

Miscibility of Dextran and Poly(ethylene glycol) in Dilute Aqueous Solutions. II. Effect of Temperature and Composition

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ABSTRACT: The miscibility of dextran (Dx) with poly(ethylene glycol) (PEG) was investigated in dilute aqueous solutions by viscometry. Homopolymers of Dx and PEG and their blends with Dx/PEG ratios of 10/90, 25/75, 50/50, 75/25, and 90/10 were studied at 25, 30, 35, 40, and 45°C in bidistilled and deionized water. Starting with the classical Huggins equation, the results of the viscosity behavior of each parent polymer and their blends were interpreted in terms of miscibility parameters, Δk , Δb , α , β , ΔB , and μ . On the basis of the sign convention involved in these criteria,

miscibility between Dx and PEG was found to increase with the weight fraction of PEG in the blend composition and temperature. The fourier transform infrared (FTIR) analysis is also used to investigate the miscibility of the polymer pairs. The existence of specific interactions between Dx and PEG was demonstrated by FTIR spectroscopy. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4587–4594, 2006

Key words: miscibility; viscosity; blends; dextran; poly(ethylene glycol)

INTRODUCTION

The miscibility between the constituents of a polymer mixture is an important factor in the development of new materials based on polymeric blends.^{1–5} In miscible polymeric blends, there are often specific interactions between groups or polymer segments that lead to decrease of the Gibbs energy of mixing. Miscible polymer blends present only one phase, while immiscible blends present separated domains. The final properties of polymer blends are directly related to the degree of their miscibilities. The majority of known polymeric mixtures are immiscible. However, several miscible polymeric blends have been found, especially in the last two decades.^{1–4}

For polymer–polymer miscibility investigations, the most useful techniques are electronic microscopy,⁵ spectroscopy,⁶ thermal analysis,⁷ and inverse gas chromatography.⁸ These techniques have been very powerful for such studies. However, most of them are very expensive. An alternative simple, inexpensive, and reliable method to analyze polymer miscibility in solution is viscometric technique. Viscometry is widely used to determine the molecular weight, molecular weight distribution, and degree of polymerization. Many researchers have attempted to correlate viscosity with miscibility of ternary polymer solutions

(polymer1/polymer2/solvent). In addition, dilute solution viscometry method provides information about both the polymer–polymer interactions and polymer–solvent interactions in solution. The effectiveness of dilute solution viscometry method is based on the assumption that mutual interactions of macromolecules in solution have a great influence on the viscosity in the ternary systems.

Many criteria have been proposed by researchers to determine polymer–polymer miscibility by the viscometry method such as intrinsic viscosity-composition plots, reduced specific viscosity-composition plots, interaction parameter, μ , thermodynamic parameter, α , and modified thermodynamic parameter, β .^{9–13} Analysis of the viscosity data with all the proposed criteria brings forth the fact that not all the criteria may simultaneously satisfy the condition for the miscibility. Further, it has been reported that the parameters such as molecular weight of polymers, solvent used, and the concentration of polymers play an important role in determining the miscibility of two polymers.

Dextran (Dx) is a high-molecular-weight polymer of D-glucose, produced by different bacterial strains. Dx and its derivatives are used as plasma expanders,¹⁴ blood substitutes,¹⁵ bone healing promoters,¹⁶ and also for dermal and subcutaneous augmentation¹⁷ and for drug delivery.¹⁸ Poly(ethylene glycol) (PEG) is used in almost all applications of aqueous phase partitioning. For biochemical separations on the laboratory scale, the most commonly used aqueous phase

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system is composed of Dx and PEG.¹⁹ In the present study, an effort has been made to investigate the miscibility of Dx and PEG in aqueous solutions and effect of temperature on their miscibilities by using several criteria based on viscosity measurements.

THEORETICAL BACKGROUND

Basically, miscibility parameters obtained by dilute solution viscometry are derived from classical Huggins equation,²⁰ which expresses the specific viscosity η_{sp} of a single-solute solution as a function of concentration c :

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

where $[\eta]$ is the intrinsic viscosity and b is related to the Huggins coefficient k_H by

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

The value of 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 molecular dimensions.

An analogue of eq. (1) proposed by Krigbaum and Wall²¹ can be applied to a ternary system (polymer 1/polymer 2/solvent)

$$\eta_{sp,m} = [\eta]_m(c_1 + c_2) + b_m(c_1 + c_2)^2 \quad (3)$$

The Huggins slope coefficient b_m , which characterizes the interactions of all polymer species, is related to the Huggins parameter k_m of the polymer blend by

$$b_m = k_m[\eta]_m^2 \quad (4)$$

The plot of reduced specific viscosity of polyblend $\eta_{sp,m}/(c_1+c_2)$ vs. total polymeric concentration ($C = c_1 + c_2$) yields a straight line, and the intercept and gradient corresponds to $[\eta]_m$ and b_m , respectively. Theoretically, $[\eta]_m(c_1+c_2)$ is the total effective specific hydrodynamic volume, which is the addition of the effective specific hydrodynamic volume of constituent polymers, and $b_m(c_1+c_2)^2$ reflects to total molecular interaction. It is composed of three terms: $b_{11}c_1^2$, $b_{22}c_2^2$, and $2b_{12}c_1c_2$, corresponding to polymer(1)–solvent, polymer(2)–solvent, and polymer(1)–polymer(2) interactions, respectively. Comparing it with eq. (1) for single component, the specific viscosity of a polyblend is

$$\eta_{sp,m} = [\eta]_1c_1 + [\eta]_2c_2 + b_{11}c_1^2 + b_{22}c_2^2 + 2b_{12}c_1c_2 \quad (5)$$

If this is compared with the analogue of eq. (3) for the mixture, it is found that the linear relationship between the intrinsic viscosities of the components holds,

$$[\eta]_m = [\eta]_1w_1 + [\eta]_2w_2 \quad (6)$$

where w_1 and w_2 are the weight fractions of polymer 1 and polymer 2, respectively.

A further expression is obtained relating to total polymer–polymer interaction for mixture and those of the components, namely

$$b_m = w_1^2b_{11} + w_2^2b_{22} + w_1w_2b_{12} \quad (7)$$

where b_{11} , b_{22} and b_{12} are the terms characterizing the interactions of same (1–1, 2–2) and different (1–2) polymer molecules, respectively. And

$$b_{11} = k_{11}[\eta]_1^2 \quad (8)$$

$$b_{22} = k_{22}[\eta]_2^2 \quad (9)$$

$$b_{12} = k_{12}[\eta]_1[\eta]_2 \quad (10)$$

where k_{12} is the Huggins coefficient between different (1–2) polymer molecules. It should be noted that k_{12} and b_{12} are different from k_m and b_m .

Combining eqs. (7) and (10), the following equation, which gives b_{12} with all experimental parameters, can be achieved:

$$b_{12} = \frac{b_m - (b_{11}w_1^2 + b_{22}w_2^2)}{2w_1w_2} \quad (11)$$

Combining eqs. (10) and (11) gives k_{12} with all experimental parameters:

$$k_{12} = \frac{b_m - (b_{11}w_1^2 + b_{22}w_2^2)}{2[\eta]_1[\eta]_2w_1w_2} \quad (12)$$

In the presence of only hydrodynamic interactions, theoretical values of b_{12} or k_{12} are calculated as geometric means of b_{11} and b_{22} or k_{11} and k_{22} :

$$b_{12,t} = (b_{11}b_{22})^{1/2} \quad (13)$$

$$k_{12,t} = (k_{11}k_{22})^{1/2} \quad (14)$$

Since experimental b_{12} or k_{12} values reflect both hydrodynamic and thermodynamic interactions between polymer segments, the difference between experimental and theoretical values, $\Delta k = k_{12} - k_{12,t}$ and $\Delta b = b_{12} - b_{12,t}$, could give information on the thermodynamic interactions of the polymers. A positive difference is an indication of attractive interactions and

miscibility, whereas a negative difference indicates repulsion and immiscibility.

Sun et al.¹² suggested a new criterion, α , based on the classical Huggins equation and Huggins coefficient k_m in the blends. According to Sun et al.'s approach for a ternary system, there are three types of interaction that might contribute to the value of k_m : long-range hydrodynamic interaction of pairs of single molecules given by k_{m1} ; 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:

$$k_m = k_{m1} + k_{m2} + k_{m3} \quad (15)$$

In the absence of strong special interactions that would encourage aggregation, and at sufficiently low concentrations, the second term k_{m2} can be neglected. Reabbreviating k_{m3} as α and rearranging the final equation then yields

$$\alpha = k_m - k_{m1} \quad (16)$$

$$\alpha = k_m - \frac{k_{11}w_1^2[\eta]_1^2 + k_{22}w_2^2[\eta]_2^2 + 2\sqrt{k_{11}k_{22}}w_1w_2[\eta]_1[\eta]_2}{(w_1[\eta]_1 + w_2[\eta]_2)^2} \quad (17)$$

where k_m is the experimentally obtained Huggins constant. The parameter α indicates the nature and strength of the intermolecular interaction ($\alpha > 0$, attraction; $\alpha < 0$, repulsion). The sign of parameter α can be used to predict the miscibility of polyblend, when $\alpha \geq 0$, miscible; $\alpha < 0$, immiscible.

Jiang and Han¹³ revised Sun's criterion by substituting an expression of k_m illustrated as in eqs. (17) and (18).

$$k_m = \frac{k_{11}[\eta]_1^2w_1^2 + k_{22}[\eta]_2^2w_2^2 + 2k_{12}[\eta]_1[\eta]_2w_1w_2}{(w_1[\eta]_1 + w_2[\eta]_2)^2} \quad (18)$$

Then, they gave a β criterion

$$\beta = \frac{2\Delta k[\eta]_1[\eta]_2w_1w_2}{(w_1[\eta]_1 + w_2[\eta]_2)^2} \quad (19)$$

where $\Delta k = k_{12} - (k_{11}k_{22})^{1/2}$. Similarly, when $\beta \geq 0$, miscibility exists and when $\beta < 0$, immiscibility exists.

In contrast, Chee¹¹ suggested that a simple measure of the intermolecular interactions in the ternary systems is the arithmetic differential interaction parameter defined as

$$\Delta B = \frac{b_m - \bar{b}}{2w_1w_2} \quad (20)$$

$$\bar{b} = w_1b_{11} + w_2b_{22} \quad (21)$$

Values of b_m , b_{11} , and b_{22} can be obtained experimentally. A positive or zero ΔB indicates miscibility, whereas $\Delta B < 0$ indicates phase separation.

Chee suggested a more effective parameter, μ , for blend solutions having sufficiently far apart $[\eta]_1$ and $[\eta]_2$ values:

$$\mu = \frac{\frac{b_m - b_{11}}{[\eta]_m - [\eta]_1} - \frac{b_{22} - b_{11}}{[\eta]_2 - [\eta]_1}}{2([\eta]_2 - [\eta]_m)} \quad (22)$$

For miscible blends $\mu \geq 0$, while immiscible blends have negative values of μ .

EXPERIMENTAL

Chemicals

Two water soluble polymers, poly(ethylene glycol) (PEG; $M_n = 5.400$ g/mol) supplied from British Drug House Ltd. (BDH) and Dextran (Dx; $M_n = 6.400$ g/mol) supplied from Pharmacia, were used in this study. Bidistilled and deionized water, having almost zero conductivity, was used as solvent.

Viscosity measurements

The relative viscosities of both homopolymers and blends were measured at five different temperatures (25, 30, 35, 40, and 45°C) by using Ubbelohde type capillary viscometer. Viscosity measurements were carried out in a constant temperature water bath. The temperatures were kept constant within $\pm 0.1^\circ\text{C}$ sensitivity by an electronically controlled thermostat. The solutions of each binary and ternary system were made by dissolving polymer samples to a polymer concentration of 0.8 g/dL. Viscosity measurements of the polymer solutions were obtained at seven compositions: 0/100, 10/90, 25/75, 50/50, 75/25, 90/10, and 100/0 of Dx/PEG, in mass, and the respective mass fractions of PEG, W_{PEG} : 0, 0.1, 0.25, 0.5, 0.75, 0.9, and 1.0, when only polymeric species are considered. Dilutions to yield at least five lower concentrations were made by adding solvent. Measurements started after an equilibrium time of 10 min. The average elution times of solutions were determined after several measurements.

FTIR measurements

The homopolymers and the blend samples were regenerated from their aqueous solutions by solvent

TABLE I
Viscometric and Thermodynamic Data for the Studied Samples

T (°C)	W_{PEG}	b (dL/g) ²	$[\eta]_m$ (dL/g)	Δb	Δk	α	β	ΔB	μ
25	1.0	0.0166	0.2525	—	—	—	—	—	—
	0.9	0.0149	0.2347	0.0003	0.0122	0.0031	0.0008	-0.0022	-0.0585
	0.75	0.0116	0.2114	-0.0022	-0.1019	-0.0207	-0.0184	-0.0046	-0.1721
	0.5	0.0067	0.1700	-0.0043	-0.2005	-0.0796	-0.0753	-0.0067	-0.2457
	0.25	0.0035	0.1242	-0.0063	-0.2959	-0.1400	-0.1479	-0.0087	-0.3037
	0.1	0.0029	0.1061	-0.0082	-0.3840	-0.1693	-0.1438	-0.0106	-0.3606
	0.0	0.0035	0.0844	—	—	—	—	—	—
30	1.0	0.0170	0.2433	—	—	—	—	—	—
	0.9	0.0156	0.2255	0.0013	0.0627	0.0093	0.0044	-0.0008	0.0007
	0.75	0.0126	0.2046	-0.0013	-0.0631	-0.0153	-0.0116	-0.0033	-0.1439
	0.5	0.0078	0.1626	-0.0037	-0.1845	-0.0673	-0.0702	-0.0058	-0.2222
	0.25	0.0048	0.1230	-0.0053	-0.2600	-0.1277	-0.1300	-0.0073	-0.2856
	0.1	0.0041	0.1009	-0.0066	-0.3256	-0.1319	-0.1203	-0.0087	-0.3374
	0.0	0.0044	0.0835	—	—	—	—	—	—
35	1.0	0.0180	0.2406	—	—	—	—	—	—
	0.9	0.0167	0.2204	0.0022	0.1136	0.0208	0.0079	0.0001	0.0661
	0.75	0.0135	0.2006	-0.0011	-0.0561	-0.0098	-0.0102	-0.0032	-0.1244
	0.5	0.0086	0.1601	-0.0035	-0.1791	-0.0644	-0.0675	-0.0056	-0.2153
	0.25	0.0056	0.1215	-0.0046	-0.2338	-0.1202	-0.1169	-0.0067	-0.2643
	0.1	0.0047	0.0969	-0.0058	-0.2964	-0.1090	-0.1105	-0.0079	-0.3100
	0.0	0.0048	0.0811	—	—	—	—	—	—
40	1.0	0.0195	0.2207	—	—	—	—	—	—
	0.9	0.0181	0.2038	0.0027	0.1551	0.0220	0.0112	0.0003	0.0729
	0.75	0.0150	0.1845	0.0001	0.0025	0.0024	0.0005	-0.0023	-0.1077
	0.5	0.0103	0.1509	-0.0015	-0.0891	-0.0453	-0.0343	-0.0039	-0.2081
	0.25	0.0065	0.1115	-0.0033	-0.1924	-0.0797	-0.0961	-0.0057	-0.2616
	0.1	0.0054	0.0920	-0.0035	-0.2021	-0.0763	-0.0738	-0.0058	-0.2862
	0.0	0.0050	0.0775	—	—	—	—	—	—
45	1.0	0.0252	0.2084	—	—	—	—	—	—
	0.9	0.0233	0.1938	0.0042	0.2701	0.0275	0.0198	0.0005	0.0775
	0.75	0.0194	0.1747	0.0015	0.0962	0.0199	0.0183	-0.0022	-0.1172
	0.5	0.0134	0.1415	-0.0001	-0.0004	-0.0006	-0.0002	-0.0037	-0.2072
	0.25	0.0084	0.1062	-0.0013	-0.0842	-0.0177	-0.0420	-0.0050	-0.2487
	0.1	0.0064	0.0871	-0.0013	-0.0806	-0.0141	-0.0292	-0.0049	-0.2527
	0.0	0.0053	0.0745	—	—	—	—	—	—

evaporation at room temperature and dried at 35°C under vacuum. Fourier transform infrared (FTIR) spectra of KBr pellets of the samples were taken by Mattson 1000 FTIR spectrophotometer in the 4000–400 cm^{-1} range, where 40 scans taken at 16 cm^{-1} resolution.

RESULTS AND DISCUSSION

Viscometric analysis

The linear and angular coefficient of $\eta_{\text{sp},m}/C$ vs. C curves were calculated by the linear regression procedure giving respectively, the intrinsic viscosity, $[\eta]$, and $b = k_H[\eta]^2$, or more properly the slope of $\eta_{\text{sp},m}/C$ vs. C curves. For all binary and ternary systems studied, reduced viscosity was found to be a linear function of concentration with correction coefficients of 0.98 at least; no crossovers appear within the range of concentration used. The results obtained by linear regression analysis and other parameters calculated

from equations mentioned earlier are summarized in Table I. As can be followed in Table I, the intrinsic viscosity value of both homopolymers and blends decreases with increasing temperature and the intrinsic viscosity values of the polymer blends vary between those of pure polymers, indicating the existence of intermolecular interactions between the unlike polymer segments when mixed together.

For the sake of simplicity and to make comparisons on the miscibility behavior of different blends of the polymers, Figure 1(a–f) depict together the miscibility parameter values presented in Table I as a function of the weight fraction of PEG in the blend samples at five temperatures studied. As can be followed from the figures, all of the different miscibility parameter values do not always agree with each other. In some cases, a miscibility parameter value tends to indicate miscibility, while another one indicates immiscibility. Generally, ΔB and μ parameters obtained for the blends studied give more negative values than the

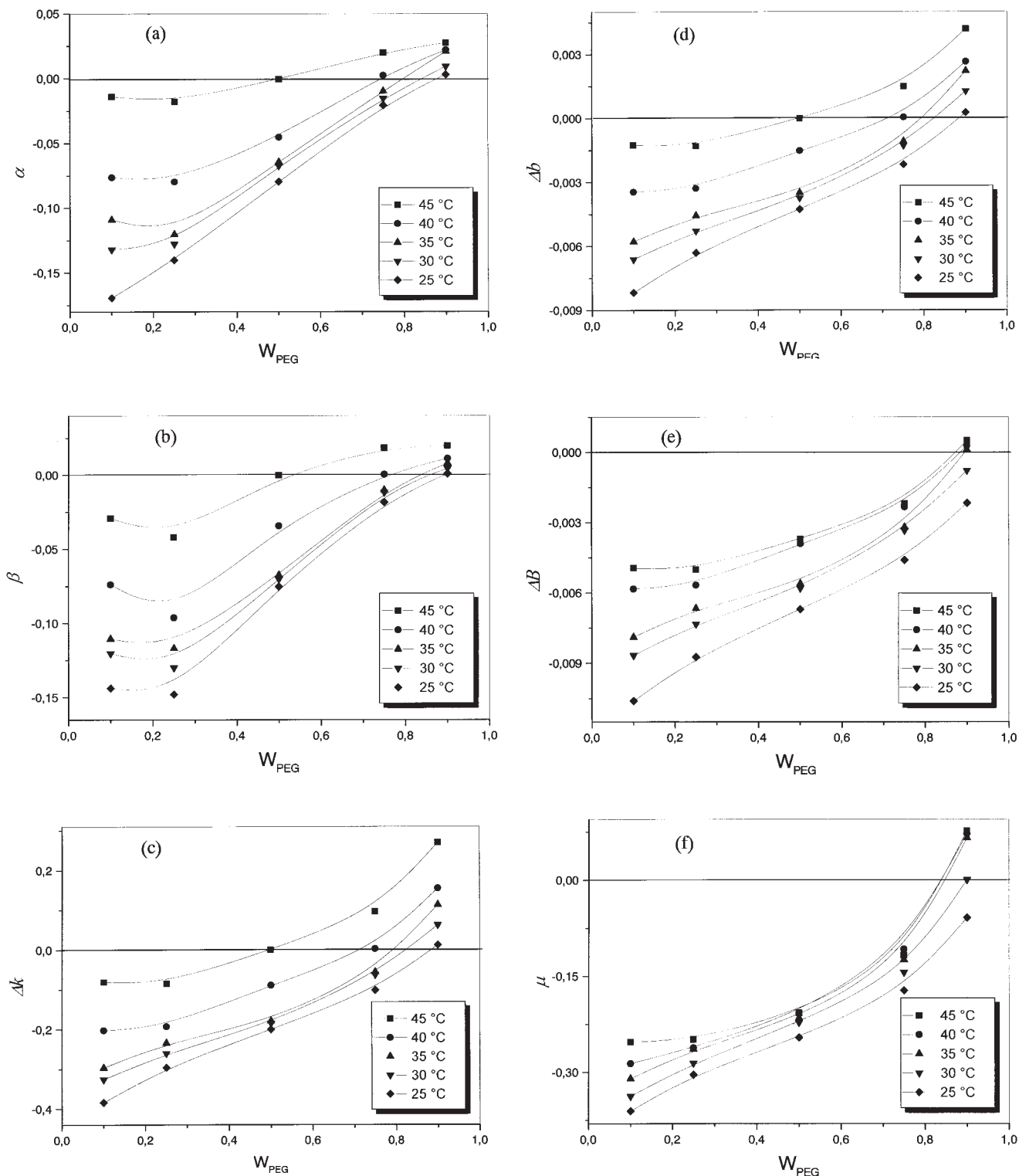


Figure 1 Concentration dependence of (a) α , (b) β , (c) Δk , (d) Δb , (e) ΔB , and (f) μ at different temperatures.

other miscibility parameters. In spite of these contradictions, a common trend is observed with all miscibility parameters. For the systems studied, miscibility of Dx and PEG shows a tendency that increases with the weight fraction of PEG in the blend samples at all temperatures studied. In same cases, Dx/PEG (90/10)

blend shows a deviation from this tendency although it is still immiscible according to all miscibility parameters at all temperatures. As can be followed from the miscibility curves, the Dx/PEG blends having 90/10, 75/25, and 50/50 compositions have negative values of all miscibility parameters at all temperatures stud-

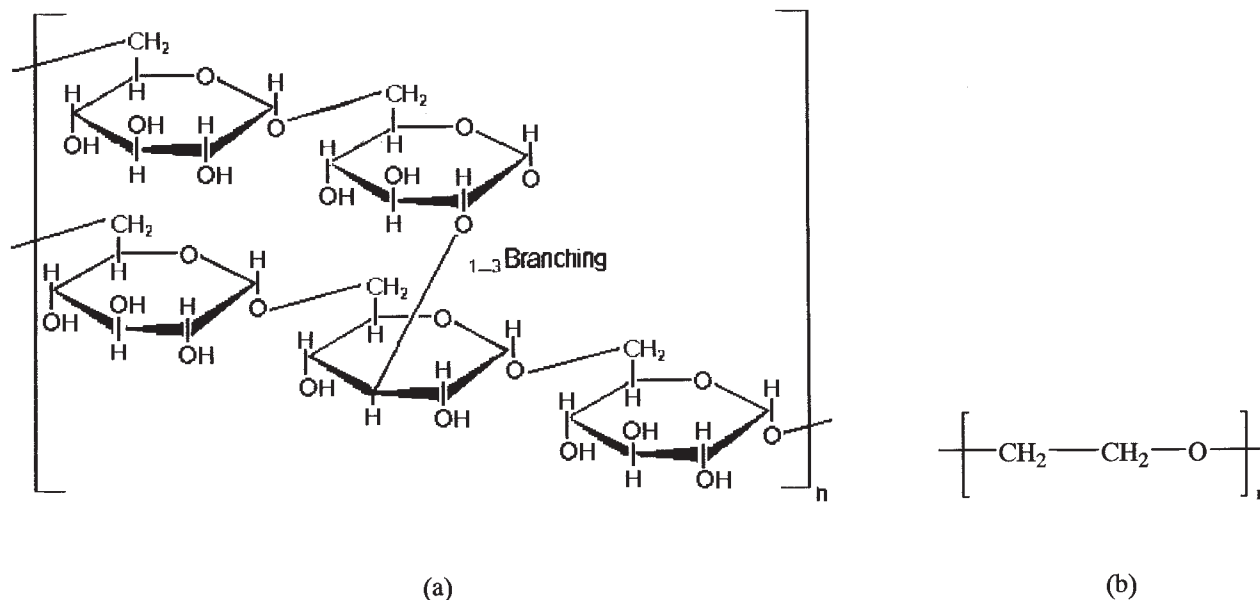


Figure 2 Structure of (a) Dx and (b) PEG.

ied, suggesting that these blend systems may exhibit phase separation and hence immiscibility. The blend Dx/PEG (25/75) shows miscibility at 40 and 45°C according to all miscibility parameters other than ΔB and μ . Dx/PEG (10/90) blend has positive values of all miscibility parameters at 35, 40, and 45°C, suggesting that Dx and PEG mixed in a ratio of 10/90 are miscible with each other at these temperatures. This blend sample is also miscible at 25 and 30°C according to α , β , Δk , and Δb parameters.

In Figures 1(a)–1(f), it can be easily seen that the miscibility of Dx and PEG increases not only with the weight fraction of PEG but also with temperature. For the systems studied, miscibility parameters for Dx/PEG blends shift to more positive values with increasing temperature. Polymer–polymer miscibility is generally known to be enhanced by specific interactions between the polymer pairs. The reason why miscibility shows a tendency to increase with the increasing weight fraction of PEG and temperature might be attributed to this fact. Specific interactions like dipole–dipole interaction or H-bonding should be responsible for the miscibility observed between Dx and PEG in solution. The functional sites present in the structure of these polymers can be seen in Figure 2. It can be proposed that favorable interactions occur between etheric oxygen or hydroxyl on the Dx backbone and etheric oxygen of PEG. Considering the structure of Dx, it is strongly expected that intra and intermolecular H-bonding will form between the polymer segments. Under the conditions where miscibility is exhibited between Dx and PEG, the interactions between the two polymers should be enough to overcome the intra and intermolecular H-bonding among Dx chains

themselves. As the weight fraction of PEG in the blend composition decreases, the probability for a Dx chain to establish H-bonding interaction with a chain of its own kind increases, since PEG chains become less available in the medium for bonding. Consequently, immiscibility between the two polymers is observed at the low weight fractions of PEG. On the contrary, at the high weight fractions of PEG, the probability of the specific interactions between Dx and PEG and hence miscibility increases, since the establishment of H-bonds between two Dx chains becomes more difficult.

Temperature helps the interactions between the two polymers to overcome the effects that prevent the miscibility. With the increasing temperature, the H-bonds among the polymer chains and between the polymer segments and water molecules are destroyed and van der Waals type interactions between the polymer pairs, because of the presence of polar —OH and C—O groups, and dipole-induced dipole-type forces are expected to become more favorable.²² Because of this fact, the interaction probability between Dx and PEG and hence miscibility increases with increasing temperature. The effect of temperature on the miscibility of Dx and PEG is more evident at the higher weight fractions of Dx. Especially for α and β parameters, the shift towards more positive values with an increment of temperature is greater at higher Dx concentrations. This behavior is an evidence of the explained effect of temperature on the breaking of H-bonds among the Dx chains and hence on the miscibility of the polymer pair. In addition, with increasing temperature, the polymer chains become more flexible and this makes miscibility easier.

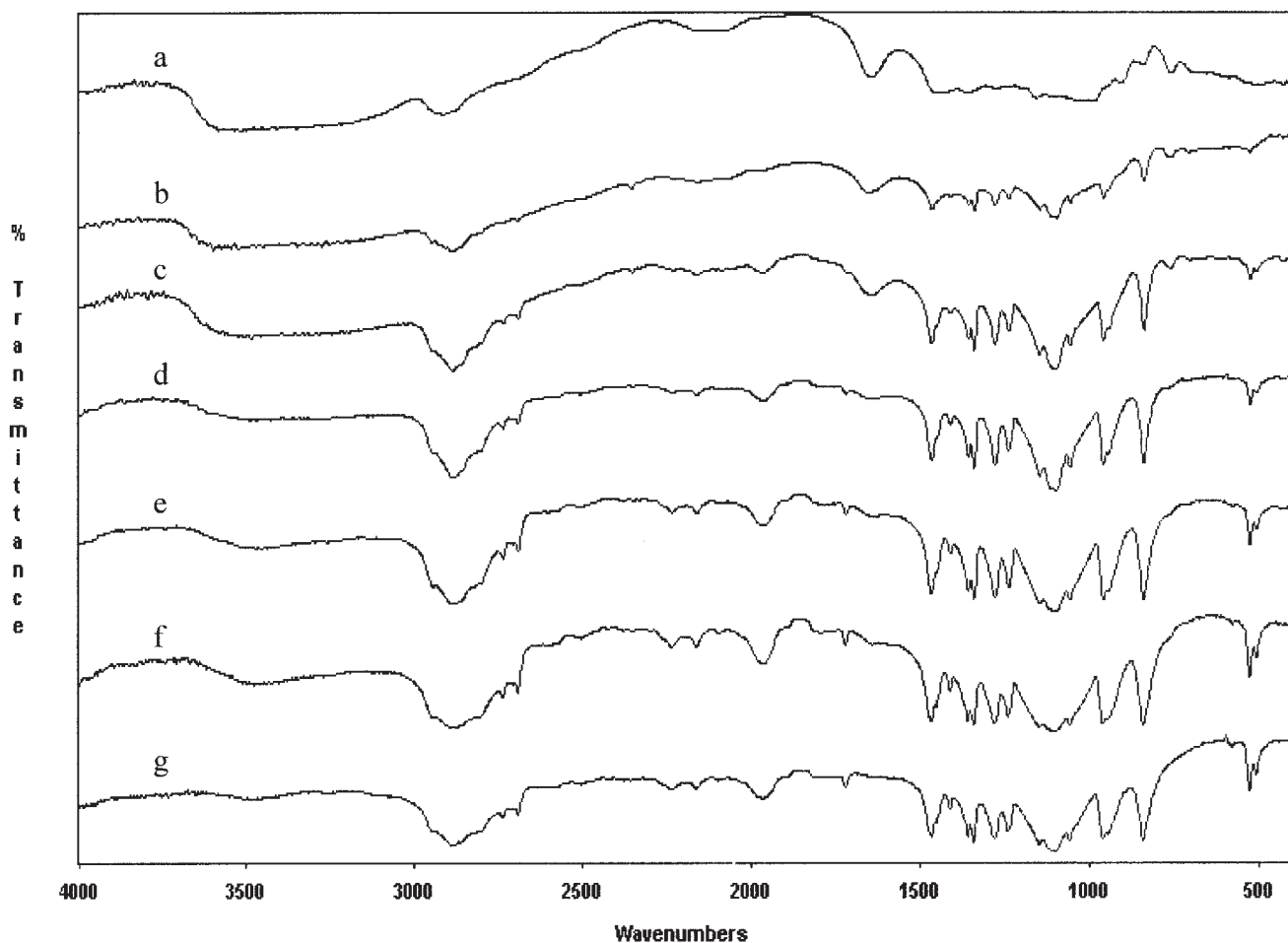


Figure 3 The FTIR spectra of (a) Dx, the blends Dx/PEG: (b) 90/10, (c) 75/25, (d) 50/50, (e) 25/75, (f) 10/90, and (g) PEG.

FTIR spectroscopy analysis

FTIR spectroscopy has been widely used by many researchers to study the formation of blends.^{23–25} FTIR spectrum provides information regarding intermolecular interaction via analysis of FTIR spectra corresponding to stretching or bending vibrations of particular bonds, and the positions at which these peaks appear depends directly on the force constant or bond strength. Hydrogen bonding or other secondary interactions between chemical groups on the dissimilar polymers should theoretically cause a shift in peak position of the participating groups. This kind of behavior is exhibited by miscible blends that show extensive phase mixing. Hydrogen bonding interactions usually move the stretching frequencies of the participating groups, e.g., O—H towards lower numbers usually with increased intensity and peak broadening. The shift in peak position will depend on the strength of the interaction.

The FTIR spectra of Dx, the blends Dx/PEG: 90/10, 75/25, 50/50, 25/75, 10/90, and PEG taken in the solid are compared with each other in Figure 3(a–g), respectively. In the spectrum of PEG, —O—H stretching

centered at 3490 cm^{-1} , multiple —C—H stretching of methylene groups at 2881 cm^{-1} , —C—H bending and rocking vibrations at 1467 , 1413 , and 961 cm^{-1} , —O—H bending vibrations at 1281 cm^{-1} , and —C—O bands at 1149 , 1100 , and 1060 cm^{-1} are observed. In the Dx spectrum, —O—H stretching centered at 3522 cm^{-1} , —C—H stretching at 2918 cm^{-1} , —C—H bending and rocking vibrations at 1465 , 1431 , and 990 cm^{-1} , —O—H bending vibrations at 1280 cm^{-1} , and —C—O stretching at 1160 and 1107 cm^{-1} are observed.

The spectra of blend samples display characteristic absorption bands of Dx and PEG. In the —O—H bending and —C—O stretching vibration bands of blend spectra, no clear evidence of specific interactions between Dx and PEG is observed. But as can be followed in Table II, as we move through to PEG spectrum, the —O—H stretching absorption band shifts to lower frequencies. The —O—H stretching absorption band of all blends except for Dx/PEG (90/10) is observed at a lower frequency than those of homopolymers. This shift towards lower energy reveals that there is a favorable interaction between

TABLE II
FTIR Data for Different Polymer Systems and —OH
Absorption Frequency

Polymer system	ν_{OH} (cm ⁻¹)
Dx	3522
Dx/PEG (90/10)	3518
Dx/PEG (75/25)	3486
Dx/PEG (50/50)	3480
Dx/PEG (25/75)	3461
Dx/PEG (10/90)	3465
PEG	3490

Dx and PEG through the hydroxyl group of Dx and etheric oxygen of PEG.

CONCLUSIONS

From our observations it is clear that although Dx and PEG were found to be immiscible at most of the studied conditions, all the miscibility parameters have a tendency to increase with the increasing weight fraction of PEG and temperature. This behavior is in conformation with the presence of hydrogen bonding sites present in the structures of these polymers. The FTIR studies also support these observations. From the FTIR peaks it is evident that the systems show a shift in peak position towards lower energy, as the weight fraction of PEG in the blend composition is increased. This observation confirms the presence of the specific interactions between Dx and PEG, and strongly supports the viscometric observations.

It can be concluded that inexpensive viscometric method can be used to within a fairly good accuracy in acquiring the miscibility/compatibility of two polymers. Further, it is also observed that the different miscibility parameters such as Δk , Δb , α , β , ΔB , and μ are in good agreement with each other for the systems studied although same contradictions exist.

In this study, the effect of blend composition and temperature on the miscibility of Dx and PEG was investigated. But it is a known fact that the selected solvents also have a great influence on the miscibility of polymer pairs in solution.²⁶ For the evaluation of the effect of solvent, this polymer pair (Dx/PEG) was also investigated in DMSO solutions. In the near fu-

ture, a comparison of the results of viscometric studies of DMSO solutions with those of aqueous solutions will be reported²⁷ on the basis of solubility parameters with regard to the theoretical methods of Hoy and Van Krevelen-Hoftyzer pair.

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