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A. Al-Kahtani Ahmed[a]; J. Jayaraju[b]; B. S. Sherigara[a]; H.S. Naik Bhojya[a]; J. Keshavayya[b]
[a] Department of Industrial Chemistry, School of Chemical Sciences, Kuvempu University, Shankaraghatta, Karnataka, India [b] Department of Chemistry, Kuvempu University, Shankaraghatta, Shimoga, India

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Miscibility Studies of Dextran/Poly(vinyl pyrrolidone) Blend in Solution

A. AL-KAHTANI AHMED,[1] J. JAYARAJU,[2] B.S. SHERIGARA,[1,*] H.S. NAIK BHOJYA[1]
and J. KESHAVAYYA[2]

[1] *Department of Industrial Chemistry, Kuvempu University, School of Chemical Sciences, Jnana Sahyadri, Shankaraghatta 577-451, Karnataka, India*
[2] *Department of Chemistry, Kuvempu University, Jnana Sahyadri, Shankaraghatta, Shimoga 577-451, India*

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The miscibility of dextran (Dex)/poly(vinyl pyrrolidone) (PVP) in solution has been investigated in different percentages of the blend components by employing viscosity, density, refractive index and ultrasonic velocity methods at 30 and 50°C, respectively. Ultrasonic velocity and adiabatic compressibility against blend compositions were plotted and found to be linear. The interaction parameters μ and α have been obtained by using the viscosity data. The results indicated that the Dex/PVP blends are miscible in the entire composition range and it was further confirmed by ultrasonic velocity, density, refractive index studies. In addition, the results revealed that the change in temperature has no significant effect on the miscibility of Dex/PVP polymer blend.

Keywords: blend, dextran, density, miscibility, refractive index, ultrasonic velocity, viscosity

1. Introduction

Blends of natural and synthetic polymers, prepared with the aim of producing new materials for applications in the biomedical field are called as 'bio-artificial polymeric materials' (1–3). The gain in newer properties depends on the degree of compatibility or miscibility of the polymer at a molecular level. Generally, the polymer-polymer miscibility is due to some specific interactions like dipole-dipole forces, H-bonding and formations of charge complexes between the polymer segments (4–6) (Scheme 1). There have been various techniques of studying the miscibility of the polymer blends (7). Some of these techniques are quite complicated, costly and time consuming. Hence, it is desirable to identify simple, low cost and rapid techniques to study the miscibility of polymer blends.

Many scientists showed that viscometry was a simple and very useful method, because it not only requires no expensive equipment, but offers very useful information about the relationship between dilute solution properties and bulk structure of polymer blends (8–12). Chee (13) and Sun et al. (14) have employed viscometry to study the miscibility of polymer blends. Paladhi and Singh (15,16) and Varada Rajulu et al. (17–20) have shown that the variation of ultrasonic velocity, viscosity and refractive index with blend composition is linear for miscible blends.

Fourier transform infrared (FTIR) spectroscopy is one of the many techniques that have been applied to investigate specific molecular bonding interactions in polymer blends (21–25). In the case of immiscible systems, the spectrum of the blend reflects the appropriate addition of the IR spectrum of the two individual components. In the case of miscible or partially miscible polymer blends, the IR spectrum would show formation of new bands as the results of miscibility; and disappearance of some component bands. Shifts in the specific bands would give information on the switches from component specific bonds to the bonds between components (26,27).

Differential Scanning Calorimetry (DSC) is one of the most commonly used thermal methods to determine glass transition temperature (*T*g). Using DSC, miscibility or immiscibility in polymer blends is determined through the measurement of *T*g of the components versus that of blends. Perfectly miscible polymer mixtures exhibit a single *T*g located between the *T*g of the individual components with a sharpness of transition similar to that of the components. On the other hand, immiscible blends show multiple *T*g, corresponding to the *T*g of each component in the mixture. DSC has been successfully used to show molecular

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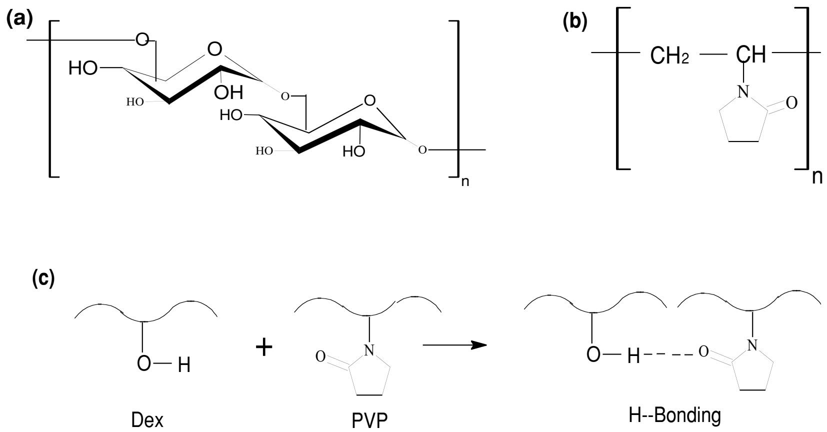
*Address correspondence to: B.S. Sherigara, Department of Industrial Chemistry, Kuvempu University, School of Chemical Sciences, Jnana Sahyadri, Shankaraghatta 577-451, Karnataka, India. E-mail: bssherigara@rediffmail.com



Sch. 1. Schematic representation of (**a**) = dextran, (**b**) = poly(vinyl pyrrolidone) and (**c**) = H-bounding between Dex and PVP.

miscibility or immiscibility in biopolymer systems (28–31), as well as in synthetic polymers (32,33).

As part of our research work, we have studied the miscibility of Dex/PVP blend in solution at different temperature by a viscosity, ultrasonic velocity, density and refractive index technique, and the miscibility of the blends is also confirmed by Fourier transform infrared (FTIR) and differential scanning calorimetric (DSC). We selected these polymers, because they have many pharmaceutical and biomedical applications in drug delivery (34,35). Dextran is a naturally occurring water-soluble polysaccharide with excellent biocompatibility. Poly(vinyl pyrrolidone) is a highly polar and amphoteric polymer and both of these Dex and PVP are used as a blood plasma expender.

2. Experimental

The blends of Dex/PVP of different composition have been prepared by mixing a solution of polymers in distilled water. Poly(vinyl pyrrolidone), ($\overline{M_w} = 58{,}000$, ACROS Organics, New Jersey) and Dextran, ($\overline{M} \cong 60,000$, ACROS Organics, New Jersey) were employed in the present study. The total weights of the two components in solution were always maintained at 1 and 2 g/dL. Stock solutions, of homopolymers and the blend of Dex/PVP of different blend compositions, 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20 and 90/10, were prepared by mixing solutions of polymers in distilled water. Viscosity measurements of 1 and 2% w/v in water at 30 and 50°C were measured

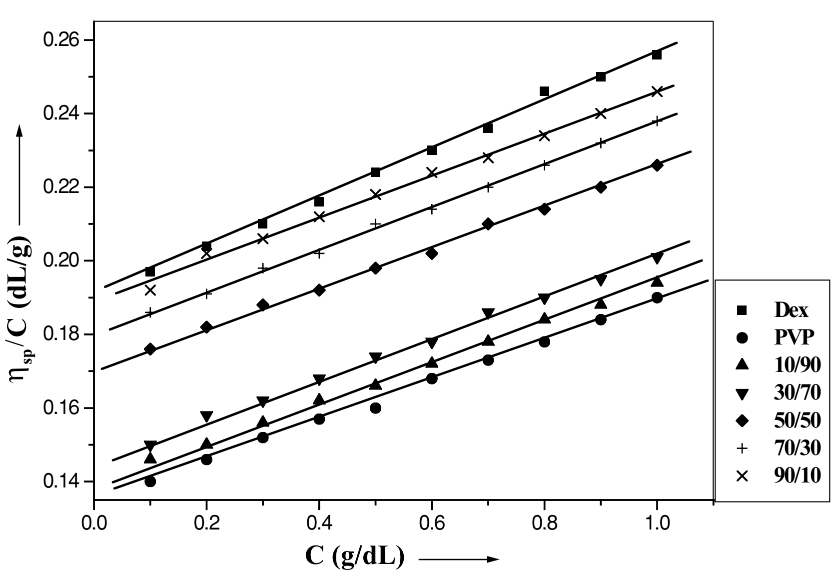


Fig. 1. The variation of reduced viscosity of 1% w/v Dex/PVP blend in solution at 30°C.

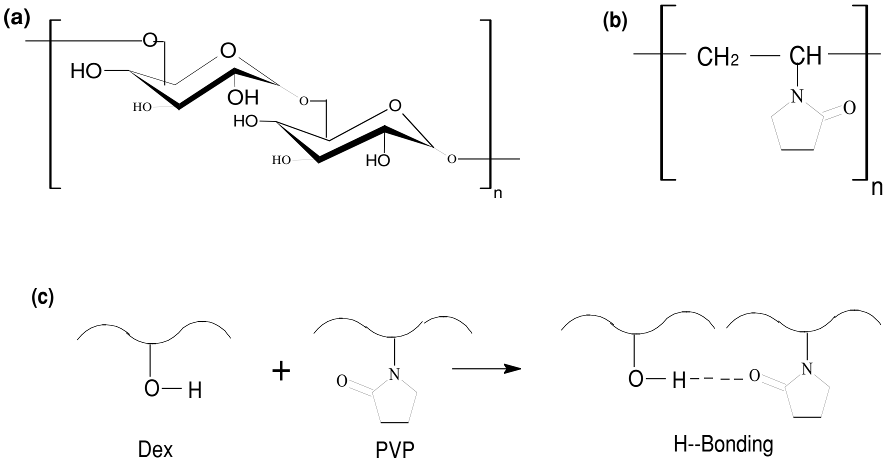


Fig. 2. The variation of reduced viscosity with composition Dex/PVP blend in solution at 50°C.

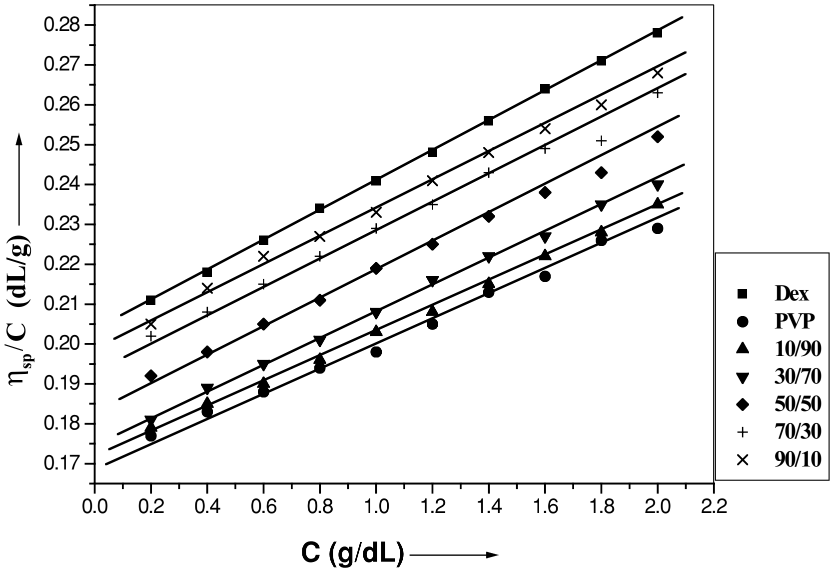


Fig. 3. The variation of reduced viscosity of 2% w/v Dex/PVP blend in solution at 30°C.

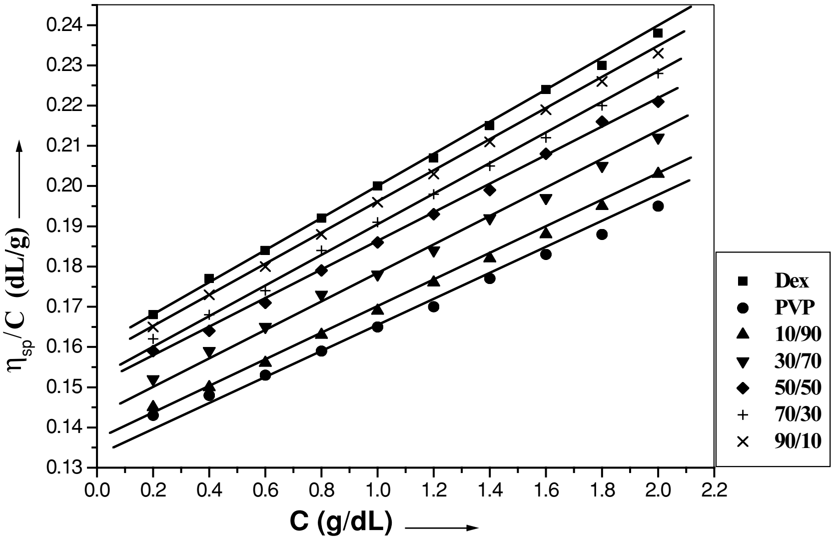


Fig. 4. The variation of reduced viscosity of 2% w/v Dex/PVP blend in solution at 50°C.

Table 1. Interaction Parameters μ and α for Dex, PVP and their blends in solution at 30 and 50°C

Composition Dex / PVP	*1% w/v*				*2% w/v*			
	30°C		*50°C*		*30°C*		*50°C*	
	μ	α	μ	α	μ	α	μ	α
10/90	−0.17	0.21	−0.12	0.09	−0.24	0.04	−0.07	0.04
20/80	0.02	0.11	0.35	0.11	0.01	0.01	0.09	0.03
30/70	−0.04	0.14	−0.06	0.06	0.04	0.05	0.01	0.02
40/60	0.02	0.21	0.01	0.10	0.02	0.04	0.02	0.02
50/50	0.04	0.12	0.13	0.06	0.30	0.07	1.23	1.52
60/40	0.07	0.15	0.04	0.10	0.01	0.01	0.02	0.03
70/30	0.06	0.20	0.09	0.04	0.21	0.02	1.04	0.03
80/20	0.02	0.18	0.01	0.07	0.02	0.03	0.02	0.02
90/10	0.08	0.21	0.02	0.09	0.03	0.01	0.12	0.13

using a Ubblehode suspended level viscometer. The required temperature was maintained in a thermostat with a thermal stability of ±0.05°C. The ultrasonic velocity measurements were carried out by an interferometric technique (17) employing an ultrasonic interferometer (Mittal Enterprises, New Delhi, India). The ultrasonic cell has a double-wall jacket, and the temperature is maintained by circulating water from a thermostat with the thermal stability of ±0.05°C. The experimental frequency was 2-MHz and the velocity measurements were accurate to better than ±0.5%. The densities of the solutions were measured at 30 and 50°C using a pycnometer. The refractive index of the blend solutions were measured with an Abbe's refractometer with a thermostat water circulation system (17) at 30 and 50°. The accuracy of the refractive index measurements was ±0.02%.

FTIR analysis was carried out using a Shimadzu-1800S FTIR spectrophotometer at 2 cm^{-1} resolution with 64 scans over the spectral range from 4000 to 400 cm^{-1}. The films of pure components and their blends were prepared by a solution casting method and dried at 40°C under vacuum for 48 h and placed in a desiccator. The highly brittle film-like flakes were crushed to make powder and mixed with KBr to make a disc for FTIR analysis.

For the differential scanning calorimetric (DSC) measurements, a Perkin-Elmer DSC-7, operating in a dynamic mode was employed. Nitrogen gas was used as an inert gas at a flow rate of 20 mL/min. *T*g values of plain Dex, PVP and mixtures prepared only at 50/50 ratio are reported, since sensitivity of DSC to monitor multiple *T*g behavior in 30/70 and 70/30 ratios, if any, would be limited. Because as one of the component ratios gets smaller, as in the case of 30/70 or 70/30, the heat flow would also get smaller at a similar ratio, which would make *T*g identification difficult. Each sample (80 mg) of (a) plain Dex, (b) Dex/PVP blends (50/50) and (c) plain PVP was placed in aluminum pan. An empty aluminum pan was used as a reference and a heating/cooling rate of 10°C/min was applied throughout the study with scan ranges between 0 and 130°C. Rescans were performed immediately after each scan, in order to erase the thermal history of the samples and to confirrm the location of the *T*g, based on the reversibility of this second-order transition. The *T*g of samples were determined from the DSC rescans, at the midpoint in the shift of the heat flow baseline, which corresponded to the temperature at which one-half of the change in the heat capacity, ΔC_p, occurred. The reported data are the averages of at least two replicate measurements.

3. Results and discussion

Figures 1–4 show the Huggins' plots for pure components and their blends of concentration 1% and 2% w/v at 30 and

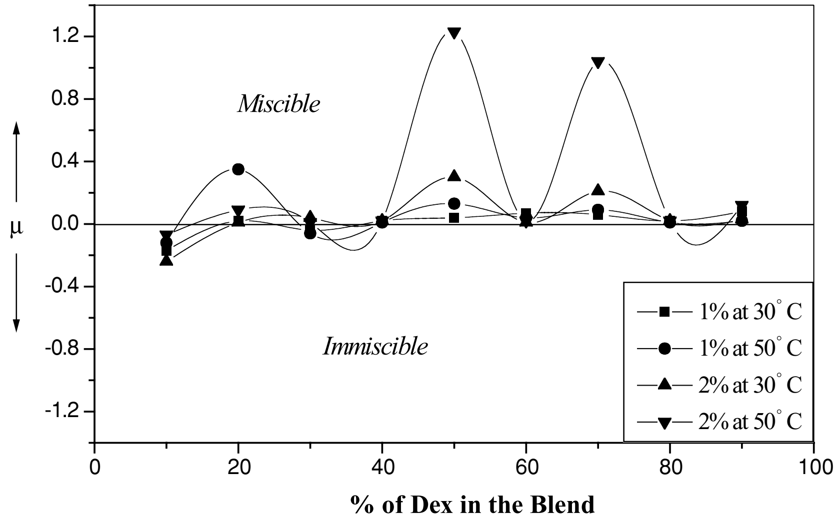


Fig. 5. Interaction Parameter μ for 1% and 2% w/v. Dex/PVP Blend in Solution at 30, 50°C.

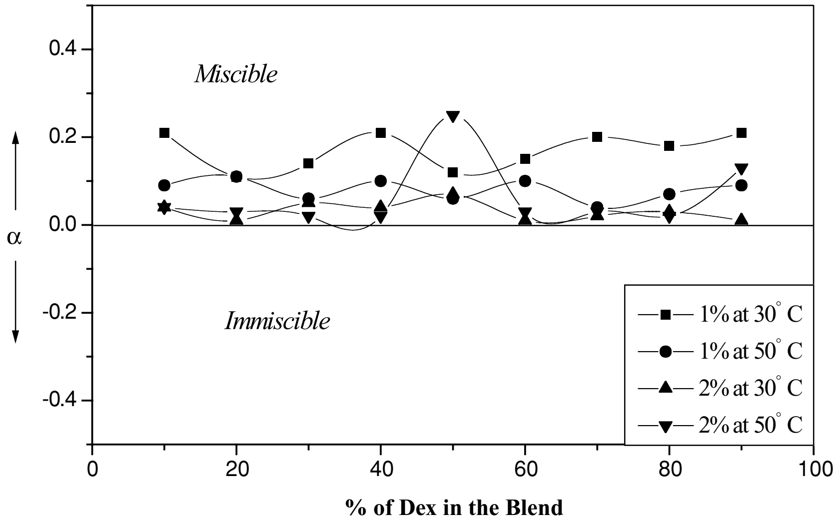


Fig. 6. Interaction Parameter α for 1% and 2% w/v. Dex/PVP Blend in Solution at 30, 50°C.

50°C. It is well known that the plots for reduced viscosity against concentration deviate from linearity according to the degree of miscibility of polymer blends. Plots for compatible blends are linear, whereas for non-compatible, they are not linear indicating that there are two phases formation with several phases at intermediate composition When the polymer blends comprising non-compatible polymer components, a sharp crossover is observed and a significant decrease in slope occurs in the plot of reduced viscosity against composition. But, in this case, the plots were linear and no crossover is seen, showing that Dex/PVP blends are miscible (36–38).

To quantify the miscibility of polymer blends, Chee (13) has given the expression for the interaction parameter when polymers are mixed in weight fractions w_1 and w_2, as:

$$\Delta B = \frac{b - \overline{b}}{2w_1w_2} \tag{1}$$

where, $\overline{b} = w_1b_{11} + w_2b_{22}$ in which, b_{11} and b_{22} are the slope of the viscosity curves for the pure components and b is related to Huggin's coefficient K_H as:

$$b = K_H[\eta]^2 \tag{2}$$

For ternary systems, the coefficient b is also given by:

$$b = w_1^2b_{11} + w_2^2b_{22} + 2w_1w_2b_{12} \tag{3}$$

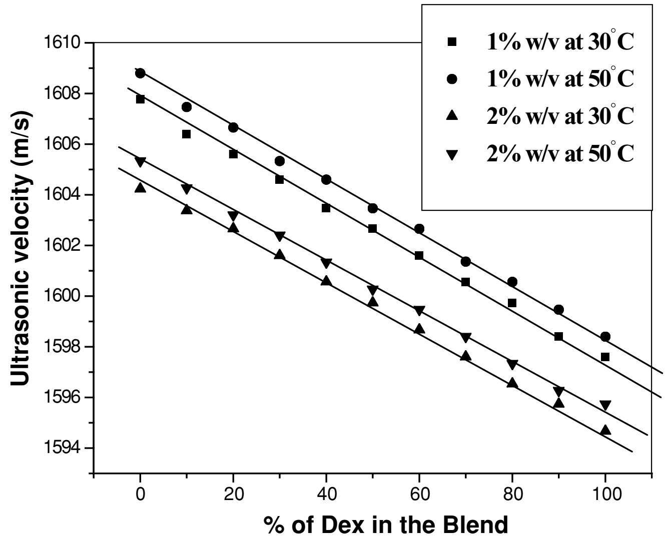


Fig. 7. Effect of temperature on the variation of ultrasonic velocity with composition of 1% and 2% w/v of Dex/PVP blend in solution at 30 and 50°C.

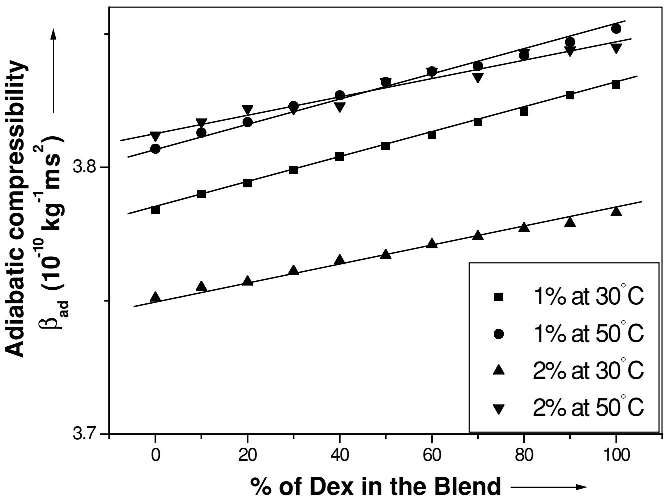


Fig. 8. Effect of temperature on the variation of adiabatic compressibility, with composition of 1% and 2% w/v of Dex/PVP blend in solution at 30 and 50°C.

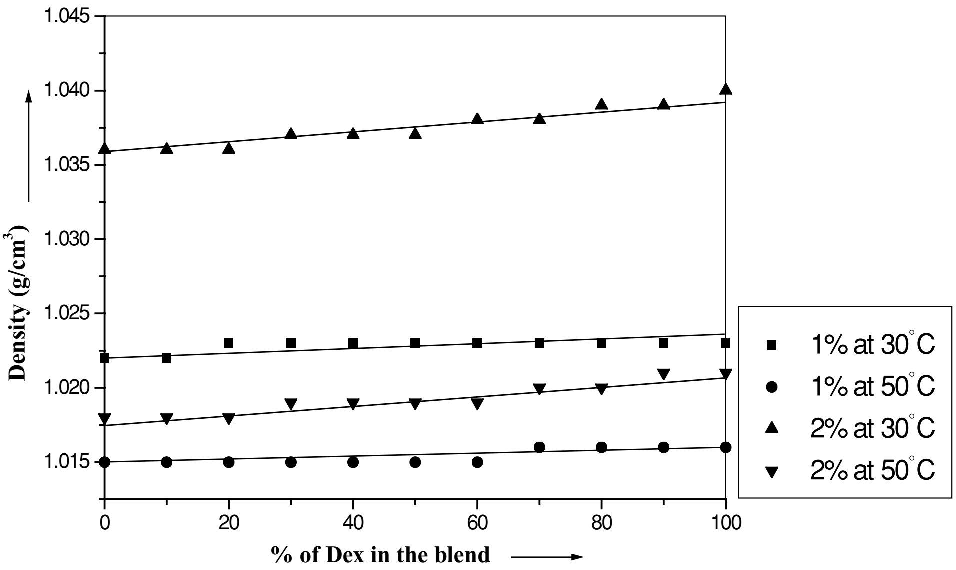


Fig. 9. Effect of temperature on the variation of density, with composition of 1% and 2% w/v of Dex/PVP blend in solution at 30 and 50°C.

where b_{12} is the slope for the blend solution. Using these values, Chee (13) defined a more effective parameter as follows:

$$\mu = \frac{\Delta \mathrm{B}}{\{[\eta]_2 - [\eta]_1\}^2} \tag{4}$$

where $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities for the pure component solutions. For miscible blend $\mu \geq 0$ and $\mu < 0$ indicates immiscible. In the present study, the μ values at 30 and 50°C for Dex/PVP blend were found to be almost positive for most blend compositions indicating that the blend is miscible and the data are given in Table 1. Recently, Sun et al. (14) have suggested a new formula for the determination of miscibility of polymer as follows:

$$\alpha = K_m - \frac{K_1\,[\eta]_1^2\,w_1^2 + K_2\,[\eta]_2^2\,w_2^2 + 2\sqrt{K_1 K_2}\,[\eta_1]\,[\eta_2]\,w_1 w_2}{\{[\eta]_1\,w_1 + \;[\eta]_2\,w_2\}^2} \tag{5}$$

where, K_1, K_2 and K_m are the Huggin's constant for individual components 1 and 2 and the blend, respectively. While deriving this equation, the long-range hydrodynamic interactions are considered. Sun et al. (14) have suggested that the blend will be miscible when $\alpha \geq 0$ and immiscible

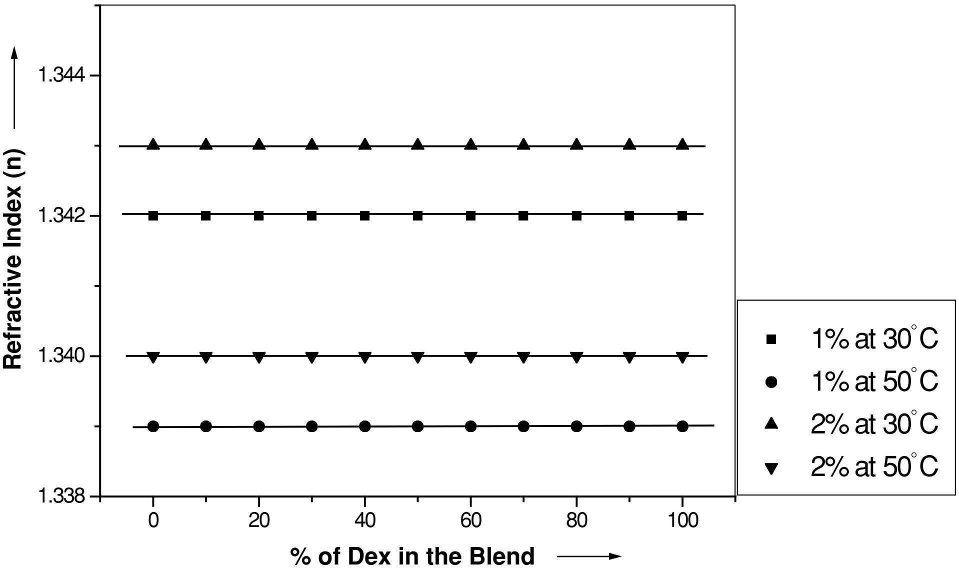


Fig. 10. Effect of temperature on the variation of refractive index, with the composition of 1% and 2% w/v of Dex/PVP blend in solution at 30 and 50°C.

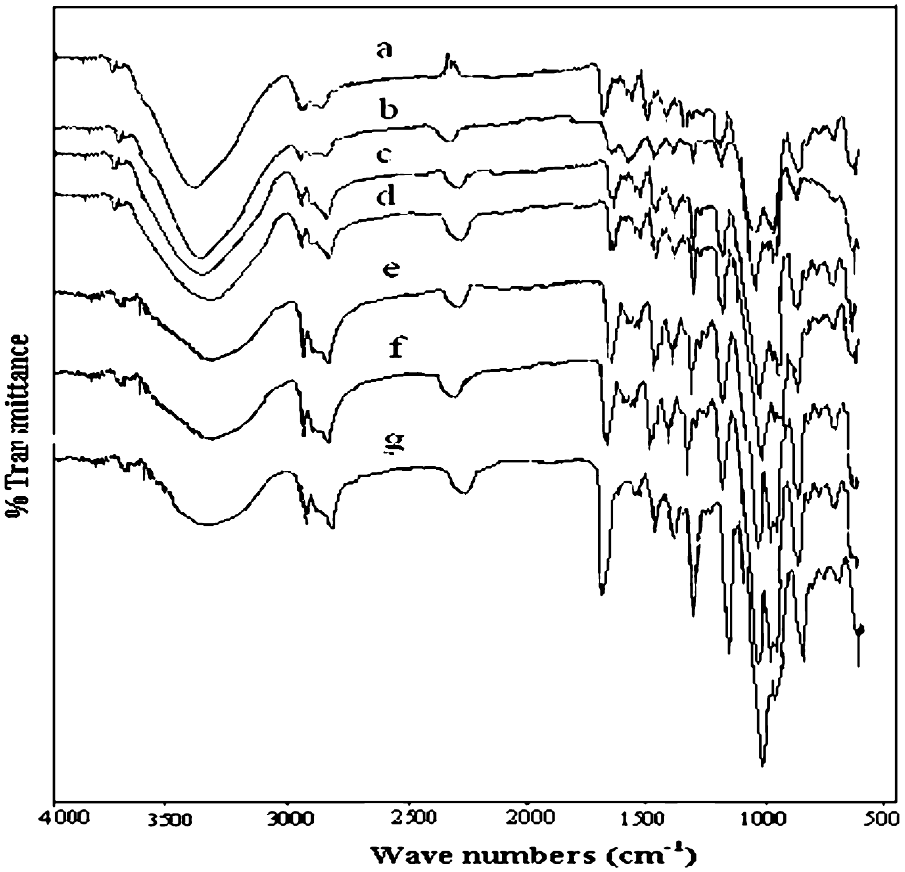


Fig. 11. FTIR spectra of (a) Dex, the blends Dex/PVP: (b) 90/10, (c) 70/30, (d) 50/50.

when $\alpha < 0$. The computed values of α were found to be almost positive at 30 and 50°C for most blend compositions indicating that the blend is miscible and the data are given in Table 1. Figures 5 and 6 show the miscibility and immiscibility regions with different compositions of Dex in the blend.

To confirm this further, we have measured the ultrasonic velocity (v), density (ρ) and refractive Index (n) of the blend under consideration of various compositions at 30 and 50°C. The variation of the ultrasonic velocity, density and refractive index with the blend compositions are shown in Figures 7–9, respectively. The adiabatic compressibility $\beta_{ad.}$ (18) of different blend compositions was evaluated by using the equation:

$$\beta_{ad} = \frac{1}{v^2 \rho} \tag{6}$$

Where, v is the velocity of sound and ρ is the density of blend solutions.

The variation of adiabatic compressibility at 30 and 50°C is as shown in Figure 10. In all cases, plots are found to be linear indicting the miscibility of the blend. For immiscible blend, the curves will be non linear because of the presence of voids at the interface between the two incompatible polymers which cause excess attenuation and non-linearity. Hence, it has already been established that the variation will be linear for miscible blends and nonlinear for immiscible blends (15–20). This observation is in agreement with μ and α values.

FTIR spectra of Dex, PVP and their blends 90/10, 70/30, 50/50, 30/70 and 10/90 are shown in Figure 11. The formation of miscible polymer blend requires the presence of specific interactions between the two polymers. Such interactions are evidenced by FTIR studies (39–42). In the Spectra of Dex, –OH stretching centered at 3445 cm^{-1}due to hydrogen bonded OH and a shoulder around 3600 cm^{-1} due to free OH groups, –CH stretching at 2918 cm^{-1}, –CH bending and rocking vibrations at 1460, 1430, and 995 cm^{-1}, –OH bending vibrations at 1280 cm^{-1}, and –C–O stretching in the 1150–1100 cm^{-1} region are observed. Another significant absorption band was the C–OH stretching region of FTIR spectra (~990–1060 cm^{-1}). The reason being, when a hydroxyl group next to a carbon atom is involved in hydrogen bond formation, the bond between C and OH would also be affected (43).

In the PVP spectrum, the strong absorption at 1670 cm^{-1} is associated with C=O absorption of tertiary amide and the five member ring. This C=O band occurs at a longer wavelength than normal carbonyl absorption due to the resonance effect. Absorption at 1286 cm^{-1} is due to –CN

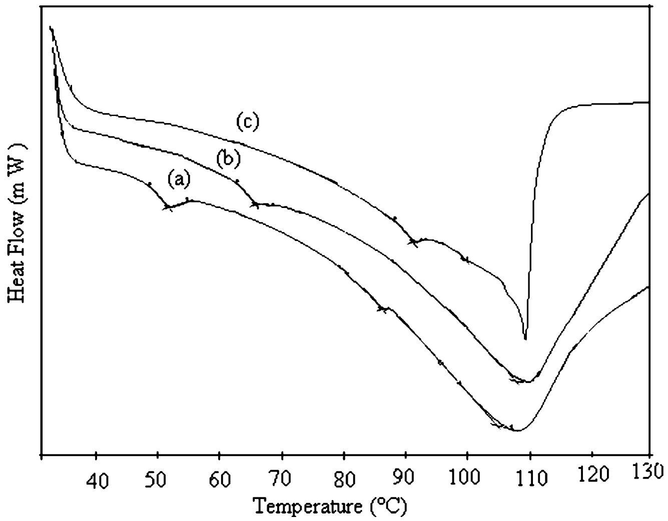


Fig. 12. DSC thermograms of (a) Dex, (b) Dex/PVP blend (50/50) and (c) PVP.

bond. The band was observed at 1450 due to $CH_2{-}C{=}O$. Besides this, the symmetrical stretching CH_2 occurs near 2930 cm^{-1}, the absorption peak around 3500 cm^{-1} can be ascribed to the C N group, –CH stretching at 2840–3000 cm^{-1}. The spectra of blend samples display characteristic absorption bands of Dex and PVP. In the –OH bending, –CN and –C–O stretching vibration bands of blend spectra, no clear evidence of specific interactions between Dex and PVP is observed. But as can be followed in Figure 2, as we move through to PVP spectrum, the –OH stretching absorption band shifts to lower frequencies. The –OH stretching absorption band of all blends is observed at a lower frequency than those of pure polymers. Also in Figure 9, as we move through to Dex spectrum, the C=O stretching absorption band shifts to lower frequencies (44,45). This shift towards lower energy reveals that there is a favorable interaction between Dex and PVP through the hydroxyl group of Dex and carbonyl group of PVP.

For further confirmation, the DSC thermograms of (a) Dex, (b) Dex/PVP blend (50/50) and (c) PVP are displayed in Figure 10. In the case of plain dextran, the Tg was obtained at 52°C. The small peak and broad peaks were observed at 86 and 105°C, respectively due to endothermic transition. In the case of plain PVP, the Tg was obtained at 90°C. The thermogram of PVP also showed a small and sharp peak at 99 and 109°C, respectively due to endothermic transition. For the Dex/PVP blend, Tg was obtained at 66°C and a broad peak was seen at 108°C, due to endothermic transition. However, there was no peak corresponding to Dex or PVP, indicating that the blend is miscible.

4. Conclusions

Using viscosity, ultrasonic velocity, density and refractive index methods the polymer blend of Dex/PVP of 1and 2% w/v in water at 30 and 50°C were found to be miscible. The miscibility of the blend in the case of Dex/PVP blend is independent of the changes in temperature and concentration. Thus, simple measurements like viscosity, ultrasonic velocity, density, and refractive index studies is an inexpensive, rapid and efficient method in exploring the miscibility of polymer blends in solution. FTIR spectroscopy provided analysis on the possible bonding interactions that was combined with thermal analysis to explain the mechanism of miscibility in the blend through formation of hydrogen bonding interactions between the Dex and PVP through the hydroxyl group of Dex and carbonyl group of PVP. Thermal analysis of system consisting of Dex and PVP (50/50) has shown miscible system with 1 Tg.

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