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Studies on Miscibility of Sodium Alginate/Polyethylene Glycol Blends

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Miscibility studies have been conducted on solutions of blends of sodium alginate (SA) and polyethylene glycol (PEG) over an extended range of concentrations and compositions in water. The ultrasonic velocity, viscosity, density, and refractive index of the blends have been measured at 30 and 50°C as a function of compositions of SA/PEG. The interaction parameters such as μ and α have been obtained using the viscosity data to probe the miscibility of the blends. The plots of reduced viscosity versus composition deviate from linearity according to the degree of miscibility of SA/PEG blends at all concentrations. The obtained miscibility results from viscosity have been confirmed by the ultrasonic velocity, density, and refractive index.

Keywords: polymer blends; viscosity; ultrasonic velocity; refractive index; miscibility

1 Introduction

Polymer blends are physical mixtures of structurally different polymers or copolymers, which interact with secondary forces with no covalent bonding such as hydrogen bond, dipole-dipole forces and charge-transfer complexes for homopolymer mixtures (1–3). Polymer–polymer miscibility can be determined by a number of techniques, such as differential scanning calorimetry (DSC), melt rheology, dynamic mechanical thermal analyzer (DMTA), neutron scattering, inverse gas chromatography and electron microscopy (4). Most of these techniques are, of course, sophisticated but costly and time consuming. Nowadays, simple, low cost and rapid techniques are available to study the miscibility of polymer blends. Chee (5) and Sun et al. (6) have employed a viscometer to study the miscibility of polymer blends. Paladhi and Singh (7, 8) and Varada Rajulu et al. (9) have shown that the variation of ultrasonic velocity, viscosity and refractive index is linear for compatible blends and non-linear for immiscible blends. Some methods used to access the miscibility were reported for the studies of the viscosities of polymer mixtures in solution, (10–15). Kuleznev et al. (12) and Hourston and Hughes (13), have reported the viscometric and sonic velocity measurements to access the miscibility of blends respectively. Singh and

Singh (16) presented the measurement of ultrasonic viscosity for compatible and Feldman and Rusu (10) presented the dynamic viscosity measurements.

Algin is a water soluble gum, found in all species of brown algae. It is an important constituent of the cell walls. The term algin is the generic designation for the salts of alginic acid, the most common is sodium alginate (17). Sodium alginate is a linear polysaccharide normally isolated from many strains of marine brown seaweed and algae (17). Recently, numerous scientists reported the miscibility of polymer blends using simple techniques (18–20).

Polyethylene glycol (PEG) is a water soluble and hydrophilic polymer. PEG series and their fatty acid esters are widely used in cosmetic and pharmaceutical industries. They have various characteristics such as water-solubility, non-volatility, physiological inertness, and lubricating properties. It can make skin moist, soft, comfortable etc. We can change the viscosity, moisture absorption and structure of the products according to their different molecular weight. The product with relative low molecular weight (not more than 2000) can be used as a wetting agent and thickness modifier for producing cream, emulsion, toothpaste, and shaving cream, etc. It can also be used for hair conditioners, the latter can make hair silky.

The authors selected sodium alginate as it is used as membrane material for dehydration studies (16, 17), in the food industry, etc. Polyethylene glycols are widely used as lubricants, binders, carriers, solvent and coatings in the cosmetics, pharmaceutical, paper, food, textile and chemical specialty fields (21).

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2 Experimental

SA [$\bar{M}_v = 4.96$ KDA by GPC method, Research grade, Thomas Baker Chemicals Limited, Mumbai, India], and PEG [$\bar{M}_v = 6000$, E. Merck (India) Limited, Mumbai, India] were used for the present study. A dilute polymer solution of 1% w/v, was prepared for all the methods. Stock solutions of homopolymers and blends of SA/PEG of different compositions viz., 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20 and 90/10 by wt%, were prepared in water. The viscosity and density measurements at 30 and 50°C were made using an Ubbelohde Suspended Level Viscometer (USLV) and specific gravity bottle, respectively. The required temperature was maintained within $\pm 0.05^\circ\text{C}$.

The ultrasonic velocities of the blend solutions with different compositions viz., 0/100, 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20 and 90/10 by wt% were measured at 30 and 50°C using an ultrasonic interferometric technique. The different temperatures were maintained by circulating water from a thermostat with a thermal stability of $\pm 0.05^\circ\text{C}$ through the double walled jacket of ultrasonic experimental cell. The experimental frequency was 2 MHz and the velocity measurements were accurate to better than $\pm 0.05\%$.

The refractive indices of blend solutions with different compositions were measured directly with a Abbe's refractometer with a thermostated water circulation system at 30 and 50°C. The accuracy of the refractive index measurement is $\pm 0.02\%$.

3 Results and Discussion

3.1 Reduced Viscosity Measurement Studies

In order to quantify the miscibility of the polymer blends, Chee (5) suggested the general expression for the interaction parameter when the polymers are mixed in weight fractions, w_1 and w_2 as;

$$\Delta B = \frac{b - \bar{b}}{2w_1w_2} \quad (1)$$

where, $\bar{b} = w_1b_{11} + w_2b_{22}$, where b_{11} and b_{22} are the slopes of the viscosity plots for the components 1 and 2 are related to Huggins coefficient K_H as;

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

For the ternary system, it is also given by;

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

where, b_{12} is the slope for the blend solution.

However, Chee's theory fails to account for the experimental data when the intrinsic viscosities for the pure components are far apart. In such cases, he defined a more efficient

interaction parameter to predict the miscibility,

$$= \frac{\Delta B}{\{[\eta]_2 - [\eta]_1\}^2} \quad (4)$$

where, $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities for the pure components. The polymer blend is miscible if $\mu \geq 0$ and immiscible when $\mu < 0$.

Recently, Sun et al. (6) suggested a most satisfactory new equation for the determination of polymer miscibility as;

$$\alpha = K_m$$

$$= \frac{k_1[\eta]_1^2w_1^2 + k_2[\eta]_2^2w_2^2 + 2\sqrt{k_1k_2}[\eta]_1[\eta]_2w_1w_2}{\{[\eta]_1w_1 + [\eta]_2w_2\}^2} \quad (5)$$

where, k_1 , k_2 and k_m are the Huggins constants for individual component 1, 2 and blend, respectively. The long-range hydrodynamic interactions are considered while deriving the equation. The polymer blend is miscible if $\alpha \geq 0$ and immiscible when $\alpha < 0$.

The measured values of reduced viscosity data for SA, PEG and their blend compositions viz., 90/10, 70/30, 50/50, 30/70 and 10/90 wt% at 30 and 50°C for different concentrations are given in Tables 1 (a, b) respectively. The Huggins plots of reduced viscosity against concentration for

Table 1. (a) The reduced viscosity data for SA, PEG and their blends in water at 30°C. (b) The reduced viscosity data for SA, PEG and their blends in water at 50°C

Concentration (g/dL)	(a) η_{sp}/c (dL/g) at 30°C						
	1%w/v, SA/PEG blend compositions						
	SA	PEG	90/10	70/30	50/50	30/70	10/90
1.0000	11.41	0.16	9.56	6.67	5.14	2.45	0.92
0.9000	10.90	0.16	9.11	6.36	5.09	2.40	0.84
0.8000	10.61	0.15	8.71	6.02	4.61	2.31	0.86
0.7000	9.94	0.14	8.02	5.71	4.50	2.21	0.82
0.6000	9.63	0.13	7.56	5.35	4.28	2.23	0.81
0.5000	9.10	0.13	7.00	5.09	4.10	2.15	0.79
0.4000	8.62	0.12	6.37	4.94	4.18	2.29	0.87
0.3000	8.23	0.11	6.59	5.35	4.42	2.59	0.89
0.2000	7.70	0.11	6.74	5.46	4.65	3.02	0.99
0.1000	7.26	0.10	6.86	5.81	4.88	3.37	1.05
(b) η_{sp}/c (dL/g) at 50°C							
1.0000	9.65	0.15	8.66	5.92	3.79	2.18	0.84
0.9000	9.22	0.14	8.18	5.66	3.61	1.97	0.82
0.8000	8.80	0.13	7.76	5.43	3.52	1.80	0.78
0.7000	8.52	0.12	7.35	5.13	3.32	1.76	0.75
0.6000	8.14	0.12	6.88	4.89	3.14	1.69	0.71
0.5000	7.74	0.11	6.48	4.62	2.95	1.64	0.72
0.4000	7.42	0.10	5.94	4.38	2.79	1.80	0.78
0.3000	7.09	0.09	6.01	4.48	3.12	2.07	0.85
0.2000	6.69	0.09	6.06	4.51	3.36	2.38	0.90
0.1000	6.39	0.08	6.23	4.75	3.61	2.62	0.98

the pure components and blends at 30 and 50°C are shown in Figures 1 (a) and (b) for SA/PEG blends, respectively. From these figures, it is evident that the Huggins plots are composed of two regions with varying slopes for SA/PEG blends.

Figures 1(a, b) indicate the considerable higher slope variation for 90/10, 70/30 and 50/50 compositions of SA/PEG blends at 30 and 50°C, respectively. Hence, SA/PEG blends are found to be miscible only when SA content is more than 50% in the blend. Below these critical concentrations, a sharp decrease in the slopes is observed in the Huggins plots due to phase separation.

In order to probe the miscibility of SA/PEG blends, the blend miscibility equations suggested by Chee (5) and Sun et al. (6) were utilized. The computed interaction parameters μ and α for SA/PEG blends at 30 and 50°C are presented in Table 2.

For the SA/PEG blend, it is observed from Table 2 that the μ values are negative when the sodium alginate content is up to 60% and then positive beyond this value. The α values are found to be negative when the sodium alginate content is up to 40% in the blend and then positive beyond this value at 30 and 50°C. For 50/50 and 60/40 blend compositions, the μ

Table 2. The interaction parameters μ and α of 1% w/v SA/PEG blends in water

% Wt Composition SA/PEG	1% w/v, SA/PEG blend			
	At 30°C		At 50°C	
	μ	α	μ	α
10/90	-0.0495	-0.7156	-0.0526	-0.5349
20/80	-0.0491	-0.3111	-0.0459	-0.3495
30/70	-0.0374	-0.0557	-0.0437	-0.2188
40/60	-0.0365	-0.0803	-0.0401	-0.1329
50/50	-0.0045	0.0883	-0.0097	0.1404
60/40	-0.0007	0.0549	-0.0032	0.0188
70/30	0.0168	0.1119	0.0238	0.0993
80/20	0.0349	0.1147	0.0385	0.1343
90/10	0.0599	0.1495	0.0715	0.1164

and α values give contradictory information. However, SA/PEG blend is found to be miscible only when sodium alginate content is more than 50% in the blend. It is also evident that the temperature has no effect on the miscibility of SA/PEG blends.

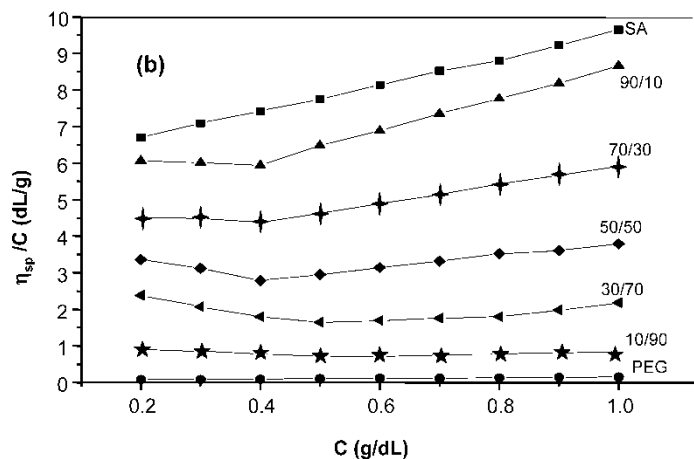
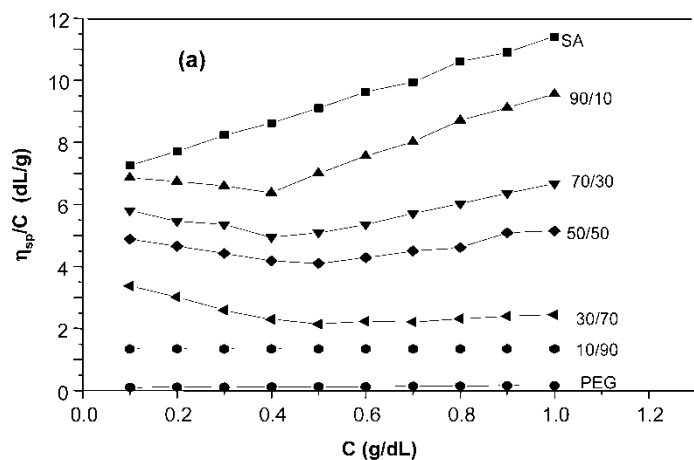


Fig. 1. The reduced viscosity data for SA, PEG and their blends in water at different temperatures; (a) 30 and (b) 50°C.

3.2 Effect of Temperature on the Reduced Viscosity

Figure 2 represents the effect of temperature on the variation of the reduced viscosity for 70/30% wt., SA/PEG blend. It is evident from the figure that the reduced viscosity decreases as the temperature increases. Figure 2 also revealed the non-linear behavior because of the semi-compatible nature of the blend. The computed interaction parameter α for 70/30% wt., SA/PEG blend, is +0.1119 and +0.0993 at 30 and 50°C, respectively (Table 2). These positive values indicate the miscibility of the blend composition at both temperatures. The plot of μ vs. composition of SA in

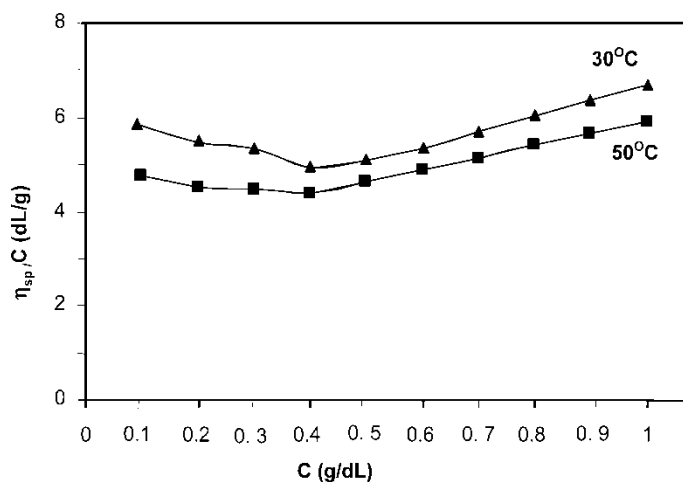


Fig. 2. Effect of temperature on the reduced viscosity for 70/30% wt., 1% w/v, SA/PEG blends in water at different temperatures.

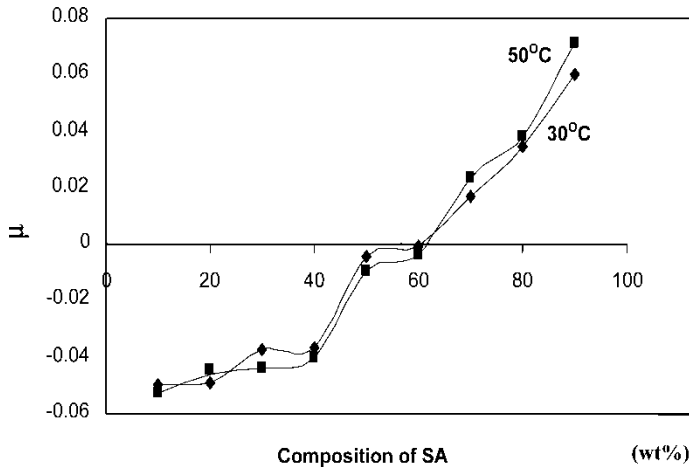


Fig. 3. Plot of interaction parameter, μ as a function of composition of SA at 30 and 50°C.

blends is shown in Figure 3. From the figure, it is clear that there is no temperature influence on the miscibility of the blends. For the sake of comparison, the plot of μ and α vs. composition of SA at 30°C is shown in Figure 4. The trend of μ and α with composition of blend is almost the same and positive values above 60% of SA.

For the sake of completion, the effect of compositions of blends on reduced viscosity is shown in Figures 5 (a, b) at 30 and 50°C, respectively. From the figure, the nonlinear behavior of reduced viscosity with compositions of blend was noticed. The order of reduced viscosity curve with reference to concentration of blend is; $0.1 \leq 0.5 < 1.0$, which is in the expected range.

The variation of theoretically predicted reduced viscosity as a function of SA composition for SA/PEG blends at both temperatures as shown in Figures 6 (a, b), respectively for 0.1, 0.5 and 1.0% concentrations of blends. From Figure 6, it was noticed that the linear behavior for theoretically predicted viscosity curves. The gap of reduced viscosity

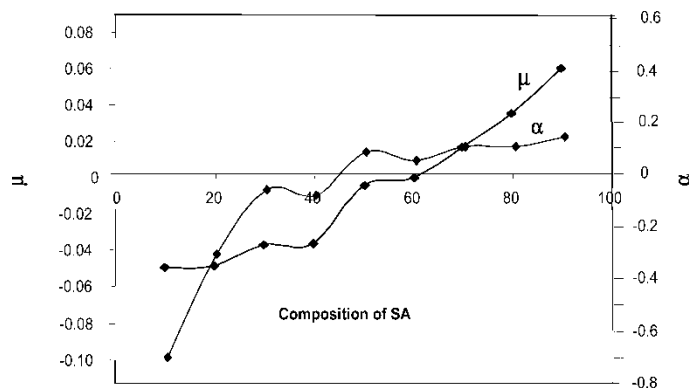


Fig. 4. Plot of interaction parameter μ and α as a function of composition of SA at 30°C.

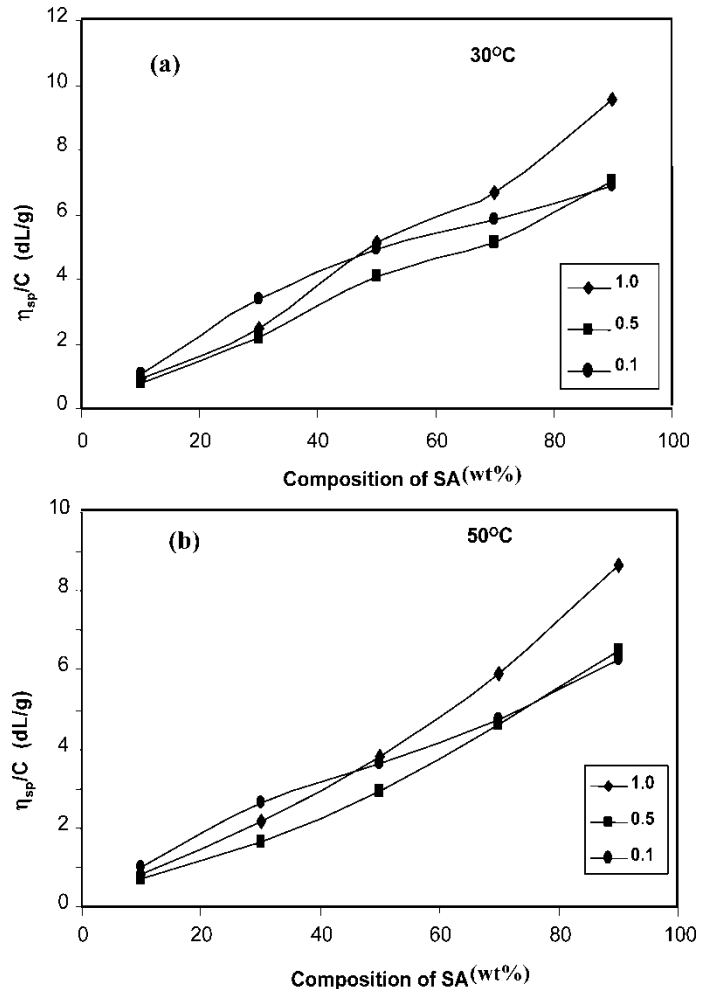


Fig. 5. Variation in reduced viscosity as a function of SA content in SA/PEG for different concentrations at; (a) 30 and (b) 50°C.

between lower concentration to higher concentration of blends increases with increase in SA concentration. This is because, increase in high viscous SA component in the blend.

The comparison of both theoretical and experimental reduced viscosity as a function of composition of SA at 30 and 50°C is shown in Figures 7 (a, b), respectively for 1% solution. From the figure, it was noticed that, the increase in SA composition increases the reduced viscosity. This is due to increase in concentration of high viscous SA component in the blends. The experimentally measured reduced viscosity values are lower compared to theoretically calculated values. This result clearly indicates less interaction between SA and PEG.

3.3 Ultrasonic Velocity, Density, Adiabatic Compressibility and Refractive Index Measurement Studies

In order to confirm the exact nature of the SA/PEG blends, ultrasonic velocity, density and refractive index at various

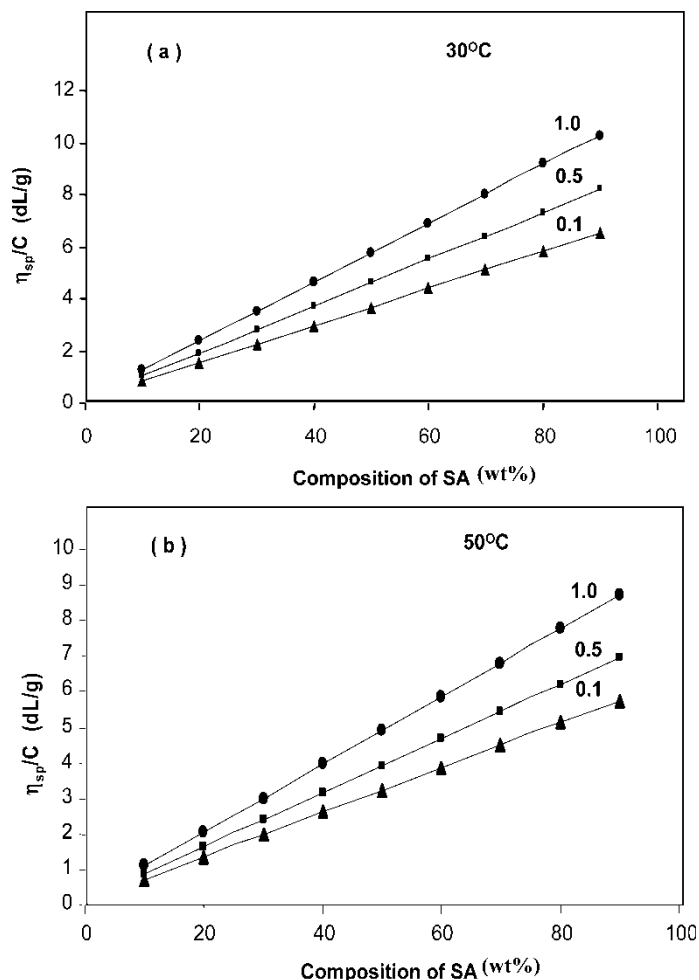


Fig. 6. Theoretically predicted reduced viscosity as a function of SA content in SA/PEG for different concentration at; (a) 30 and (b) 50°C.

blend compositions and at different temperatures were measured (Table 3). The adiabatic compressibility (β_{ad}) of different blend compositions was evaluated. The variations of ultrasonic velocity, density, adiabatic compressibility and refractive index as a function of blend compositions for SA/PEG blends is shown in Figures 8–11 respectively. These graphs showed both linear and non-linear regions indicating the semi-compatible nature of the blends. In the present investigation, the variation is found to be linear when the SA content is more than 50% in SA/PEG blend at both these temperatures. Below the critical concentration, the variations are found to be non-linear due to phase separation in the blend. The linearity in the graphs may be due to possible specific interactions like hydrogen bonding to some extent between the hydroxyl groups of sodium alginate and ether groups of polyethylene glycol (1–3) in the SA/PEG blend. Departure from linearity has been indicated in the sonic velocity measurements in the solid incompatible blends (13).

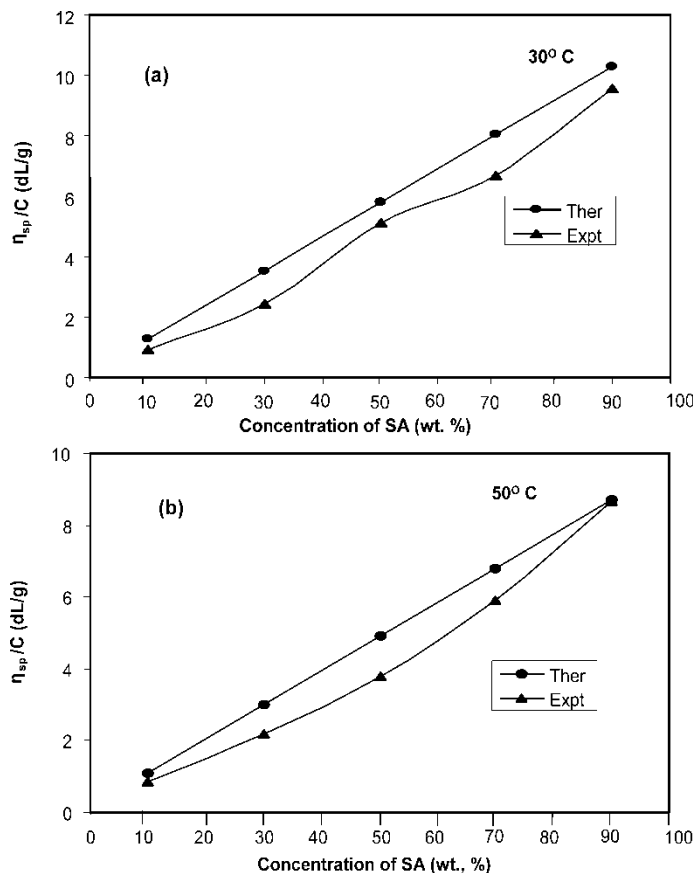


Fig. 7. The experimental and theoretically calculated reduced viscosity data as a function of PEG concentration in SA/PEG (1% solution) blends in water at different temperatures: (a) 30 and (b) 50°C.

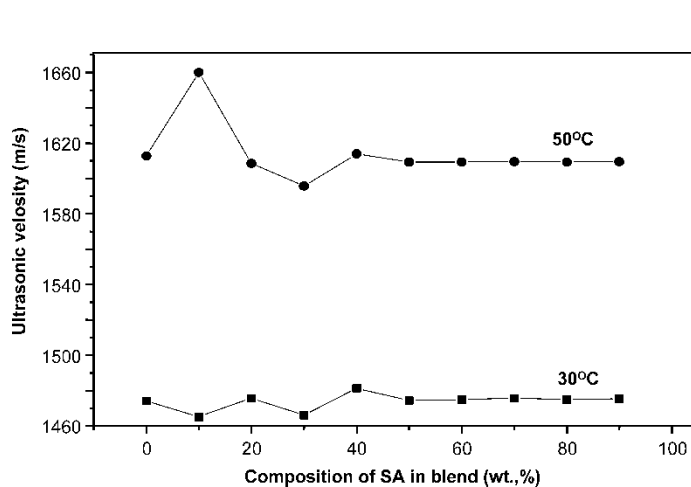
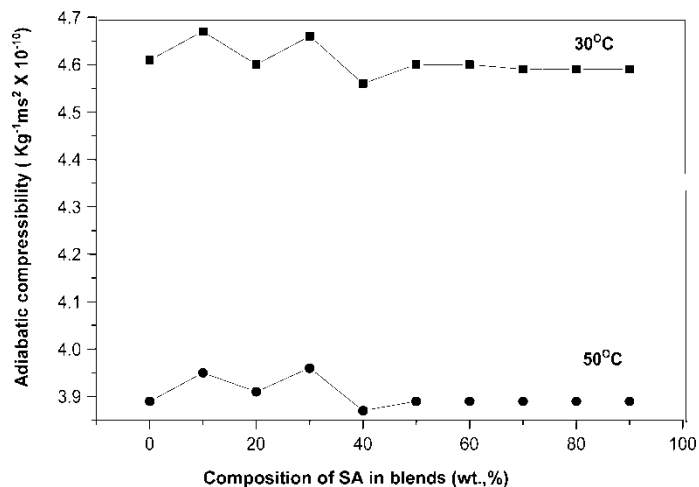
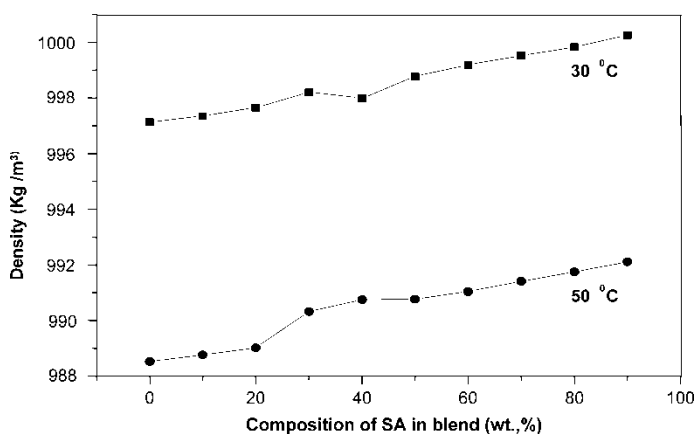
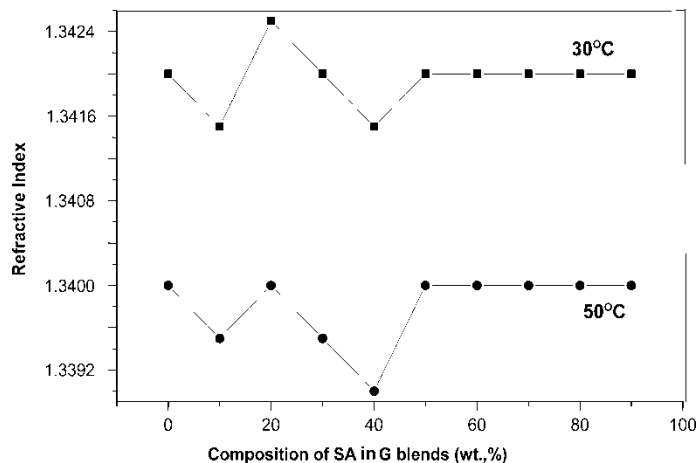
These observations are in conformity with the obtained α values based on the Sun et al. (6) method. Hence, the present study indicates the existence of miscibility windows only when sodium alginate content is more than 50% in SA/PEG blends.

3.4 Effect of Temperatures on the Ultrasonic Velocity, Density, Adiabatic Compressibility and Refractive Index

From Figures 8–11 for SA/PEG blends, it can be observed that the ultrasonic velocity increases and the density, adiabatic compressibility and refractive index decreases as the temperature increases. With the change in temperature, the shape of curve is not altered. This result clearly indicates that the temperature has no effect on the miscibility of the blends. The SA/PEG blends are found to be miscible when SA content is more than 50% in the blend. Thus, SA/PEG blends are found to be semi-compatible at both temperatures.

Table 3. The ultrasonic velocity, density, adiabatic compressibility and refractive index data for 1% w/v, SA/PEG blends in water at 30 and 50°C

% wt Composition SA/PEG	At 30°C				At 50°C			
	Ultrasonic velocity (m/s)	Density (kg/m ³)	Adiabatic compressibility β (kg ⁻¹ ms ²) $\times 10^{-10}$	Refractive index	Ultrasonic velocity (m/s)	Density (kg/m ³)	Adiabatic compressibility β (kg ⁻¹ ms ²) $\times 10^{-10}$	Refractive index
0/100	1474.13	997.13	4.61	1.3420	1612.80	988.53	3.89	1.3400
10/90	1465.06	997.35	4.67	1.3415	1670.00	988.77	3.95	1.3395
20/80	1475.73	997.65	4.70	1.3425	1708.53	989.02	3.91	1.3400
30/70	1466.13	998.21	4.66	1.3420	1595.73	990.32	3.96	1.3395
40/70	1481.33	997.99	4.56	1.3415	1613.86	990.75	3.87	1.3390
50/50	1474.40	998.77	4.70	1.3420	1709.33	990.77	3.89	1.3400
60/40	1474.93	999.19	4.70	1.3420	1709.33	991.04	3.89	1.3400
70/30	1475.73	999.52	4.59	1.3420	1709.70	991.41	3.89	1.3400
80/20	1474.93	999.83	4.59	1.3420	1709.33	991.75	3.89	1.3400
90/10	1475.46	1000.25	4.59	1.3420	1709.70	992.11	3.89	1.3400

**Fig. 8.** Variation of ultrasonic velocity with composition of SA/PEG blends in water at 30 and 50°C.**Fig. 10.** Variation of adiabatic compressibility with composition of SA/PEG blends in water at 30 and 50°C.**Fig. 9.** Variation of density with composition of SA/PEG blends in water at 30 and 50°C.**Fig. 11.** Variation of refractive index with composition of SA/PEG blends in water at 30 and 50°C.

4 Conclusions

Based on viscosity, density, ultrasonic velocity and refractive index measurements, the SA/PEG blends are found to be miscible only when the SA content is more than 50% in the blends at both these temperatures. Hence, SA/PEG blends in water at 30 and 50°C are said to be semi-compatible in nature. Also, the temperatures have no effect on the miscibility of these blends. But, as the temperature increases, reduced viscosity, density, adiabatic compressibility and refractive index decreases while ultrasonic velocity increases. It may be concluded that the simple measurements like viscosity, ultrasonic velocity, density and refractive index provide a information to the semi miscibility of SA/PEG blends, generally which is obtained by sophisticated techniques such as thermal and SEM techniques.

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