density increment $(\partial \rho / \partial c_2)_\mu^\circ$ increased almost linearly with the density of the dialysate. In column 6 are listed the values of the apparent volume ϕ'. ϕ' decreases sharply with increasing borax concentration and appears to level off at a higher concentration (see Figure 1). These changes of ϕ' are appreciably large in comparison with the denaturation of proteins in moderately concentrated salt solutions, where ϕ' initially decreased and then increased somewhat on addition of salt.[13,14] The large observed decrease in ϕ' suggests a strong interaction between PVA and borax, though the borax concentration is not so high. This also indicates that the use of ϕ' as a constant, independent of borax concentration, leads to se-

Table I. Density characteristics of poly(vinyl alcohol) at 25°C in borax solutions at constant molality and at constant chemical potentials

Borax	ρ°	$(\partial \rho / \partial c_2)^\circ_{w_3}$	$\bar{v}_2^\circ$	$(\partial \rho / \partial c_2)_\mu^\circ$	ϕ'	ξ_3°	ξ_1°
$mol\,l^{-1} \times 10^2$	$g\,ml^{-1}$		$ml\,g^{-1}$		$ml\,g^{-1}$	g (3)/g (2)	g (1)/g (2)
0	0.99707	0.247_8	0.754				
0.46	0.99799			0.274_8	0.725	0.039	−42
0.48	0.99806			0.278_8	0.722	0.042	−44
0.60	0.99824	0.234_5	0.767				
0.77	0.99863			0.286_5	0.715	0.054	−35
0.80	0.99863			0.290_7	0.710	0.059	−36
1.00	0.99896	0.232_6	0.768				
1.49	0.99982	0.225_1	0.775				
1.56	1.00016			0.310_9	0.690	0.089	−28
1.61	1.00028			0.312_9	0.687	0.090	−27
2.99	1.00268	0.226_7	0.771				
3.94	1.00472			0.336_1	0.661	0.133	−16.7
4.09	1.00483			0.340_1	0.657	0.139	−16.8
4.98	1.00647	0.210_8	0.777				
5.69	1.00782			0.360_4	0.635	0.169	−14.7

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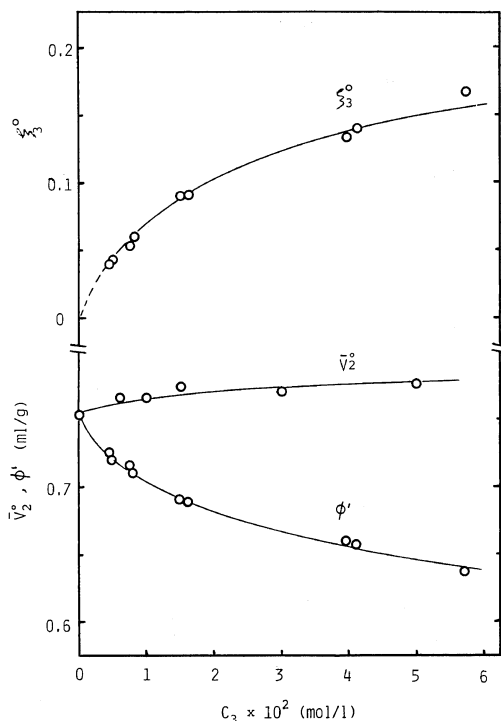
Figure 1. Preferential interaction parameter ξ_3° and the partial specific $\bar{v}_2^\circ$ and apparent ϕ' volumes, of PVA in borax solutions at 25°C, as a function of borax concentration C_3 (mol l^{-1}).

rious error in the determination of molecular weight by ultracentrifugation. Thus, the dependence of $\bar{v}_2^\circ$ and ϕ' on the borax concentration and difference between these values in the presence and absence of borax may be interpreted in terms of interactions of PVA with borax and/or solvent water.

The preferential interaction parameter ξ_3° at various borax concentrations was calculated from eq 1, using the values of $(\partial\rho/\partial c_2)_\mu^\circ$, $\bar{v}_2^\circ$, and $\bar{v}_3$. The value of $\bar{v}_3$ was estimated from the separately determined specific volume of an aqueous borax solution at 25°C:

$$v = 1.00294 - 0.88638\omega + 0.63548\omega^2$$

where ω is the weight fraction of borax. The results (column 7) are shown in Figure 1, along with the values of $\bar{v}_2^\circ$ and ϕ', as a function of borax concentration. The value of ξ_3° is positive throughout the range of borax concentrations studied and increased with borax concentration, in contrast to the case of ϕ'. Both the magnitude (expressed in

molar base) and the increasing trend in ξ_3° are in close agreement with the binding isotherms of borax to PVA, previously determined by chemical titration of borax for the dialysed systems.[16] Furthermore, the increasing trend in ξ_3° observed here is very similar to the increase in the intrinsic viscosity $[\eta]$ of an aqueous PVA solution upon addition of borax. The viscosity of this solution increases sharply on adding a small amount of borax and becomes almost saturated in the presence of *ca.* 0.05 mol l^{-1} borax.[17] This similarity of increasing trends of $[\eta]$ and ξ_3° with borax concentration apparently suggests that the thickening of dilute PVA solution by borax may be ascribed to the binding of borax with the PVA chain.

The positive ξ_3° value apparently indicates the binding of borax to PVA but this does not exclude the possibility of interactions with other solvent components. In other words, bindings of borax and water may be occurred in different domains of the PVA chain. If we follow the physical model proposed by Reisler *et al.*,[14] for describing the mutual interactions in the three-component system at dialysis equilibrium, ξ_3° can be expressed in terms of the relevant model parameters as follows,

$$-\xi_3^\circ/w_3 = \xi_1^\circ = B_1 - (B_3 - E_3)/w_3 \qquad (4)$$

where $\xi_1^\circ = (\partial w_1/\partial w_2)_\mu^\circ$, which is sometimes called the net hydration. B_1 and B_3 express bindings of water (1) and borax (3) to PVA (2). E_3 is the Donnan exclusion of borax (3). All quantities are expressed in grams per gram of PVA. Positive B_3 means the removing of borax from the bulk of solvent, or an influx of borax across a membrane from the outer solvent compartment, freed of PVA. On the contrary, the binding of water B_1 corresponds to an effective increase in borax concentration and, thus implies an outflow of borax into the outer solvent compartment. The Donnan effect acts in the same direction as B_1. The binding parameters B_1, B_3, and E_3 may be estimated from other types of experiments, in which the definitions for binding, different from those used here may be introduced.

In Figure 2, the value of ξ_1° (column 8) is plotted against $1/w_3$, according to eq 4. ξ_1° is negative and further decreases with decreasing w_3, indicating a net dehydration from the PVA moiety. The plot is significantly concaved throughout range of borax concentrations studied. From the initial slope and
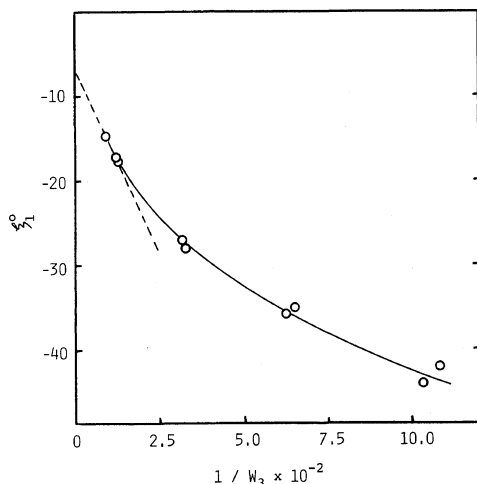
Figure 2. Net hydration ξ_1° as a function of the reciprocal borax concentration w_3 (g of borax/g of water).

intercept at a limit of $1/w_3 \to 0$, though the extrapolation is not very definite, we can deduce $(B_3 - E_3)$ as being about 0.085 and B_1 about -7.0. These values can be expressed on equivalent basis, i.e., $(B_3 - E_3)M_u/M_3 = 0.019$ borax molecule bound and $-B_1 M_u/M_1 = 17$ water molecules dehydrated, per monomer unit of PVA at an infinite concentration of borax, (M_1, M_3, and M_u are the molecular weights of water, borax, and monomer unit of PVA, respectively). The value of 0.019 for the $(B_3 - E_3)M_u/M_3$ term is considerably small in comparison to the maximum net binding of borax with PVA (0.03), estimated from the binding isotherms previously obtained.[16] The definitions for binding and experimental conditions were nearly the same as those in the present case except at a finite polymer concentration of about 5×10^{-3} g ml^{-1}.

Although the parameters used here are thermodynamically operational quantities, not reflecting any direct molecular mechanism themselves, the following discussion may be permissible. Generally, a PVA chain in an aqueous media must have many water molecules, which may be hydrated by hydrogen bonds on the OH groups of PVA and hydrophobically hydrated around the chain (iceberg formation).[18–20] These hydrogen bonding and hydrophobic hydrations usually contribute toward a decrease in the partial specific volume of PVA and

to an increase in the present B_1 term. Such hydrated structures of the PVA chain are probably destroyed by the binding of borax to it, and many water molecules liberated from the chain and the surrounding vicinity. This water liberation (dehydration) may fully account for the present very large negative value of the B_1 term. Furthermore, since the actual binding species to the PVA chain seems to be the borate ion rather than borax itself,[21,22] the present PVA chain can behave as a negatively charged polyion when borate ion is bound to it, even though PVA is a typical non-dissociating polymer. Thus, the electrostrictional hydration on the chain due to these charges should be also taken into consideration; this hydration may positively contribute to the B_1 term. However, it is difficult to separate the B_1 value obtained into the respective contributions from various hydrations, since the present ξ_1° is defined as the net hydration. The same situation may also applied to the bonding term of borax, $(B_3 - E_3)$, i.e., a discussion based on the separate B_3 and E_3 terms may be impossible using only the present data. But, it may at least be said that the E_3 term has a positive value smaller than the B_3 term, because of the possible Donnan exclusion owing to the charges on the chain. An experiment on the system containing a large amount of additional neutral salt, where the Donnan effects can be neglected, would be helpful for separating the $(B_3 - E_3)$ term into its respective components. Thus, the observed density characteristics of PVA in a borax solution can be semi-quantitatively interpreted in terms of the net binding of borax and net dehydration on the basis of a simple model consideration, though some speculative discussion may be contained. Furthermore, the thickening of aqueous PVA by borax may be ascribed to the above-mentioned binding of borate ion to the PVA chain, accompanied by changes in the water structures around it.

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