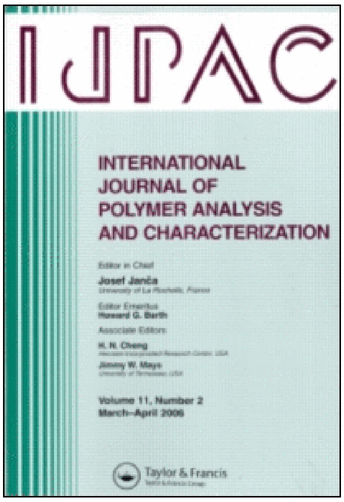

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Věra Halabalová[a]; Lubomír Šimek[a]
[a] Faculty of Technology, Tomas Bata University, Zlín, Czech Republic

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A Study of Blends of Amphiphilic Polymers in Solution

Věra Halabalová and Lubomír Šimek
Faculty of Technology, Tomas Bata University, Zlín, Czech Republic

Abstract: The viscometric coefficient, k_{AB}, characterizing the interaction of chemically dissimilar polymer segments was estimated from changes of the intrinsic viscosity of poly(vinyl alcohol) (PVA) measured in "pseudo-solvents," i.e., dilute solutions of poly(ethylene glycol) (PEG) in water and dimethyl sulfoxide (DMSO). The results provide evidence of the compatibility of these polymers in both solvents. The effects of hydroxyl end groups and the character of solvents has been found. The aggregation of PVA molecules in water is not significantly suppressed by PEG.

Keywords: Compatibility; Intrinsic viscosity; Huggins coefficient; Interaction parameter; Poly(vinyl alcohol); Poly(ethylene glycol); Amphiphilic polymer

INTRODUCTION

The study of the solution properties of polymer mixtures is interesting for several reasons. First, polymer blends are often processed in solutions and then concentrated by evaporation. Dissolving polymer mixtures in a good solvent is a convenient way of mixing immiscible components. The properties of the mixtures can be greatly influenced by the structure of polymer coil formed in solution in dependence on processing conditions. Therefore, an understanding of the solvent-mediated interactions

Address correspondence to Věra Halabalová, Faculty of Technology, Tomas Bata University, TGM 275, 762 72 Zlín, Czech Republic. E-mail: halabalova@ft.utb.cz

between unlike monomers is of great interest. Second, polymers are often synthesized in solution. The polymerizing mass itself is a polymer mixture, containing both reactive growing chains and nonreactive "dead" chains, together with small molecules, such as solvent, nonreacted monomer, and inhibitors.

Information on compatibility is thus necessary in modeling the reaction kinetics. Third, in the dilute solution, the effects of interactions can be investigated between a relatively small number of coils. In addition, the time range of solution properties measurements is usually short. The obtained information can be a good base for the estimation of properties of concentrated polymer mixtures.

Several solution methods have been focused so far on finding a suitable procedure to obtain Flory-Huggins parameter, χ_{AB}, characterizing the interaction between different polymers.[1–12] As most of them are time consuming, a simple viscometric method has been proposed.[13–15] It is referred to as the method of "polymeric solvents or pseudo-solvents." The intrinsic viscosity, $[\eta_A]_B$, of polymer A is measured in mixed solvents consisting of a low-molecular weight solvent and polymer B in various concentrations, c_B. The interaction is characterized by coefficient k_{AB} evaluated from the dependence of $[\eta_A]_B$ versus $[\eta_B]c_B$ or, more precisely, as $k_{AB} = \text{slope}/2$ from the slope of the plot of $p^*(\eta_r)_B$ versus $[\eta]_B c_B$, where $p^* = [\eta_A]_B/[\eta_A]$. The symbol $(\eta_r)_B$ stands for the relative viscosity of the pseudo-solvent, $[\eta_A]_B$ is the intrinsic viscosity of polymer A in the pseudo-solvent, and $[\eta_A]$ and $[\eta_B]$ are, respectively, the intrinsic viscosities of polymer A and polymer B in the low-molecular weight solvent. A necessary condition for good estimation of the coefficient k_{AB} is the linearity of the above plot.

The coefficient k_{AB} is an analogy to the Huggins coefficient, k_H, which is frequently used in studies of binary systems. While the latter reflects the interaction of two molecules of the same polymer, the former is characteristic of the interaction of two molecules of polymers A and B.

The Huggins coefficient contains contributions from the hydrodynamic and thermodynamic interactions. Since under Θ-conditions, the thermodynamic contribution vanishes, the value $k_H = 0.5$ may be associated with the hydrodynamic interaction. Under Θ-conditions, polymer molecules can overlap without restriction. As the thermodynamic quality of the solvent improves, the overlapping is reduced due to the domination of "repulsive" interactions and manifests itself in a decrease of the k_H to values lower than 0.5. Below the Θ-temperature, the attractive interactions prevail and the Huggins coefficient becomes larger than 0.5.

In the analogy with the Huggins coefficient, the k_{AB} parameter will probably be dependent on the solvent. There is no theory for this parameter, and so the same picture is accepted for unlike polymer molecules.[14]

The method of pseudo-solvents has been applied to a variety of systems.[13–15] Most of them consisted of nonpolar or weakly polar polymers. No systematic study, however, has been devoted to amphiphilic polymer containing hydrophobic and hydrophilic groups, where complicated interactions can be expected at various concentrations. The pair poly(vinyl alcohol) (PVA) and poly(ethylene glycol) (PEG) is an example of such a system. The studies of phase equilibria performed by Inamura and coworkers[16–18] confirm this hypothesis.

In this work, water and dimethyl sulfoxide (DMSO) were used as low-molecular weight solvents, PVA was polymer A, and three samples of PEG (molecular weights 300, 1000, and 6000 g/mol) with different molecular weights were used as polymer B. The purpose of the study was to estimate the k_{AB} coefficient and its dependence on the solvent and molecular weight of PEG. Such effects have not been observed with nonpolar polymers but may be expected with systems where hydrogen bonds and hydrophobic interactions occur.

The following rules have been deduced from preceding articles:[13–15]

(1) If $k_{AB} < 0.5$, the intrinsic viscosity of polymer A in the "pseudosolvent" is a decreasing function of $[\eta_B]c_B$. If $k_{AB} > 0.5$, the dependence exhibits a maximum.
(2) Incompatibility (repulsive interaction) of chemically dissimilar polymer segments is indicated by $k_{AB} < 0.5$. If $0.5 < k_{AB} < 0.6$, the segments are compatible. The values of $k_{AB} >> 0.6$ indicate stable polymer complexes.

The accuracy of the k_{AB} parameter is not high. On the other hand, the k_{AB} values can give rough qualitative information about the interaction of dissimilar polymers, and values lying above 0.5 are a good indication of compatibility of polymers.

EXPERIMENTAL SECTION

Materials

Poly(vinyl alcohol) (PVA), polymer A, Sloviol P9805, and poly(ethylene glycol) (PEG), polymer B, with average molecular weights 300, 1000, and 6000 g/mol were provided by Chemické závody (Nováky, Slovak Republic). The number of acetate groups in PVA is determined by the degree of hydrolysis (98.3 mol%). Dimethyl sulphoxide (DMSO) and distilled water were used as solvents.

Table I. Concentration of polymer solvent

Polymer	Solvent	Concentration [g/dL]
PEG 6000	Water	1, 2, 3, 4, 5
PEG 1000	Water	2.5, 5, 7.5, 10, 13
PEG 300	Water	5, 7.5, 10, 12.5, 15
PEG 6000	DMSO	0.5, 1, 2, 3, 4, 5
PEG 1000	DMSO	5, 10, 15, 20, 30
PEG 300	DMSO	2.5, 5, 7.5, 10, 15

Preparation of Solutions

Solutions used in the viscosity measurements were prepared in the following way. Polymer B, whose solution was used as the "polymer solvent," was dissolved to give a series of solutions having different concentrations, c_B (Table I).

Stock solutions of PEG were prepared by heating samples with DMSO or distilled water for 1 h at 90°C in volumetric flasks. After dissolution and filtration through a glass filter (S2), the second polymer, A (concentration $c_A = 1\,g/dL$), was dissolved in this "polymer solvent" by shaking for 2 h. Then the mixture was left standing for 24 h at room temperature and heated again for 1 h at 90°C.

Viscometry

The relative viscosity, η_r, of solutions was measured at 25 ± 0.05°C in Ubbelohde capillary viscometers adapted for subsequent dilutions. The intrinsic viscosity, $[\eta_A]_B$, and Huggins coefficient, k_H, were calculated from viscosities measured for given systems polymer A-polymer B-solvent, each at five polymer B concentrations, c_B. The data $\{[\eta(c_A, c_B) - \eta(c_B)]/\eta(c_B)c_A\}_{\text{fixed}c_B}$ are extrapolated to $c_A = 0$ to obtain $[\eta_A]_B$. The Huggins coefficient, k_H, is derived from this dependence in the usual way. The Heller method was used to estimate the intrinsic viscosities.[13–15] Plots of reduced viscosity values against concentration were linear for all samples, with correlation coefficients of 0.99.

RESULTS AND DISCUSSION

System PVA–PEG–DMSO

As can be seen in Figure 1 the plots of $[\eta_A]_B$ versus $[\eta_B]c_B$ exhibit the maxima. The sharpest maximum is found with PEG 6000, followed by

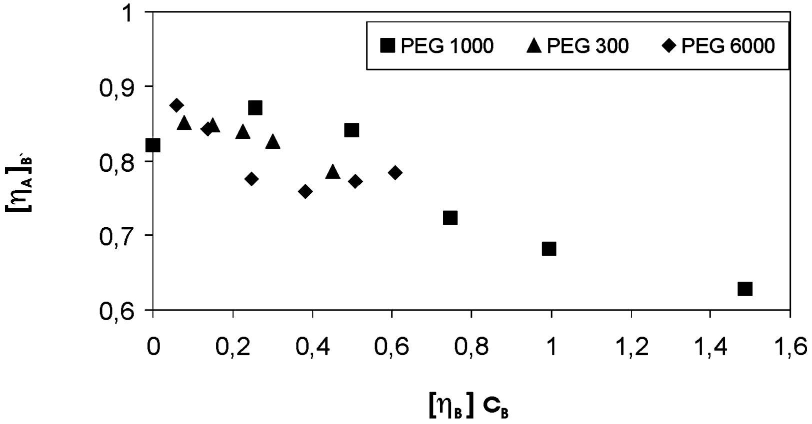

Figure 1. Variation of intrinsic viscosity $[\eta_A]_B$ of PVA with composition of pseudo-solvents PEG-DMSO.

a shallow minimum. For other systems, PEG 300 and PEG 1000, no minimum was found. The maximum is an indication of $k_{AB} > 0.5$, i.e., of the compatibility of units of PVA and PEG. This is at variance with the results of the study by Inamura and coworkers.[16–18] The differences can be attributed to the solvent effect on this interaction.

Figure 2 represents a "sensitive" plot of experimental data. Data for samples PEG 300 and 1000 lie on the same line with slope 1.23,

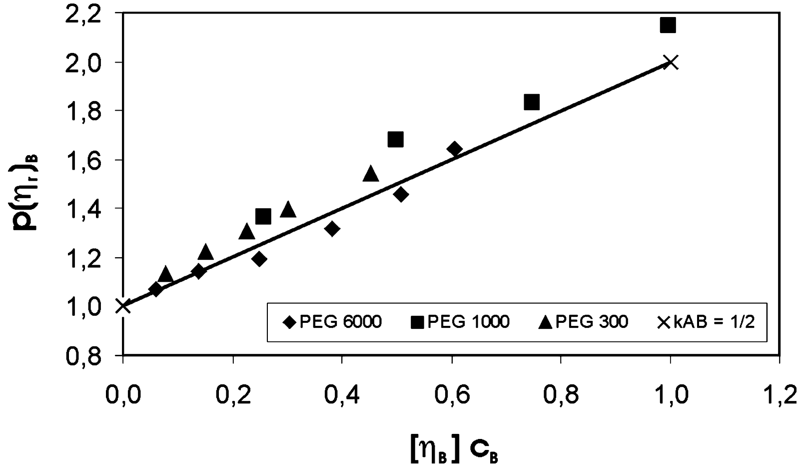

Figure 2. Estimation of interaction coefficient k_{AB} for PVA and PEG from the results presented in Figure 1. The straight line corresponds to $k_{AB} = 0.5$.

which corresponds to $k_{AB} = 0.61$ and indicates a favorable compatibility interaction. The slope ($s = 0.9$) and the interaction coefficient ($k_{AB} = 0.45$) for PEG 6000 are lower. The samples differ in the molecular weight and in the content of hydroxyl end groups. The mole fraction of these groups is high (0.24) in PEG 300, lower (0.08) in PEG 1000, and very low (0.014) in PEG 6000. The difference in values of k_{AB} can be attributed to the effect of end groups. Their interaction with OH groups of PVA is probably stronger than the interaction of PEG units.

System PVA–PEG–Water

The plots of $[\eta_A]_B$ versus $[\eta_B]c_B$ (Figure 3) are almost identical for all systems with PEG samples of different molecular weights. They differ from Figure 1 in that the maximum is almost unnoticeable and the decreasing branches of the plots are less steep. In view of the scatter of data points in Figure 4, the slope s and the coefficient k_{AB} cannot be estimated with the same precision as with the solutions in DMSO. Lower precision is due to experimental difficulties (foaming of aqueous solutions of PVA). Nevertheless, the interaction coefficient is $0.5 < k_{AB} < 0.6$ and shows that these polymers are compatible in water.

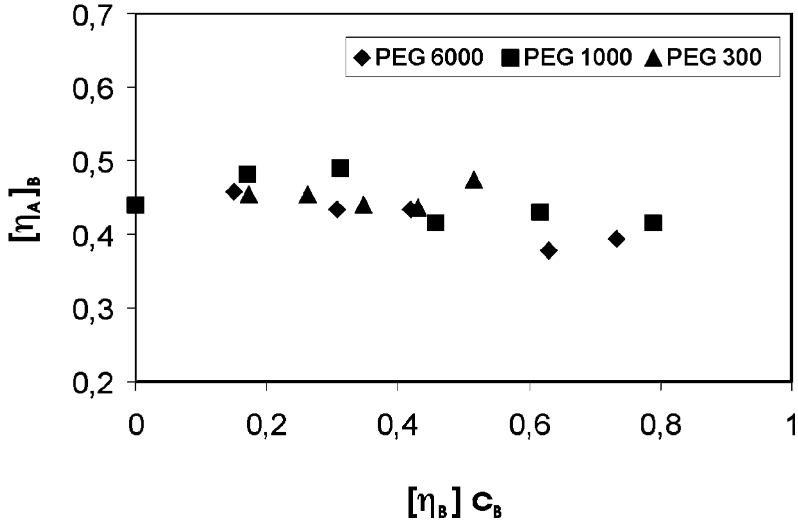

Figure 3. Variation of intrinsic viscosity $[\eta_A]_B$ of PVA with composition of pseudo-solvents PEG–water.

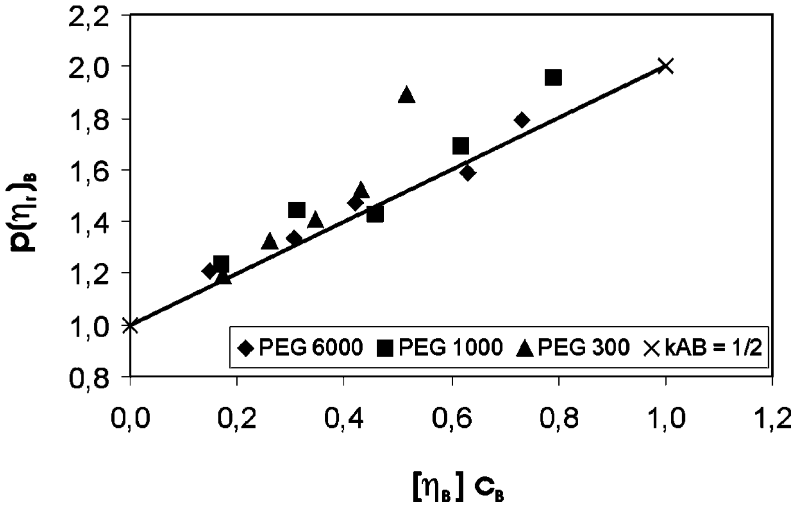

Figure 4. Estimation of interaction coefficient k_{AB} for PVA and PEG from the results presented in Figure 3. The straight line corresponds to $k_{AB} = 0.5$.

Huggins Coefficient k_H

Figure 5(a), (b) represents a plot of the Huggins coefficient k_H of ternary solutions versus $[\eta_B]c_B$. The precision of these values is lower than that of the intrinsic viscosity. This explains the scatter of data points. Nevertheless, two differences between the plots for solution in DMSO and water can clearly be seen. The k_H values in the former solvent (Figure 5(a)) are in range 0.24–0.35 and are similar to the value for PVA in DMSO. Although water is also a good solvent for PVA, the Huggins coefficient is higher ($k_H = 0.54$). This is a consequence of aggregation of PVA chains. The dependence presented in Figure 5(b) for this system has a decreasing trend. The PEG molecules seem to limit the degree of aggregation of PVA molecules.

Staszewska and Bohdanecký[14] investigated the system polyacrylamide–polyvinylalcohol–water. The value $k_{AB} = 0.28$ was slightly lower than the k_H of polyacrylamide in water (0.3–0.32) and considerably lower than the value for polyvinylalcohol (0.45–0.5). They found that the k_{AB} values are close to the value of the Huggins coefficient for polymer in good solvent systems.

In contrast to the findings obtained by the above mentioned authors, we have estimated for the system PVA–PEG–water the value of k_{AB} in the range 0.5–0.6 for different molar weights of PEG. The value of k_H of PVA in water, 0.54, lies in the same range as the value k_{AB} and k_H values of PEG of 300, 1000, 6000 g/mol in water were slightly lower or

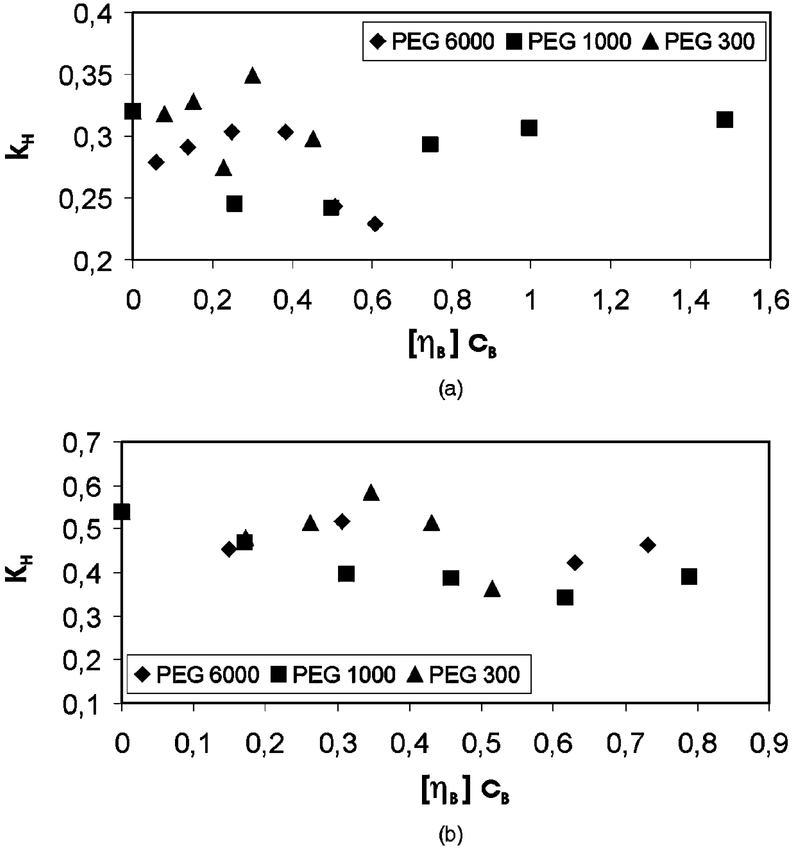

Figure 5. Huggins coefficient k_H of ternary systems PVA–PEG–DMSO (a) and PVA–PEG–water (b).

higher (0.45–0.65) than k_{AB} of this system. As can be seen from these measurements, the k_{AB} values are close to the value of the Huggins coefficient. The data obtained by viscosimetric method can thus be useful for the estimate of the compatibility of the polymer mixtures in solution.

CONCLUSION

The results of this study show that PVA and PEG in dilute solutions in DMSO and water exhibit compatibility interactions. The values of the interaction coefficient in water ($0.5 < k_{AB} < 0.6$) are independent of the molecular weight of PEG. In DMSO, the value is higher ($k_{AB} = 0.6$) in solutions of PEG 300 and 1000 than in solutions of PEG 6000

($k_{AB} = 0.45$). The difference is attributed to the effect of hydroxyl end groups. The values of the Huggins coefficient k_H are systematically higher in water and aqueous pseudo-solvent than in DMSO and pseudo-solvent solutions containing DMSO. This is explained by the aggregation of PVA molecules in aqueous media.

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