

Polymer 2–Polymer 3 Interactions in Water 1/Polymer 2/Polymer 3 Ternary Systems

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ABSTRACT: The polymer 2–polymer 3 interactions Δb_{23} , for water–poly(ethylene glycol) (PEG)–poly(vinyl alcohol) (PVA), water–poly(*N*-vinylpyrrolidone) (PVP)–PVA, water–dextran (Dex)–PVA, water–pullulan (Pul)–PVA, water–PVP–PEG, water–Dex–PEG, water–Pul–PEG, water–PVP–Dex, water–Pul–PVP system were studied. For only the water–Dex–PVA system, Δb_{23} is positive, but for the other systems negative. This indicates that most polymer pairs have repulsive interactions and are incompatible in water.

KEY WORDS Interaction / Polymer / Compatibility / Incompatibility /

Viscometry is a simple and reliable method to investigate interactions of macromolecules in solution. Using Huggins' plots, the polymer 2–polymer 3 interaction parameter, Δb_{23} was introduced for solvent 1–polymer 2–polymer 3 ternary systems by the method of Krigbaum and Wall.^{1,2} According to Krigbaum and Wall, positive Δb_{23} values indicate attractive interactions and compatibility, whereas negative values repulsive interactions and indicate incompatibility. Here, attractive, repulsive, compatible and incompatible have only relative meaning.

Recently, one of the authors obtained negative Δb_{23} for water 1–polymer 2 (PVA)–polymer 3 (PEG), though the absolute values were small.³ Therefore, it can be inferred that weak repulsive interaction exists between PVA and PEG in water–PVA–PEG system. Suto *et al.*⁴ investigated the viscometric behavior of aqueous solutions of polymer mixtures involving a liquid crystalline polymer, and reported repulsive interactions between hydroxypropyl cellulose (liquid crystalline polymer) and hydroxyethyl cellulose.

In this paper, Δb_{23} were determined for various polymer pairs in water, of poly(vinyl alcohol) (PVA), polyethylene glycol (PEG), poly(*N*-vinylpyrrolidone) (PVP), dextran (Dex), and pullulan (Pul), at various temperatures. Δb_{23} for water–Dex–PVA was positive, and Δb_{23} for the other systems were negative.

EXPERIMENTAL

Materials

The characterization of the water–soluble polymers are shown in Table I. PVA, PEG, and PVP were purified by reprecipitation in water–methanol, benzene–acetone, and water–acetone, respectively. Dex and Pul were used without further purification. The degree of saponification of PVA is 98.5 mol%.

Measurement of Viscosity

Ubbelohde viscometer was used to obtain viscosity. Measurement of viscosity was performed at 10, 20, 30, or 40°C.

The Method of Calculation of Δb_{23}

Polymer 2–polymer 3 interaction parameter, Δb_{23} was calculated as follows.²

$$\frac{(\eta_{sp})_m}{c_m} = [\eta]_m + b_m c_m \quad (1)$$

c_m the total concentration of polymer, $c_m = c_2 + c_3$, and $[\eta]_m$ the intrinsic viscosity of the mixture, theoretically defined as

$$[\eta]_m = [\eta]_2 x_2 + [\eta]_3 x_3 \quad (2)$$

x_i is the weight fraction of polymer *i*. Equation 2 is only valid for non-interacting systems. b_m defines global interactions between all polymeric species

$$b_m = [\sum x_i (b_i)^{1/2}]^2 = x_2^2 b_{22} + 2x_2 x_3 b_{23} + x_3^2 b_{33} \quad (3)$$

interactions of the b_{ii} type may be expressed as

$$b_{ii} = k'_i [\eta]_i^2, \quad (4)$$

k'_i , the Huggins constant of the *i* component.

b_{23} is a complex interaction parameter in which hydrodynamic and thermodynamic interactions as well as possible associations are included. Assuming the absence of thermodynamic interactions of *i*–*i* and *j*–*j* types in the corresponding binary systems

$$b_{23}^* = (b_{22} b_{33})^{1/2}, \quad (5)$$

where superscript * means “theoretical”, b_{23} may be obtained experimentally by insertion in eq 3 of the experimental value previously obtained from eq 1.

$$\Delta b_{23} = b_{23} - b_{23}^* \quad (6)$$

Table I. Characterization of water–soluble polymers

Polymer	Molecular weight (M_w)	Supplier
PVA	77000	Kuraray Co., Ltd.
PEG	20000	Kishida Chemical Co., Ltd.
PVP	40000	Kishida Chemical Co., Ltd.
Dex	60000–90000	Wako Pure Chemical Industries
Pul	200000	Sanwa Denpun Co., Ltd.

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RESULTS AND DISCUSSION

Figure 1 shows η_{sp}/C vs. C for dilute water-Dex-PVA system at 30°C. All Huggins' plots gave straight lines. The intrinsic viscosity $[\eta]$ and Huggins' constant k' were evaluated from the intercept and slope of the plots, respectively. Other $[\eta]$ and k' were evaluated for other polymer pairs in water. Polymer composition dependence of $[\eta]$ and k' for all water 1-polymer 2-polymer 3 systems were obtained. $[\eta]$ and k' , and polymer composition dependence are not shown here. The additivity of $[\eta]$ was obtained in all systems with respect to polymer composition. As the temperature increased, $[\eta]$ decreased for all systems. Therefore, as temperature increased, the random coil of the polymer shrank. k' for all systems gave the curves, and increased with temperature. Therefore, as the temperature increased,

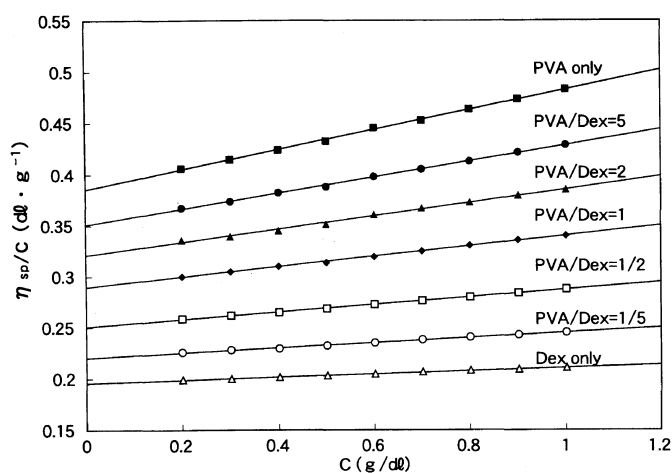


Figure 1. Huggins' plots for the water-Dex(2)-PVA(3) system at 30°C.

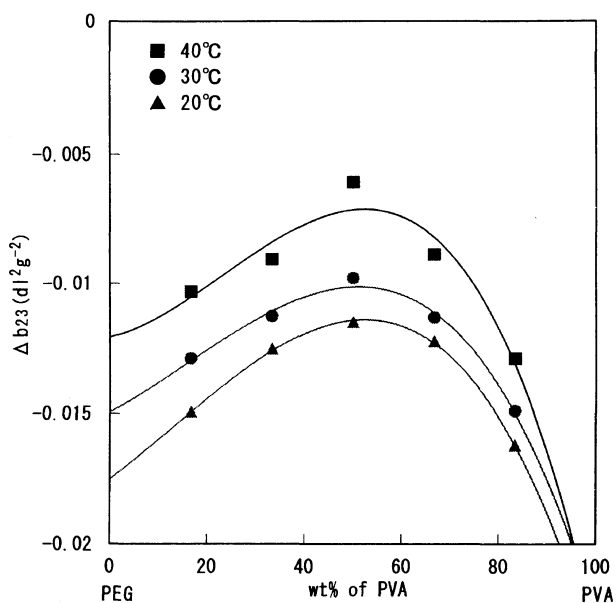


Figure 2. Polymer composition dependence of interactions for the water-PEG-PVA system.

interactions between polymer and polymer, or polymer and solvent increased.⁵

Figures 2–10 show the polymer 2-polymer 3 interaction parameters, Δb_{23} , against polymer content for water-PEG-PVA, water-PVP-PVA, water-Dex-PVA, water-Pul-PVA, water-PVP-PEG, water-Dex-PEG, water-Pul-PEG, water-PVP-Dex, and water-Pul-PVP systems. For only the water-Dex-PVA system, Δb_{23} is positive, but for the other systems Δb_{23} negative. This indicates that most polymer pairs have repulsive interactions and are incompatible, and the water-Dex-PVA system has attractive interactions and shows compatibility. This seems related to the finding in this study that all water-soluble polymer pairs show liquid-liquid phase separations in water.³ There seems to exist domains of polymer 2 or polymer 3. As the temperature increased, only the water-Dex-PVA system showed

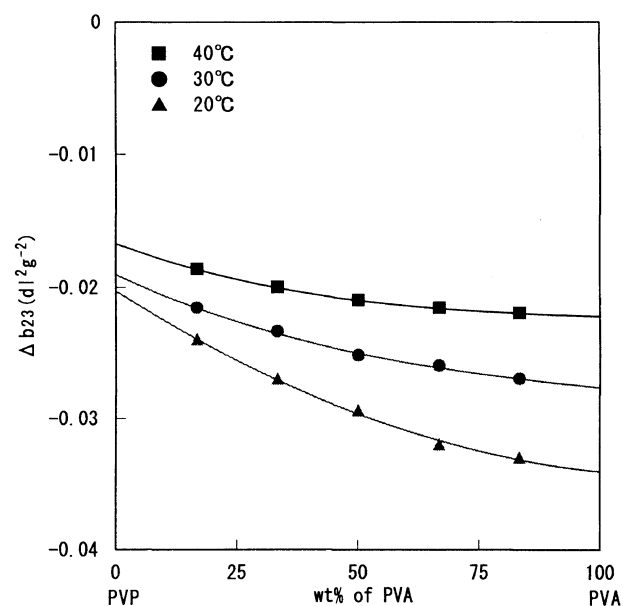


Figure 3. Polymer composition dependence of interactions for the water-PVP-PVA system.

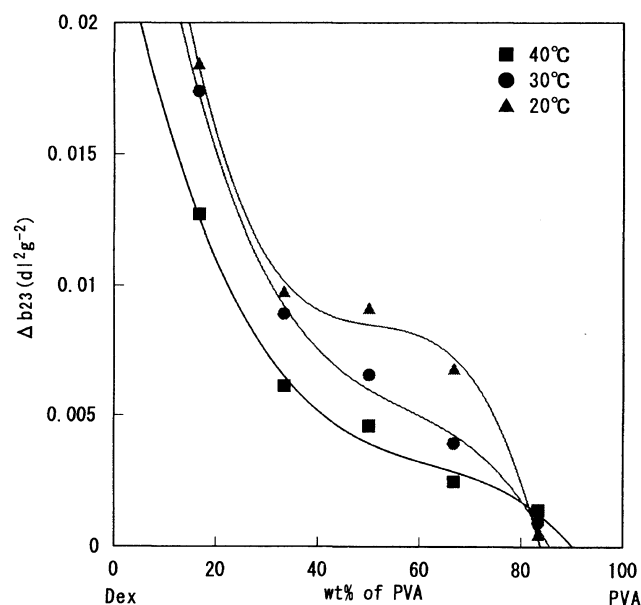


Figure 4. Polymer composition dependence of interactions for the water-Dex-PVA system.

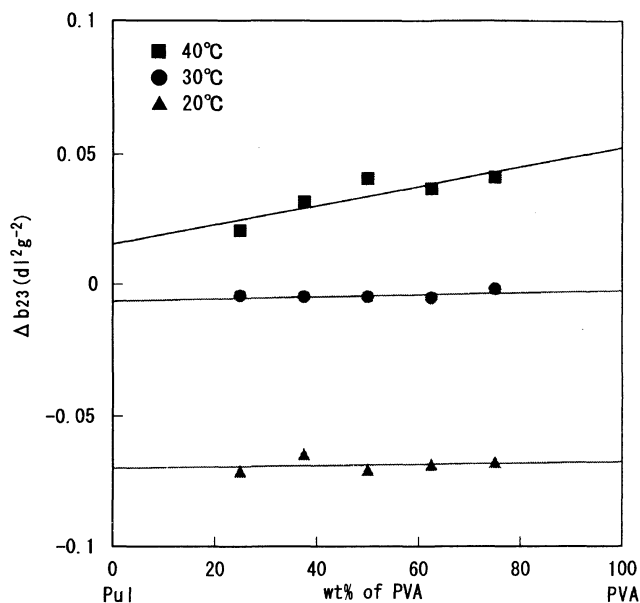


Figure 5. Polymer composition dependence of interactions for the water-Pul-PVA system.

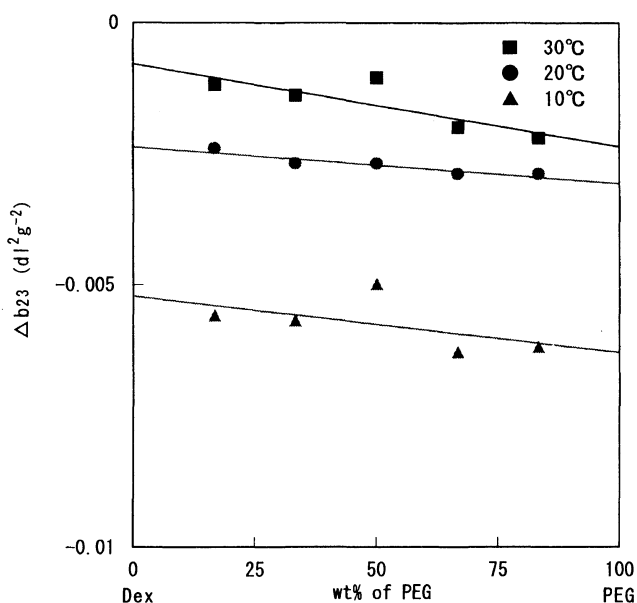


Figure 7. Polymer composition dependence of interactions for the water-Dex-PEG system.

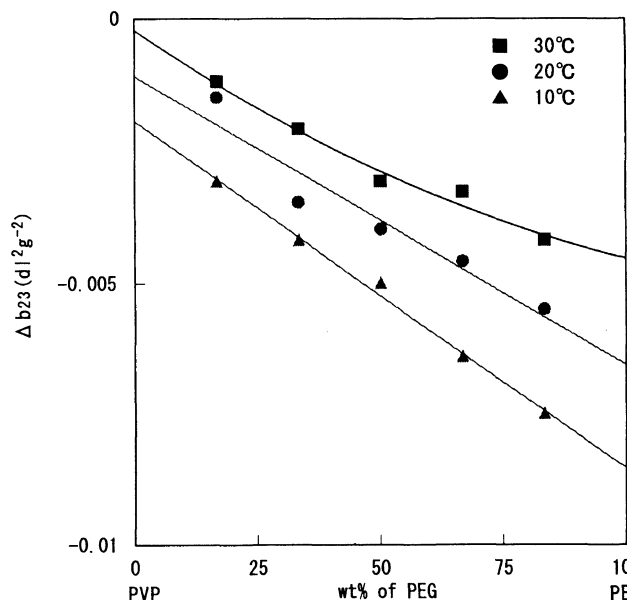


Figure 6. Polymer composition dependence of interactions for the water-PVP-PEG system.

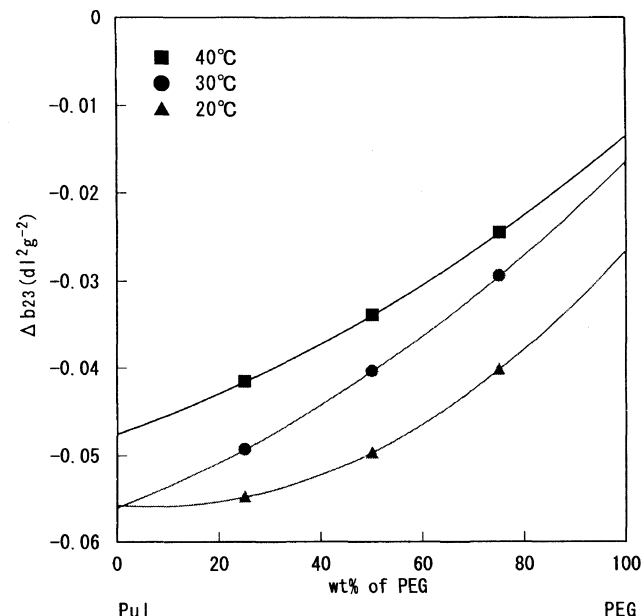


Figure 8. Polymer composition dependence of interactions for the water-Pul-PEG system.

decreased Δb_{23} , but the other systems showed increased Δb_{23} . This indicates that for most listed polymer pairs, as the temperature increased, attractive interactions and compatibility were enhanced. Only for the water-Dex-PVA system, as temperature increased, the repulsive interaction and incompatibility grew. Perhaps, this may be due to more hydrogen bonds between Dex and PVA.⁶ The interactions of hydrogen bonds become weaker as the temperature increases.

Effects of polymer composition on Δb_{23} are stated as follows. For the water-PEG-PVA system as shown in Figure 2, Δb_{23} shows the curve with maximum at 50 wt% of PVA. For the water-PVP-PVA system shown in Figure 3, Δb_{23} decreased as wt% of PVA increased. Therefore, repulsive interactions increase as wt% of PVA increases. For the water-Dex-PVA system shown in Figure 4, Δb_{23} increased as wt% of Dex increased.

Therefore, attractive interactions increase as wt% of Dex increases. For water-Pul-PVA system shown in Figure 5, Δb_{23} shows a straight line. Δb_{23} hardly changed, as wt% of PVA increased. For the water-PVP-PEG system (Figure 6), Δb_{23} shows a straight line. Δb_{23} decreased as wt% of PEG increased. For the water-Dex-PEG system (Figure 7), Δb_{23} shows a straight line. Δb_{23} decreased as wt% of PEG increased. For the water-Pul-PEG system (Figure 8), Δb_{23} shows a curved line. As shown here, Δb_{23} decreased as wt% of Pul increased. For the water-PVP-Dex system (Figure 9), Δb_{23} shows a curved line. Δb_{23} decreased as wt% of PVP increased. For the water-Pul-PVP system (Figure 10), Δb_{23} shows a curve with a maximum at 50 wt% of PVP. Figure 2 and Figure 10 show curves with maximum at 50 wt% of PVA and PVP, respectively. A mixture of

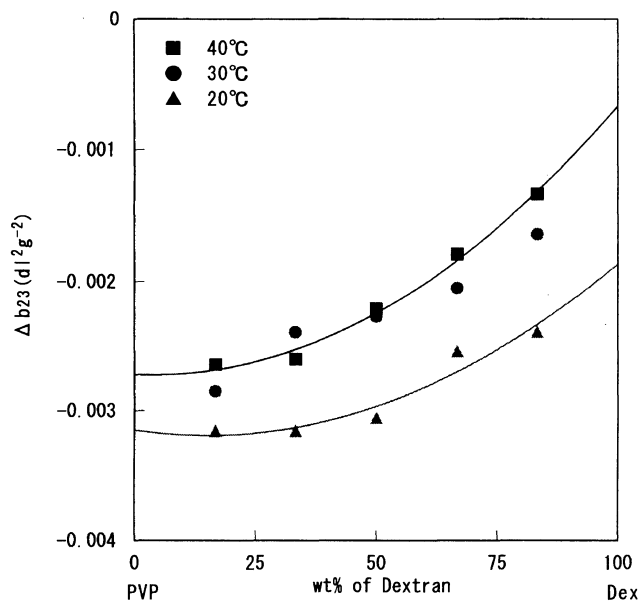


Figure 9. Polymer composition dependence of interactions for the water-PVP-Dex system.

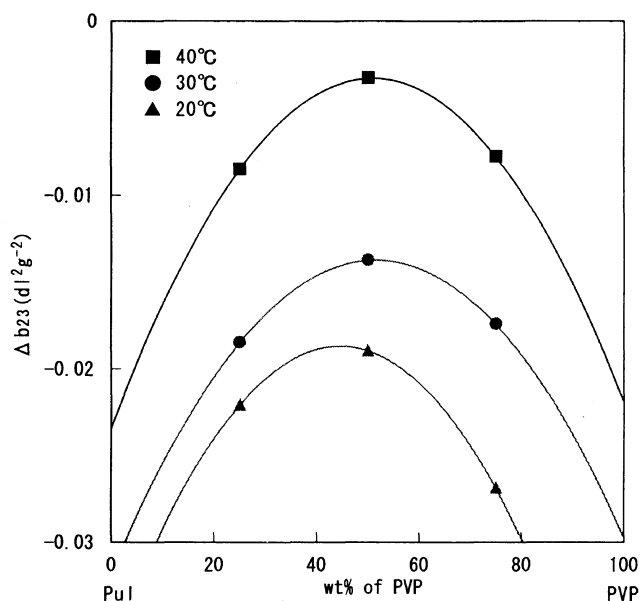


Figure 10. Polymer composition dependence of interactions for the water-Pul-PVP system.

polymers at 1 : 1 enhanced compatibility.

CONCLUSIONS

For only the water-Dex-PVA system, Δb_{23} is positive, whereas for the other systems, negative. This indicates that most polymer pairs have repulsive interactions and show incompatibility.

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