

Notes

Relation between Huggins Constant and Compatibility of Binary Polymer Mixtures in the Aqueous Ternary Systems

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Abstract: We have classified a number of aqueous ternary systems containing two different polymers into three types by focusing on the deviation of the Huggins constant k' from the additivity line. Systems of type I have negative deviations of k' ; the repulsive interaction between the two different polymers dominates. In systems of type II, k' almost follows the additivity relation; the repulsive and attractive interactions between the two different polymers are balancing. Type III systems have positive deviations of k' ; the attractive interactions are relatively dominant. This classification of systems is supported by the fact that the positive and negative deviations of k' from the additivity line also correspond to the sign of interaction parameter between polymer 2 and 3, Δb_{23} . Furthermore, we have verified the relatively high compatibility between dextran and poly(vinyl alcohol) by determining the binodal concentration of a liquid-liquid phase separation for a water/dextran/poly(vinyl alcohol) system, which is classified as type III. Thus, we found that the compositional dependence of k' closely relates to the compatibility of binary polymer mixtures in aqueous ternary systems.

Keywords: Huggins constant, viscosity, compatibility, liquid-liquid phase separation, water-soluble polymer, additivity, attractive interaction, repulsive interaction.

Introduction

When two polymer solutions with the same solvent are mixed, the two different polymers are dissolved each other up to some concentration or cause a liquid-liquid phase separation according to the interaction between two different polymers.^{1,2} This intermolecular interaction is one of significant factors for polymer blending. When the attractive interaction is dominant, the different polymers in blend sample are highly compatible and can be mixed uniformly even in the solid state. Contrary, when the repulsive interaction is dominant, the blend sample causes a micro phase separation which characterizes generally the physical properties of samples.

Recently, we have reported the temperature and composition dependence of the intrinsic viscosity $[\eta]$, the Huggins constant k' , and the interaction parameter between two different polymers Δb_{23} in various ternary systems.³ In the

systems, water was used as a common solvent and two of following water-soluble polymers were blended: poly(ethylene glycol) (PEG), poly(vinyl alcohol) (PVA), poly(*N*-vinylpyrrolidone) (PVP), dextran (Dex), and pullulan (Pul). In high polymer-concentration regions of all the systems, we have observed a liquid-liquid phase separation.⁴⁻⁷

It is well known that k' reflects overall hydrodynamic interactions among polymer chains in solution, whereas Δb_{23} is restricted to the interaction between two different polymer species. A positive or negative sign of Δb_{23} corresponds to the attractive or repulsive interaction, respectively, and its magnitude indicates the strength of interaction.^{8,9} In this paper, the typical results of k' and $[\eta]$ are graphically presented, and the relation between k' and Δb_{23} is detailed. As a result, the aqueous ternary systems investigated so far could be classified into three types by examining whether k' follows the additivity line or not. It has been also found that the composition dependence of k' closely relates to the compatibility between two different polymers in the aqueous ternary systems.

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Table I. Characteristics of Polymer Samples

Sample	$M_w/10^4 \text{ g mol}^{-1}$	M_w/M_n	Supplier
PVP	4.0	-	Kishida Chemical Co., Ltd.
PEG	2.0	1.10	Kishida Chemical Co., Ltd.
PVA	2.4	-	Kuraray Co., Ltd.
Dex	7.5	-	Wako Pure Chemical Industries

Experimental

Materials. The weight-averaged molecular weight M_w of polymer samples used is presented in Table I. PVA, PEG and PVP samples were purified by a reprecipitatorial method using a water-methanol, benzene-acetone and water-acetone mixed solvent, respectively. Due to a probable slight difference in the condition of the reprecipitatorial purification, there exists probably a little difference in M_w value of one of these polymers for each system investigated. Dex was used without further purification. The degree of saponification of PVA sample was 98.5%.

Viscometry. Viscosity measurements for PVP/PVA, PEG/PVA, and Dex/PVA mixed systems were made at 20, 30, and 40°C with a conventional capillary viscometer of the Ubbelohde type. In the evaluation of the intrinsic viscosity $[\eta]$ and the Huggins constant k' , the following three equations were used.

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \quad (1)$$

$$\ln(\eta_{sp} + 1)/c = [\eta] + \left(k' - \frac{1}{2}\right)[\eta]^2 c \quad (2)$$

$$\{2[\eta_{sp} - \ln(\eta_{sp} + 1)]\}^{1/2}/c = [\eta] + \left(k' - \frac{1}{3}\right)[\eta]^2 c \quad (3)$$

Eq. (1) is well known as the Huggins formula, and eq. (2) and eq. (3) are the derivative formula by Mead-Fuoss and Billmeyer, respectively.

Determination of Δb_{23} . Interaction parameter Δb_{23} between polymer 2 and polymer 3 in the ternary solution was calculated as follows.⁹

The specific viscosity of binary polymer mixtures was expressed as

$$(\eta_{sp})_m/c_m = [\eta]_m + b_m c_m \quad (4)$$

Here $(\eta_{sp})_m$ and c_m denote the specific viscosity and total mass concentration of the mixed polymer solution, respectively, and $[\eta]_m$ is the intrinsic viscosity of the mixture which is theoretically defined as

$$[\eta]_m = [\eta]_2 w_2 + [\eta]_3 w_3 \quad (5)$$

where $[\eta]_i$ is the intrinsic viscosity of binary solution of

polymer i and w_i is the weight fraction of i component of polymer in the mixture. The quantity b_m is defined as total interactions between all polymeric species and represented as⁹

$$b_m = \left[\sum w_i (b_i)^{1/2}\right]^2 = b_{22} w_2^2 + 2b_{23} w_2 w_3 + b_{33} w_3^2 \quad (6)$$

with

$$b_{ii} = k'_i [\eta]_i^2 \quad (7)$$

where k'_i is the Huggins constant of the i component.

It is known that b_{23} is a complex interaction parameter in which hydrodynamic and thermodynamic interactions as well as possible other interactions are included. Assuming the absence of thermodynamic interactions of $i-i$ and $j-j$ types in the corresponding binary systems, we can evaluate the intermolecular interactions of the $i-j$ type as

$$b_{23}^* = (b_{22} b_{33})^{1/2} \quad (8)$$

where superscript * means "theoretical". Value of Δb_{23} can be obtained by subtracting the calculated value of b_{23}^* from the value of b_{23} experimentally obtained by eq. (6).

$$\Delta b_{23} = b_{23} - b_{23}^* \quad (9)$$

Liquid-Liquid Phase Separation. The binodal concentration of a liquid-liquid phase separation for water/Dex/PVA system was determined according to the method previously reported by us.⁷

Results and Discussion

Intrinsic Viscosity. The lower sides of Figures 1 through 3 show results of the polymer-composition and temperature dependence of $[\eta]$ for water/PVP/PVA, water/PEG/PVA, and water/Dex/PVA system, respectively. It is seen in these figures that $[\eta]$ follows each additivity line of eq. (5), which was also observed in all systems examined.³ This result seems to be reasonable because $[\eta]$ reflects the hydrodynamic volume of a single polymer chain at infinite dilution where any intermolecular interactions vanish. In addition, $[\eta]$ becomes small as the temperature increases. This behavior was also observed in all systems examined.³ It may be caused by a reduction in the amount of hydration around a polymer chain. Discussion about this assignment is given in the reference of [6].

Huggins Constant. k' becomes large with increasing temperature for all systems investigated,³ as demonstrated in the upper side of Figures 1-3. This suggests that overall attractive interactions among polymers in solution become strong as the temperature increases. Cragg *et al.*¹⁰ also mentioned that the attractive interaction among polymers in solvent 1/polymer 2/polymer 3 ternary systems became

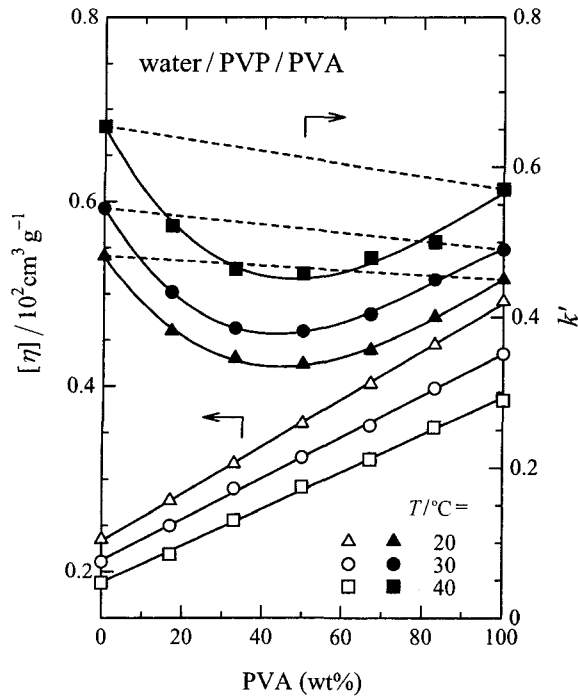


Figure 1. Polymer-composition and temperature dependence of $[\eta]$ (unfilled symbols) and k' (filled symbols) for water/PVP/PVA system. Broken lines indicate the additivity line of k' calculated by eq. (10).

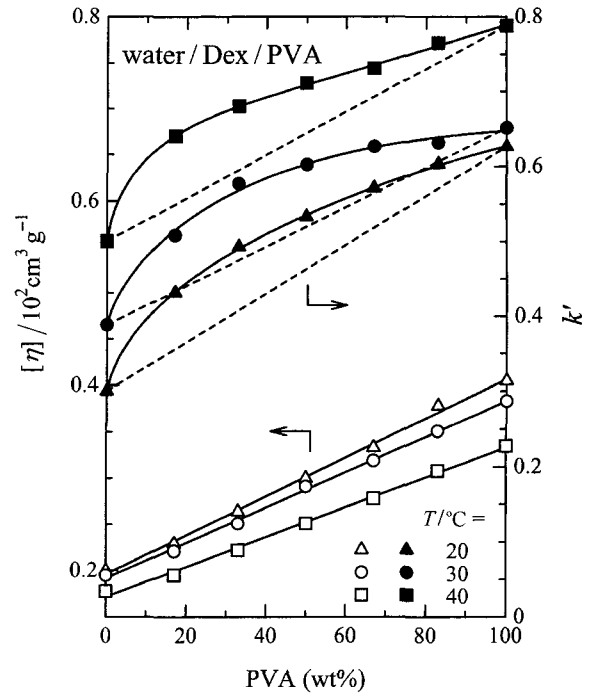


Figure 3. Polymer-composition and temperature dependence of $[\eta]$ and k' for water/Dex/PVA system. Symbols are the same as used in Figure 1.

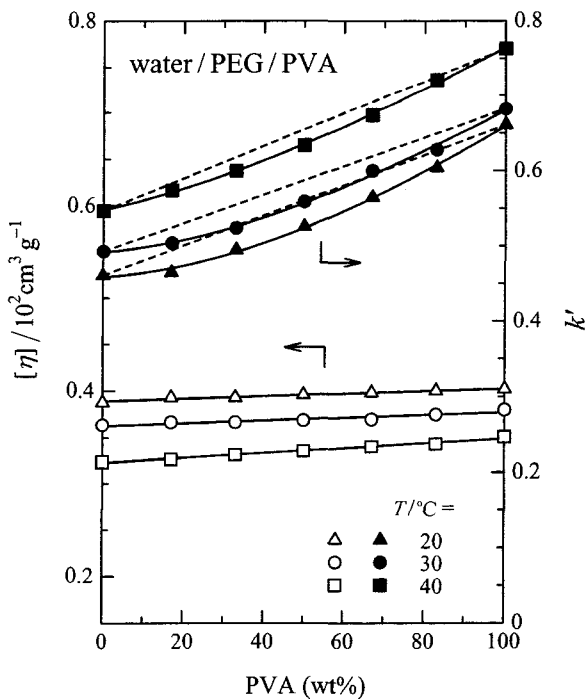


Figure 2. Polymer-composition and temperature dependence of $[\eta]$ and k' for water/PEG/PVA system. Symbols are the same as used in Figure 1.

strong as the temperature increases.

However, It is well known that behaviors of k' for multi-component systems are so sophisticated that any appropriate molecular theory has not been developed so far to explain experimental results of k' . It is considered that k' should be influenced by the following factors; the conformational change of each polymer chain with mixing, the thermodynamic or hydrodynamic interactions among polymers, the structural change of hydration or solvation, and so on.

Therefore, we have tried to explain the k' behaviors phenomenologically by focusing on deviation of k' from the additivity line, which is simply calculated by

$$k' = k'_2 w_2 + k'_3 w_3 \quad (10)$$

and drawn by broken lines in all figures. When the attractive interaction between two different polymer chains plays an important role, specific viscosity η_{sp} at a finite concentration will take a relatively large value compared with the non-interacting state where the additivity of k' holds, which brings larger values of k' . On the contrary, the repulsive interaction will bring smaller values of k' . Here, it can be assumed that the strength of interaction between the same polymer species should always take the constant value regardless of polymer-mixing composition. Therefore, the positive and negative deviation of k' from the additivity line should reflect indirectly the attractive and repulsive interaction between two

different polymers, respectively, as the positive and negative sign of Δb_{23} do.

Focusing on the deviation of k' from the additivity line, we could classify all ternary systems investigated³ into following three types.

Type I: k' deviates negatively from the additivity line as illustrated in Figure 1. In this Figure, the typical result for water/PVP/PVA system at 20, 30 and 40 °C belonging to type I is shown. The deviation of k' from the additivity line comes up to 21%. Besides the binary mixture of PVP/PVA, the following polymer mixtures in water belonged to Type I: PVP/PEG at 10, 20 and 30 °C; Dex/PEG at 10, 20 and 30 °C; PVP/Dex at 20, 30 and 40 °C; Pul/Dex at 20, 30 and 40 °C; Pul/PEG at 20, 30 and 40 °C; Pul/PVP at 20 and 30 °C; Pul/PVA at 20 °C. In these systems, Δb_{23} had negative values at any polymer composition.³ This result means that the attractive interaction between two different polymers is relatively weak and the repulsive interaction becomes dominant. It is also expected that the aqueous ternary solutions of type I easily cause a liquid-liquid phase separation at high concentration regions. Thus, the compatibility between two different polymers in these solutions is expected to be low.

Type II: k' coincides with the additivity line. In Figure 2, the result for water/PEG/PVA system are given as an example, although k' only slightly deviates from the additivity line (2~6%). The following polymer mixtures in water belonged to type II: PEG/PVA at 20, 30 and 40 °C; Pul/PVA at 30 °C, and Pul/PVP at 40 °C. In these systems, although Δb_{23} was still negative, its absolute values were fairly close to zero.³ It can be considered, therefore, that in these systems the attractive and repulsive interaction between two different polymers are almost balancing and then each polymer is unperturbed by mixing. In the systems of type II, the compatibility is expected to be intermediate.

Type III: k' deviates positively from the additivity line as demonstrated in Figure 3. Here the results for water/Dex/PVA system are shown. The deviation of k' from the additivity line extends to 19%. The following polymer mixtures in water belonged to type III: Dex/PVA at 20, 30 and 40 °C; Pul/PVA at 40 °C. These systems had positive Δb_{23} values.³ In these systems, the attractive interaction between two different polymers is rather strong compared with the other polymer pairs. The compatibility between two different polymers in these systems is expected to be relatively high. It may be caused by the formation of effective hydrogen-bond between two different polymers through hydroxyl groups of monomers.

In addition, water/Dex/PVA system showed a unique temperature dependence of Δb_{23} .³ Δb_{23} became small as the temperature increased, contrary to the other systems where it became large with increasing temperature. Therefore, the attractive interaction between Dex and PVA and then the compatibility between them are expected to weaken as the

temperature increases. Such a unique temperature dependence of Δb_{23} is well explained by the temperature dependence of strength of hydrogen bond. Here, it is very interesting to note that k' does not show a unique temperature dependence in water/Dex/PVA system, compared with the other systems.

Also, the following two systems studied by Suto *et al.*¹¹ belong to type III: water/PVP/hydroxypropyl cellulose system and water/glucose/hydroxypropyl cellulose system. In these systems, k' deviated positively from the additivity line, while Δb_{23} was positive and it weakened with increasing temperature.

Compatibility between Dex and PVA. From the above results, it is expected that the compatibility between Dex and PVA is relatively high among the polymer pairs investigated.³ In deed, we could verify in the present work the relatively high compatibility by determining the binodal concentration of a liquid-liquid phase separation for water/Dex/PVA system. A value of 19.9% for the binodal concentration of the polymer mixture (weight ratio Dex/PVA = 1) was obtained. This concentration is rather high compared with those for the other aqueous ternary systems containing Dex or PVA with a similar molecular weight M_w and the same degree of saponification of PVA.^{4,6,12} Therefore, this result suggests the relatively high compatibility between Dex and PVA. We have also found, in the above experiment, that at higher temperature the aqueous solution of Dex/PVA tends to cause more easily a liquid-liquid phase separation. This tendency seems to be consistent with the argument, noted in type III section, that the compatibility between Dex and PVA is expected to weaken with increasing temperature.

Conclusions

The values of $[\eta]$ always coincided with the additivity line, and they became small as the temperature increased. Focusing on the deviation of k' from the additivity line, we could classify a number of aqueous ternary systems into following three types. Type I: negative deviation of k' ; the repulsive interaction works between two different polymers, and the compatibility between them is relatively low. Type II: additivity of k' holds; each of two different polymers exists as an unperturbed state after mixing, and the compatibility is intermediate. Type III: positive deviation of k' ; the attractive interaction works between two different polymers, and the compatibility is relatively high. Such a classification is supported by the fact that the positive and negative deviation of k' from the additivity line just corresponded to the sign of Δb_{23} . The relatively high compatibility between Dex and PVA was verified by determining the binodal concentration of a liquid-liquid phase separation for water/Dex/PVA system. Hereafter, one can easily judge the compatibility of binary polymer mixtures in the aqueous ternary systems by examining the composition dependence of k' .

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