

Miscibility Studies on Poly(Ethylene Glycol)/Dextran Blends in Aqueous Solutions by Dilute Solution Viscometry

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Received 5 March 2004; accepted 25 April 2004

DOI 10.1002/app.20871

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Miscibility of poly(ethylene glycol) (PEG) with dextran (Dx) was investigated by dilute solution viscometry. Dilute solution viscosity measurements were made on ternary systems, polymer (1)/polymer (2)/solvent (H_2O), for four different average molecular weights of PEG and Dx. The intrinsic viscosity and viscometric interaction parameters were experimentally measured for the binary (solvent/polymer) as well as for the ternary systems by classical Huggins equation. Degree of miscibility of these polymer systems was estimated on the basis of the four following criteria: (1) the sign of the Δk_{AB} , (2) the sign of α , (3) the sign

of ΔB , and (4) the sign of the μ . Based on the sign convention involved in these criteria, immiscibility was observed in most systems. The miscibility of all these systems in accordance with the interactions between the unlike polymer chains rather than the polymer-solvent interactions were investigated depending on molecular weight of polymer sample. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 453–460, 2004

Key words: viscosity; hydrophilic polymers; miscibility; dextran

INTRODUCTION

In search of new polymeric materials, either new monomers are polymerized or copolymerization technique is used to tailor-make a new product. An alternative method has been to blend existing polymers to produce materials with desired properties. An obvious advantage of this approach is that it usually requires little or no extra capital expenditure relative to new polymers. It is also possible to produce a range of materials with properties completely different from those of the blend constituents.¹

The miscibility between the constituents of polymer mixture is an important factor in the development of new materials based on polymeric blends. In recent years, blends of homopolymers with graft copolymer have assumed importance as toughened plastics.² However, two components in a polymer-polymer blend are in general not miscible. In addition to the similarity in chemical structure, miscibility^{3–4} may arise from specific interactions, such as hydrogen bonding,⁵ dipole-dipole forces,⁶ and charge transfer complexes⁷ for homopolymer mixtures or segment-segment repulsion inside the blends. However, due to very small entropy gain in mixing long polymer chains and because of the usually encountered posi-

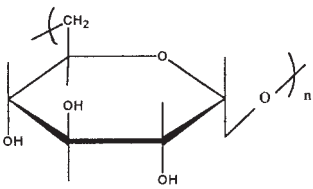
tive heat of mixing, most polymer blends form two phases.

Miscibility is defined as the ability to be mixed at a molecular level to produce one homogenous mixture. The miscible polymeric blends are those which satisfy the thermodynamic criteria for a single-phase system. (i.e., free energy of mixing ΔG is negative).

The majority of known polymeric mixtures are immiscible; however, several miscible polymer blends were found in the last three decades. The miscibility of polymer blend is calculated theoretically as well as being estimated experimentally by dynamic mechanical, thermal, electron-microscopic, neutron scattering, spectroscopic, and viscometric techniques.^{1–8} Because of its simplicity, viscometry is an attractive and very useful method for studying the miscibility of the polymer blends.⁸ Additional advantages (i.e., that no sophisticated equipment is necessary and that the crystallinity or the morphological states of the polymer blends do not affect the result) make the viscometric more convincing for characterizing polymer mixtures. Also, the retarded diffusion of polymers in the solid state makes it difficult to attain a condition of true thermodynamic equilibrium and so the behavior of a polymer mixture in solution is the best method of assessing the miscibility.^{9,10} In addition, dilute solution viscometry method provides information about both polymer-polymer interactions and polymer solvent interactions in solution. The effectiveness of dilute solution viscometry method is based on the as-

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TABLE I
Structures of Polymers Used

Polymer	Structure
Dextran (Dx)	
Poly(ethylene glycol) (PEG)	OH-(CH ₂ -CH ₂ -O)- _n H

sumption that mutual interactions of macromolecules in solution have a great influence on the viscosity in the ternary systems. A lot of work has been reported on systems involving neutral or uncharged polymers in organic solvents, complex mixtures of polymers and microemulsions, neutral and water-soluble polymers in water, and mixtures of polyanions in aqueous solvents.¹¹⁻¹⁴

In this study, four different average molecular weight poly(ethylene glycol) and dextran polymer samples were selected to examine these pairs of miscibility.

THEORETICAL

Miscibility parameters obtained by dilute solution viscometry and derived from the classical Huggins equation¹⁵ are given by

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

where η_{sp} is the specific viscosity of a single-solute solution, c is the mass concentration, $[\eta]$ is the intrinsic viscosity, and b is related to the Huggins coefficient k by

$$b = k[\eta]^2 \quad (2)$$

where b is believed to reflect the binary interactions between polymer segments. Huggins coefficient is a measure of the interpenetration of polymer coils, the extent of which depends upon the segment-segment and segment-solvent interactions. This, in turn, affects

the intermolecular hydrodynamic interaction and the molecular dimensions. Krigbaum and Wall¹⁶ derived an expression for the ideal mixture viscosity by redefining η_{sp} in the classical Huggins equation as

$$\eta_{sp,m} = [\eta]_m c_m + b_m c_m^2 \quad (3)$$

where $[\eta]_m$ is the intrinsic viscosity of the mixture, c_m is the total polymer concentration, and b_m is the Huggins slope coefficient which characterizes the interactions of all polymer species. The slope b_m for a mixture of polymer A/polymer B is given by

$$b_m = b_A w_A^2 + b_B w_B^2 + 2b_{AB} w_A w_B \quad (4)$$

where w_A and w_B are weight fractions of the polymers, b_A , b_B , and b_{AB} are the terms characterizing the interactions of the same (A-A, B-B) and different (A-B) polymer molecules, respectively, and the b_{AB} term, which is a complex parameter including the thermodynamic and hydrodynamic interactions in the system, is given by

$$b_{AB} = k_{AB} [\eta]_A [\eta]_B \quad (5)$$

where k_{AB} is the Huggins coefficient between different (A-B) polymer molecules.

In contrast, eq. (4) yields

$$b_{AB} = [b_m - (b_A w_A^2 + b_B w_B^2)] / 2w_A w_B \quad (6)$$

Combining eqs. (5) and (6) gives k_{AB} with all experimental parameters

$$k_{AB} = [b_m - (b_A w_A^2 + b_B w_B^2) / [\eta]_A [\eta]_B] w_A w_B \quad (7)$$

In the presence of only hydrodynamic interactions, theoretical values of b_{AB} or k_{AB} are calculated as geometric means of b_A and b_B or k_A and k_B

$$b_{AB,t} = (b_A b_B)^{1/2} \quad (8)$$

$$k_{AB,t} = (k_A k_B)^{1/2} \quad (9)$$

Because experimental b_{AB} or k_{AB} values reflect both hydrodynamic and thermodynamic interactions between polymer segments, the difference between ex-

TABLE II
Viscometric Data for Different Molecular Weights of Dx/H₂O and PEG/H₂O Binary Systems at 25°C

Polymer sample	Dx (T 10)	Dx (T 40)	Dx (T 70)	Dx (T 110)	PEG (2000)	PEG (4600)	PEG (8000)	PEG (10000)
$[\eta]$ (dL g ⁻¹)	0.0829	0.1698	0.2260	0.2819	0.0881	0.1360	0.1930	0.2445

$[\eta]$: Intrinsic viscosity.

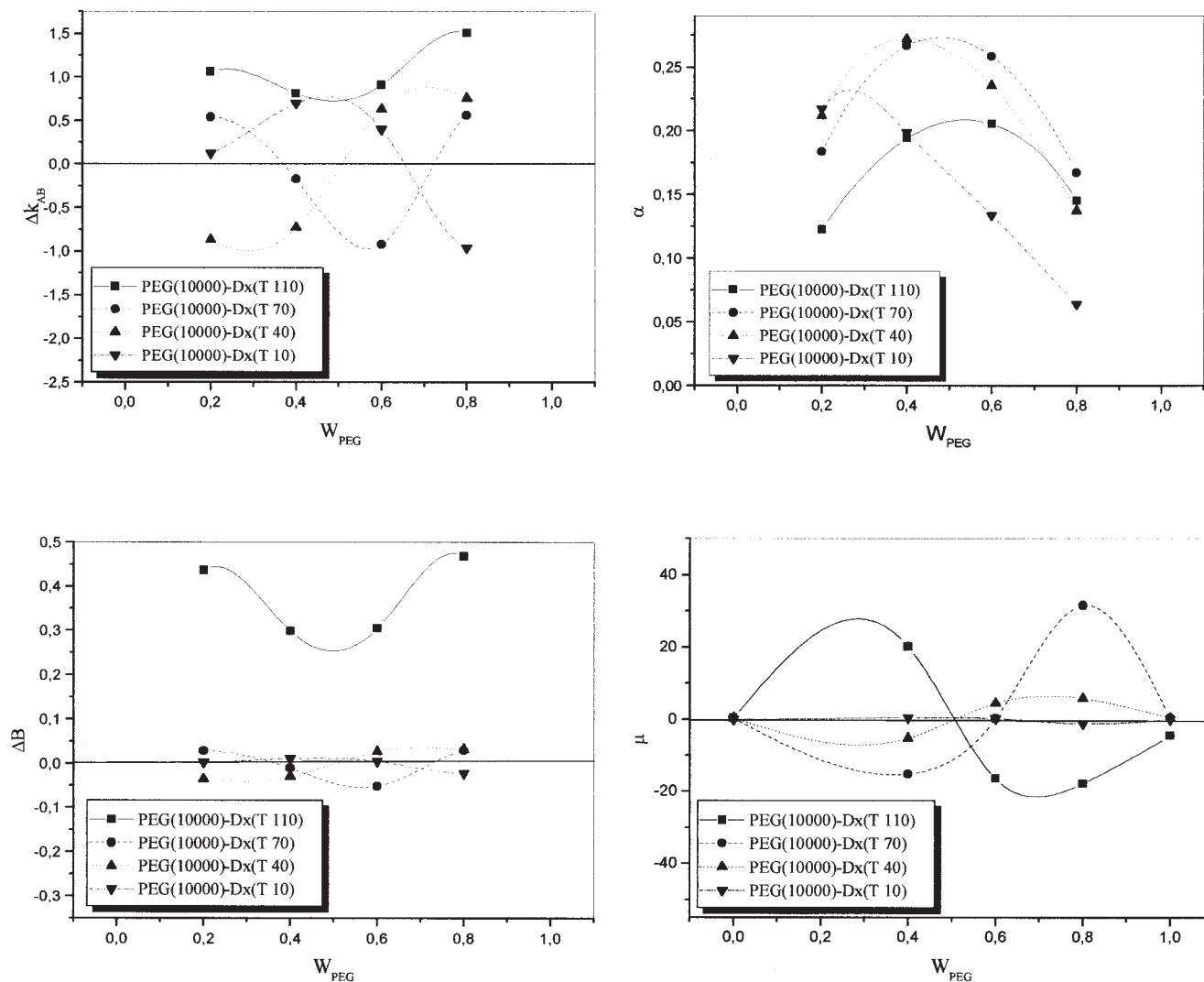


Figure 1 Plots of Δk_{AB} , ΔB , α , and μ as a function of weight fraction of PEG, W_{PEG} , for PEG (10,000)/Dx (T 110)/H₂O, PEG (10,000)/Dx (T 70)/H₂O, PEG (10,000)/Dx (T 40)/H₂O, and PEG (10,000)/Dx (T 10)/H₂O systems.

perimental and theoretical values, $\Delta k_{AB} = k_{AB} - k_{AB,1}$ could give information on the thermodynamic interactions of the polymers. Accordingly, $\Delta k_{AB} \geq 0$ signifies attractive interactions and miscibility, whereas $\Delta k_{AB} < 0$ indicates repulsion and immiscibility.

Sun et al.¹⁷ suggested a new criteria for polymer-polymer miscibility in terms of a thermodynamic parameter, α , based on the classical Huggins coefficient k_m in the blends by using the equation

$$k_m = \{k_A[\eta]_A^2 w_A^2 + k_B[\eta]_B^2 w_B^2 + 2\sqrt{k_A k_B}[\eta]_A[\eta]_B w_A w_B\} / \{[\eta]_A w_A + [\eta]_B w_B\}^2 + \alpha \quad (10)$$

According to Sun et al.'s approach for a ternary, polymer A/polymer B/solvent system, three types of interactions might contribute to the value k_m . These are long-range hydrodynamic interaction of pairs of single molecules, defined by k_{m1} , which is the same as k_m

given in eq. (10): the formation of double molecules given by k_{m2} and intermolecular attraction or repulsion given by k_{m3} . Thus, the overall k_m turns out to be

$$k_m = k_{m1} + k_{m2} + k_{m3} \quad (11)$$

The second term k_{m2} can be neglected at sufficiently low concentrations and in the absence of strong specific interactions that would encourage aggregation. Reabbreviating k_{m3} as α and rearranging eq. (11), α is given as

$$\alpha = k_m - k_{m1} \quad (12)$$

Based on the term k_m , Sun et al. thought that α can be used to determine the miscibility of polymer blends: when $\alpha < 0$, immiscible; $\alpha \geq 0$, miscible.

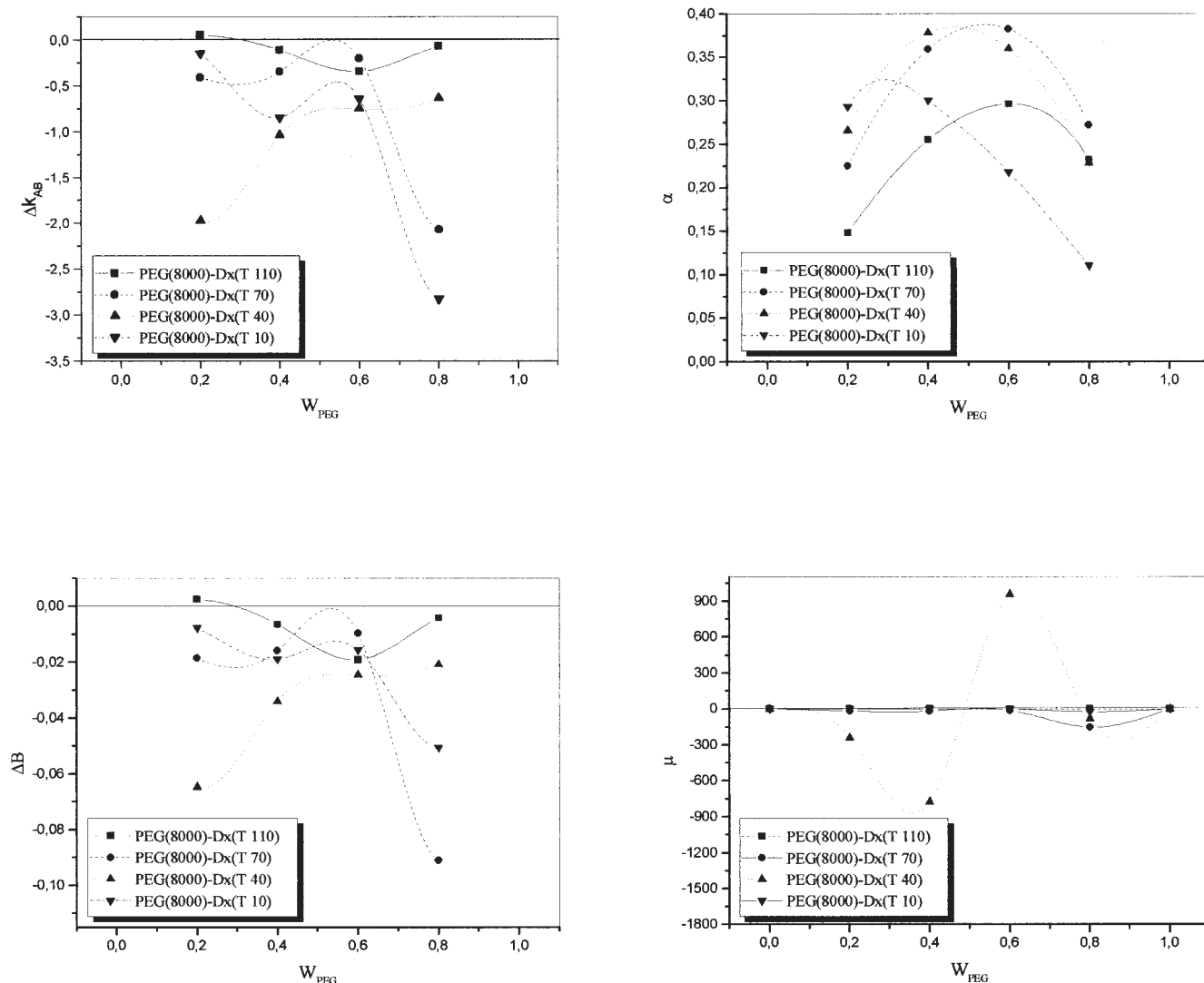


Figure 2 Plots of Δk_{AB} , ΔB , α , and μ as a function of weight fraction of PEG, W_{PEG} , for the PEG (8000)/Dx (T 110)/H₂O, PEG (8000)/Dx (T 70)/H₂O, PEG (8000)/Dx (T 40)/H₂O, and PEG (8000)/Dx (T 10)/H₂O systems.

In contrast, Chee⁹ proposed another criterion to determine polymer–polymer miscibility described as

$$\Delta B = (b_m - \bar{b}) / (2w_A w_B) \quad (13)$$

$$\bar{b} = w_A b_A + w_B b_B \quad (14)$$

where b_m is the observed interaction parameter for the polymer mixture. b_m , b_A , and b_B values can be obtained experimentally. Accordingly, $\Delta B \geq 0$ indicates miscibility; $\Delta B < 0$ indicates phase separation in the blend system. Chee suggested a more effective parameter, μ for blend solutions having sufficiently far apart $[\eta]_A$ and $[\eta]_B$ values

$$\mu = \frac{(b_m - b_A) / ([\eta]_m - [\eta]_A) - (b_B - b_A) / ([\eta]_B - [\eta]_A)}{2([\eta]_B - [\eta]_m)} \quad (15)$$

A positive or zero μ value indicates miscibility and a negative μ value indicates phase separation.¹⁸

EXPERIMENTAL

Materials

The dextran (Dx) polymer samples studied in this work were obtained from Pharmacia Fine Chemicals AB (Uppsala, Sweden). The molecular weight characteristics are determined by Pharmacia (except in T 70) and are given as for T 10 sample: $\bar{M}_n = 6200$; T 40 sample: $\bar{M}_n = 29,500 \text{ g mol}^{-1}$; and T 110 sample: $\bar{M}_n = 74,000 \text{ g mol}^{-1}$. The number-average molecular weight of T 70 Dx sample is determined as $\bar{M}_n = 46,800 \text{ g mol}^{-1}$ by Knauer membrane osmometer in aqueous solution at room temperature.

The poly(ethylene glycol) (PEG) polymer samples studied in this work were obtained from British Drug

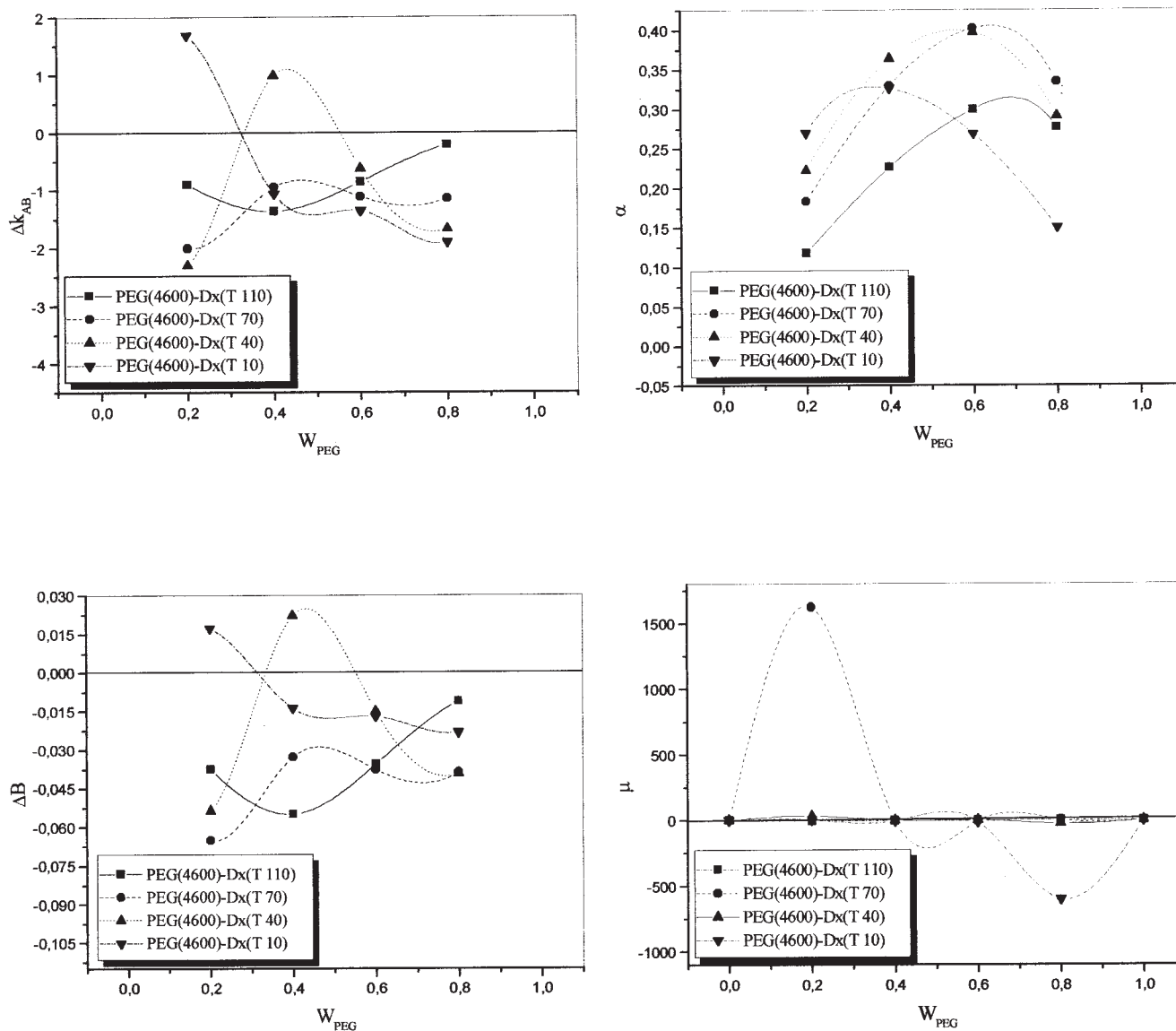


Figure 3 Plots of Δk_{AB} , ΔB , α , and μ as a function of weight fraction of PEG, W_{PEG} , for PEG (4600)/Dx (T 110)/H₂O, PEG (4600)/Dx (T 70)/H₂O, PEG (4600)/Dx (T 40)/H₂O, and PEG (4600)/Dx (T 10)/H₂O systems.

House, BDH (Poole, United Kingdom). The molecular weights of PEG samples are determined by viscometric measurement in aqueous solution at room temperature and are given as for PEG 2000 sample: $\bar{M}_v = 3190 \text{ g mol}^{-1}$; PEG 4600 sample: $\bar{M}_v = 7600 \text{ g mol}^{-1}$; PEG 8000 sample: $\bar{M}_v = 15,306 \text{ g mol}^{-1}$; PEG 10,000 sample: $\bar{M}_v = 24,565 \text{ g mol}^{-1}$.

The structures of these polymers are given in Table I. The water used as solvent was deionized and bidistilled.

Experimental method

The viscometric behaviors of PEG, Dx, and PEG/Dx/H₂O solutions were performed at 25°C by using a Ubbelohde-type capillary viscometer. The tempera-

ture of the thermostat was controlled within the range of $\pm 0.1^\circ\text{C}$ and the flow times were measured with a digital accuracy of $\pm 0.01 \text{ s}$. The stock solution of each binary and ternary system was made by dissolving polymer samples to a polymer concentration of 0.8 g dL^{-1} . Dilutions to yield six lower concentrations were made by adding solvent. Measurements were started after an equilibrium time of 10 min. The average elution times of solutions were determined after several measurements.

RESULTS AND DISCUSSION

Viscometry is a simple and effective technique for monitoring complexation and interaction of polymer blend solutions. Generally, if no specific interaction

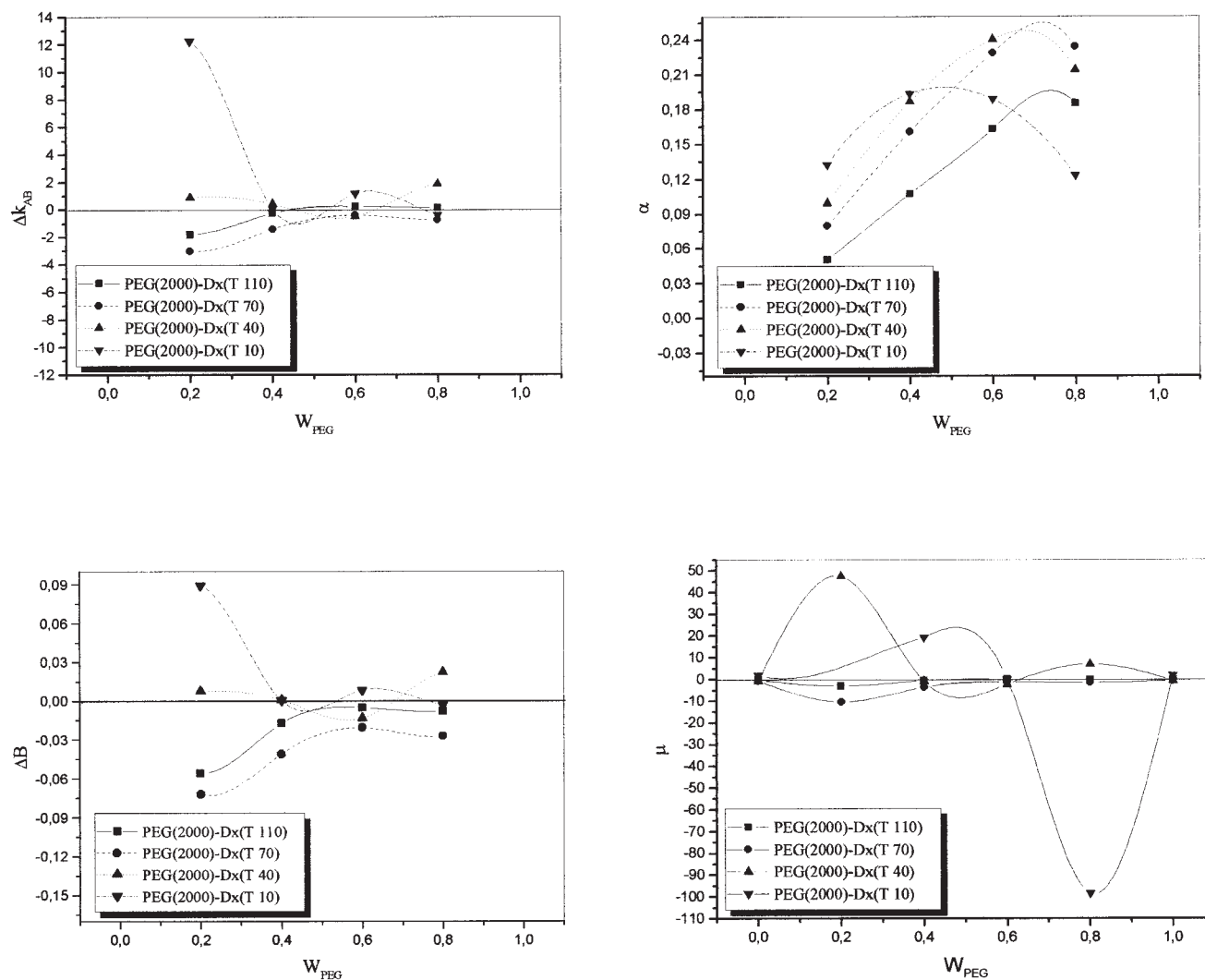
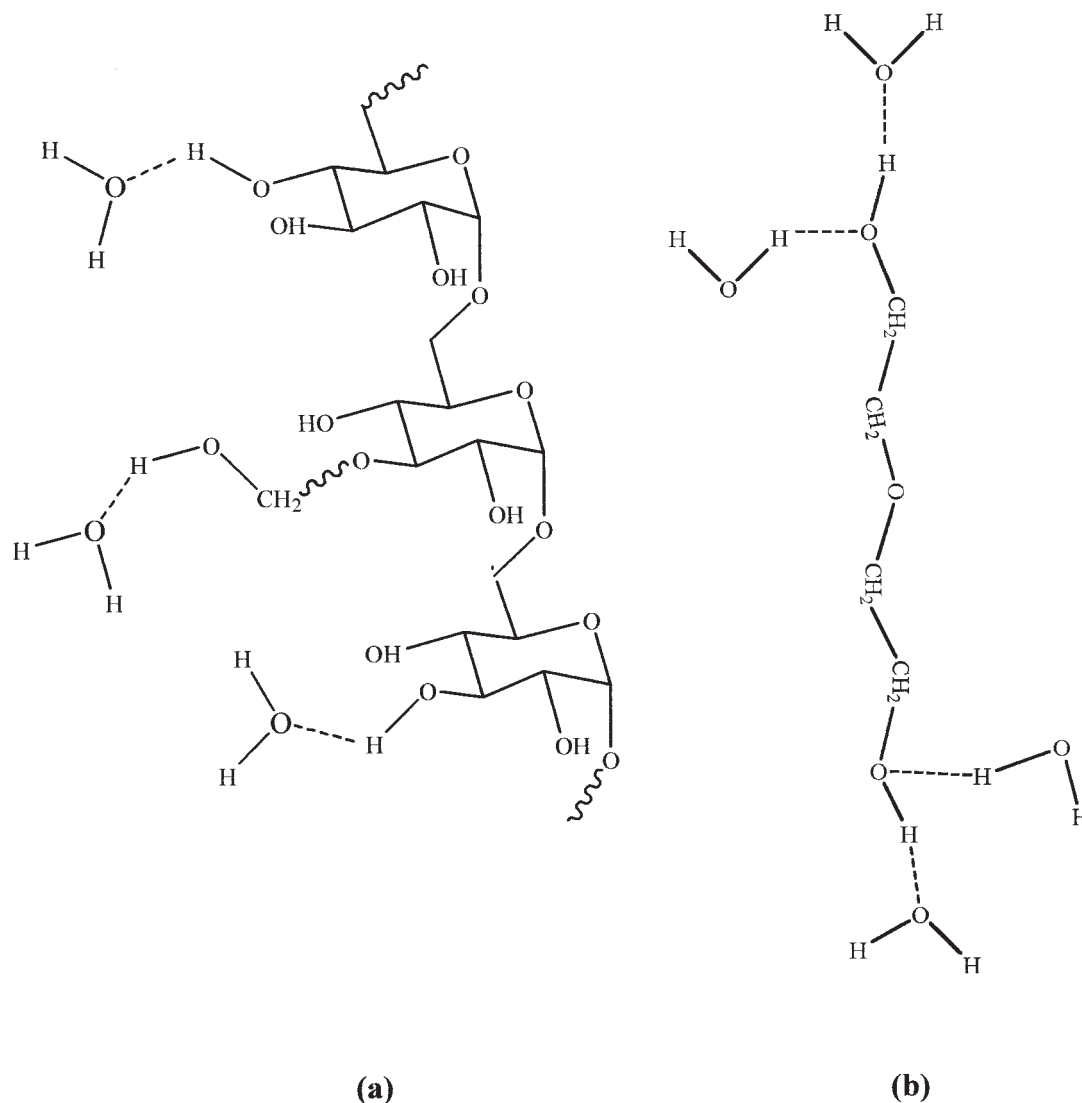


Figure 4 Plots of Δk_{AB} , ΔB , α , and μ as a function of weight fraction of PEG, W_{PEG} , for PEG (2000)/Dx (T 110)/H₂O, PEG (2000)/Dx (T 70)/H₂O, PEG (2000)/Dx (T 40)/H₂O, and PEG (2000)/Dx (T 10)/H₂O systems.

exists in polymer pair, the component polymer coils spatially isolate from each other in dilute solutions, and the reduced viscosity of the polymer pair is close to the additivity law of the component viscosity. However, positive or negative deviations from the additivity law may occur if the specific interactions between the polymer pair are strong enough, suggesting intermolecular complexation.¹⁹ H-bond complexation is dependent on many factors such as molecular weight and its distribution of the component polymers, the level of the interaction, and the solvent used. In these polymer systems, H-bond complexation was investigated depending on the molecular weight of the Dx and PEG. Miscibility is generally known to be enhanced by specific interactions between the polymer pairs (i.e., van der Waals type interactions between polymers, due to the presence of relatively polar, and polarizable groups and hydrogen bonding if there is sufficient hydrogen bonding sites present in the structures of polymer pairs).

Before discussion of data on PEG–Dx mixtures, it is necessary to characterize the viscometric behavior of each polymer separately in aqueous solutions. By using the Huggins equation, intrinsic viscosities obtained for the binary systems (PEG/H₂O and Dx/H₂O) at 25°C are tabulated in Table II. The intrinsic viscosities, $[\eta]$, of polymers with higher molecular weights have higher intrinsic viscosity values.

Based on the experimentally observed $[\eta]$ for the binary (polymer/water) and ternary (polymer 1/polymer 2/water) systems, the parameters of the miscibility criteria proposed by Krigbaum and Wall, Sun et al., and Chee were computed related equations. The plots of miscibility parameters ΔB , μ , α , and Δk_{AB} versus weight fraction of PEG (i.e., W_{PEG}) are illustrated in Figures 1–4. According to Figure 1, viscometric study shows that ΔB and Δk_{AB} values are positive for the PEG (10,000)/Dx (T 110) blend for the all weight fractions. This indicates that these blends are miscible only



Scheme 1 A schematic representation of the possible H-bond interaction between (a) Dx and H₂O, (b) PEG and H₂O.

for these molecular weights. Miscibility of the polymer mixtures decreases as the molecular weight of Dx decreases. In PEG (10,000)/Dx (T 70) blend systems, miscibility decreases with an increasing weight fraction of PEG (W_{PEG}). However, ΔB and Δk_{AB} values are negative for the PEG (10,000)/Dx (T 10) blends, for the weight fractions 0.5 and below, and these are positive for the weight fractions above 0.5. μ values of all PEG/Dx blend systems are positive and miscible up to weight fractions 0.5 and are negative and immiscible for the weight fractions above 0.5. Although ΔB , μ , and Δk_{AB} have mostly negative values, α , which is proposed by Sun et al.,¹⁸ has always positive values for all blend systems.

ΔB and Δk_{AB} parameters of all blends of PEG (8000) almost have negative values. μ values are nearly zero except for PEG (8000)/Dx (T 40) blend systems. However, α values of all blends again have positive values (see Fig. 2). In Figures 3 and 4 some deviations are

observed. Most ΔB and Δk_{AB} values are small, especially at higher weight fractions of PEG but α are also positive for these blend systems.

In different molecular weights of PEG/Dx/H₂O ternary systems, there is sufficient hydrogen bonding sites present in these polymer 1/polymer 2/solvent (H₂O) systems. However, the analysis of the miscibility criteria indicates that PEG/Dx blend systems do not satisfy the miscibility criteria (except α parameter), thus suggesting immiscibility between these two polymers especially at lower molecular weights of Dx. According to Figures 1–4, in PEG/Dx/H₂O ternary systems polymers prefer to interact with H₂O molecules individually, because H₂O is a small molecule compared with PEG and Dx and it also has two hydrogen bonding units. For the blend solutions, composed H-bond interacting groups, being nonionic, do not possess sufficient contrast homogeneously in the coils of the solution. The H-bonding between the un-

like chains not only makes an interchain connection but also influences the chain conformation; namely, it causes the unlike-segment interaction pairing and thus the chains lose their solvation ability.

ΔB values of the all polymer mixtures are negative values. μ values of all PEG/Dx blend systems are especially zero and in some cases, it can be positive and negative with changing of the content of the polymer blend. It can be seen that the values of parameter α are positive in all molecular weights of the polymer samples and each polymer mixture content. This approach makes miscibility criteria unreliable. Δk_{AB} value of the system predicted that in some cases they should be miscible but in some cases they should be immiscible.

The possible reason for the disagreement between these four methods of Δk_{AB} , μ , ΔB , and α is probably the fact that viscometric criteria do not take into account interactions between the polymer and solvent but attribute the miscibility of two polymers only to the specific interactions between the unlike polymer molecules. Namely, in addition to the H-bond interaction and H-bond formation between the PEG and Dx molecules in aqueous solutions, there is the possibility of the hydrogen bond formation between the water and each of the polymers. H-bond interaction should be responsible for the miscibility of the PEG and Dx. It can be proposed that favorable interactions occur between —OH groups of the dextran and —OH groups and etheric oxygen of PEG. Under the conditions where immiscibility is exhibited between the PEG and Dx, H-bonding interaction between the two polymers should be strong enough to overcome the intra- and intermolecular H-bonding among the polymer and solvent (Scheme 1).

CONCLUSION

The present investigation clearly indicates that the interaction in the blends studied by simple measurements based on viscometry and interactions provides valuable information about the miscibilities of the blends. Miscibility parameters Δk_{AB} , ΔB , and μ demonstrate that PEG/Dx blend systems do not satisfy the miscibility criteria especially at lower molecular weights of Dx. However, α parameter showed miscibility in all blend systems and we can say that this miscibility criterion is unreliable.

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