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Miscibility studies of HPMC/PEG blends in water by viscosity, density, refractive index and ultrasonic velocity method

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ABSTRACT

Hydroxy propyl methyl cellulose (HPMC)/polyethylene glycol (PEG) blends are edible polymer films used for food packing and directly in foodstuffs. However, they are water-soluble in ordinary temperature and have good mechanical properties. The miscibility of HPMC/PEG blend in water was studied by viscosity, ultrasonic velocity, density and refractive index techniques at 30 and 50 °C. Using viscosity data, the interaction parameters μ and α were calculated. These values revealed that HPMC/PEG blend is miscible when the HPMC content is more than 60 wt.% in the blend at 30 and 50 °C, below which is immiscible. Further the result was also confirmed by ultrasonic velocity, density, refractive index measurements, which also revealed that the change in temperature has no significant effect on the miscibility of HPMC/PEG polymer blend.

1. Introduction

The importance of polymer blending has been increased in recent years, because of the preparation of polymeric materials with desired properties, low basic cost and improved process ability. Polymer blends are physical mixtures of structurally different polymers or copolymers, which interact through secondary forces with no covalent bonding (Krause, 1978) and are miscible at molecular level. The basis of polymer–polymer miscibility may arise from any specific interactions, such as hydrogen bonding, dipole–dipole forces and charge transfer complexes for homopolymer mixtures (Varnell & Coleman, 1981; Varenell, Runt, & Coleman, 1983; Woo, Barlow, & Paul, 1986). There have been various techniques of studying the miscibility of the polymer blends (Cabanclas, Serrano, & Baselga, 2005; Crispim, Rubira, & Muniz, 1999; Jiang & Han, 1998; Patel, 2004; Ping, 1997). Some of these techniques are complicated, costly and time consuming. Hence it is desirable to identify simple, low cost and rapid techniques to study the miscibility of polymer blends. Chee (1990) and Sun, Wang, and Fung (1992) have suggested a viscometric method for the study of polymer–polymer miscibility in solution. Singh and Singh (1983, 1984)) have suggested the use of ultrasonic velocity and viscosity measurements for investigating the polymer miscibility in solution. Palladhi and Singh (1994a, 1994b) have shown that the variation of ultrasonic velocity and viscosity with blend composition is linear for miscible blends and non-linear for immiscible blends. Recently, (Varada Rajulu, Reddy, and Ranga Reddy (1998) and Varada Rajulu, Siddaramaiah, and Reddy (1998) have used ultrasonic and refractometric technique to study the miscibility of polymer blend.

As part of our research work, we have studied the miscibility of HPMC/PEG blend in water at different temperatures by viscosity, ultrasonic velocity, density and refractive index techniques (Demappa, Basavaraju, & Rai, 2006, 2007). We selected these polymers, because they have many pharmaceutical and biomedical applications (Jumel, Harding, & Hayter, 1996; Zeng, Fang, & Xu, 2004). Hydroxy propyl methyl cellulose (HPMC) is a polysaccharide prepared from cellulose. It contains both methyl and hydroxy propyl substitutes. Poly(ethylene glycol) (PEG) is a synthetic water-soluble polymer with good film forming property, which offers good tensile strength (TS), flexibility and barrier properties to oxygen and aroma (Schellekens & Bastiansen, 1991). Poly(ethylene glycol) (PEG) is used in all applications of aqueous phase partitioning. For biochemical separations on the laboratory scale, the most com-

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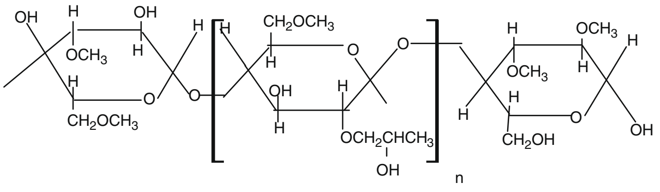
monly used aqueous phase system is composed of Dextron and PEG (Albertson, 1986). The structures of both HPMC and PEG are shown in Schemes 1 and 2, respectively.

2. Experimental

HPMC (E 15 LV premium; LOBA CHEMIE Pvt. Ltd) and PEG ($\overline{M_w} = 200$; AR grade, Merck India Ltd., India) were used for this work. A dilute polymer solution of 1% w/v was prepared for viscometric studies. Stock solutions of homopolymers and the blends of HPMC/PEG of different compositions, 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20 and 90/10, were prepared in water. Viscosity measurements at 30 and 50 °C were made using an Ubbelohde suspended level viscometer with the flow time of 98 s for distilled water. The total weight of the two components in the solution was always maintained at 1 g/dL. And the different temperatures were maintained in a thermostat bath, with a thermal stability of ±0.05 °C. The ultrasonic velocity measurements were performed by an ultrasonic interferometric technique (Varada Rajulu & Mabusab, 1996). The temperatures were maintained at 30 and 50 °C by circulating water from a thermostat, with a thermal stability of ±0.05 °C, through the double-walled jacket of the ultrasonic experimental cell. 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 by specific gravity bottle. The refractive indices of the HPMC/PEG blend solutions were measured using an Abbe's refractometer, with a thermostat water-circulation system (Varada Rajulu & Mabusab, 1998) at 30 and 50 °C (Singh & Singh, 1984). The accuracy of the refractive index measurements is ±0.02%.

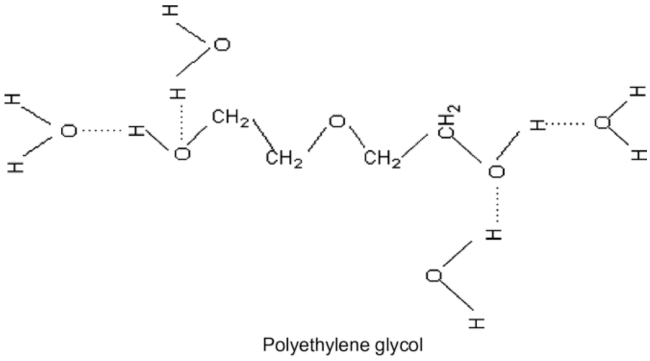
3. Results and discussion

HPMC, however, is known to be a flexible non-ionic polymer, which obeys the classical Huggin's equation. The Huggin's plots for the pure components (HPMC and PEG) and their blends at 30 and 50 °C are shown in Figs. 1, 2 and Tables 1, 2, respectively. The figure indicates the considerable higher slope variation for 80/20 and 60/40 HPMC/PEG blend compositions. This may be attributed to the mutual attraction of macromolecules in solution, because of the increase of hydrodynamic and thermodynamic interaction. Hence HPMC/PEG blend is found to be miscible, only when the HPMC content is more than 60% in the blend. Below this critical concentration, a sharp decrease in the slope is observed in the Huggin's plot because of the phase separation.



$C_8H_{16}O_8\ (C_{10}H_{18}O_8)_nC_8H_{16}O_8$

Scheme 1. Structure of HPMC.



Scheme 2. Structure of PEG.

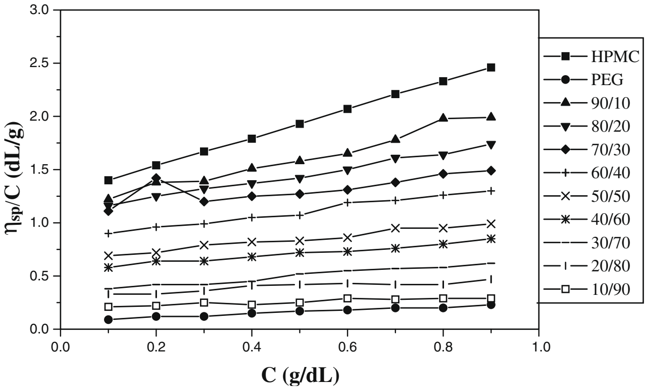


Fig. 1. Huggin's plots for 1% w/v HPMC/PEG blend in water at 30 °C.

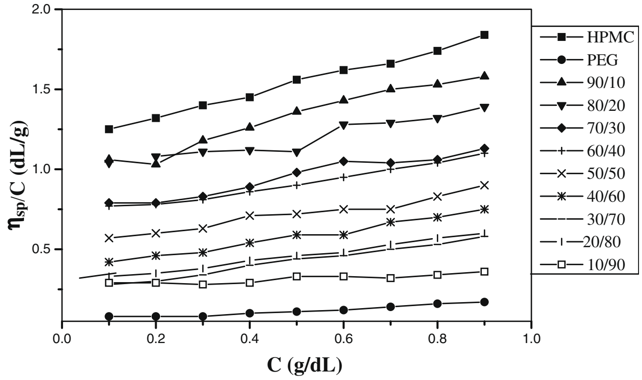


Fig. 2. Huggin's plots for 1% w/v HPMC/PEG blend in water at 50 °C.

To quantify the miscibility of the polymer blends Chee (1990) suggested that the general expression for interaction parameter when polymers are mixed in weight fractions w_1 and w_2 is as follows:

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

where $\bar{b} = w_1b_{11} + w_2b_{22}$ in which, b_{11} *and* b_{12} are the slopes of the viscosity curves for the pure components. The coefficient b is related to the Huggin's coefficient K_H as

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

for ternary systems, the coefficient b is also given by

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

where b_{12} is the slope for the blend solution. Using these values, Chee (1990) defined a more effective parameter as follows:

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

where $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities for the pure component solutions. The blend is miscible when $\mu \geqslant 0$ and immiscible

Table 1
The reduced viscosity data for HPMC/PEG and their blends in water at 30 °C

Concentration (g/dL)	η_{sp}/C (dL/g) at 30 °C									
	HPMC	PEG	HPMC/PEG blend composition							
			90/10	80/20	70/30	60/40	50/50	40/60	30/70	20/80	10/90
0.1	1.40	0.09	1.22	1.16	1.11	0.90	0.69	0.58	0.38	0.33	0.21
0.2	1.54	0.12	1.38	1.25	1.42	0.96	0.72	0.64	0.42	0.33	0.22
0.3	1.67	0.12	1.39	1.32	1.20	0.99	0.79	0.64	0.42	0.36	0.25
0.4	1.79	0.15	1.51	1.37	1.25	1.05	0.82	0.68	0.45	0.41	0.23
0.5	1.93	0.17	1.58	1.42	1.27	1.07	0.83	0.72	0.52	0.42	0.25
0.6	2.07	0.18	1.65	1.50	1.31	1.19	0.86	0.73	0.55	0.43	0.29
0.7	2.21	0.20	1.78	1.61	1.38	1.21	0.95	0.76	0.57	0.42	0.28
0.8	2.33	0.20	1.98	1.64	1.46	1.26	0.95	0.80	0.58	0.42	0.29
0.9	2.46	0.23	1.99	1.74	1.49	1.30	0.99	0.85	0.62	0.47	0.29

Table 2
The reduced viscosity data for HPMC/PEG and their blends in water at 50 °C

Concentration (g/dL)	η_{sp}/C (dL/g) at 50 °C									
	HPMC	PEG	HPMC/PEG blend composition							
			90/10	80/20	70/30	60/40	50/50	40/60	30/70	20/80	10/90
0.1	1.25	0.08	1.06	1.04	0.79	0.77	0.57	0.42	0.28	0.33	0.29
0.2	1.32	0.08	1.13	1.08	0.79	0.78	0.60	0.46	0.30	0.35	0.29
0.3	1.40	0.08	1.18	1.11	0.83	0.81	0.63	0.48	0.34	0.38	0.28
0.4	1.45	0.10	1.26	1.12	0.89	0.86	0.71	0.54	0.40	0.43	0.29
0.5	1.56	0.11	1.36	1.11	0.98	0.90	0.72	0.59	0.44	0.46	0.33
0.6	1.62	0.12	1.43	1.28	1.05	0.95	0.75	0.59	0.46	0.48	0.33
0.7	1.66	0.14	1.50	1.29	1.04	1.00	0.75	0.67	0.50	0.53	0.32
0.8	1.74	0.16	1.53	1.32	1.06	1.04	0.83	0.70	0.53	0.57	0.34
0.9	1.84	0.17	1.58	1.39	1.13	1.10	0.90	0.75	0.58	0.60	0.36

when $\mu < 0$ (Chee, 1990). The values of μ, calculated with the aforementioned expression at 30 and 50 °C are represented in Table 3.

Recently, Sun et al. (1992) have suggested a new formula for the determination of polymer miscibility as follows:

$$\alpha = K_m - \frac{K_1[\eta]_1^2 w_1^2 + K_2[\eta]_2^2 w_2^2 + 2\sqrt{K_1K_2}[\eta_1][\eta_2]w_1w_2}{\{[\eta]_1 w_1 + [\eta]_2 w_2\}^2} \tag{5}$$

where K_1, K_2 and K_m are the Huggin's constants for individual components 1, 2 and the blend, respectively. The long-range hydrodynamic interactions are considered while deriving this equation. Sun et al. (1992) have suggested that a blend will be miscible when $\alpha \geqslant 0$ and immiscible when $\alpha < 0$.The computed values of μ and α are found to be negative when the HPMC content is up to 50% and then positive beyond this value at 30 and 50 °C, respectively, and the data are given in Table 3 and Fig. 3 shows the miscibility windows of the HPMC/PEG blend in water. As the long-range hydrodynamic interactions are considered in the equation for α, Eq. (5) is more accurate than Eq. (4). A similar

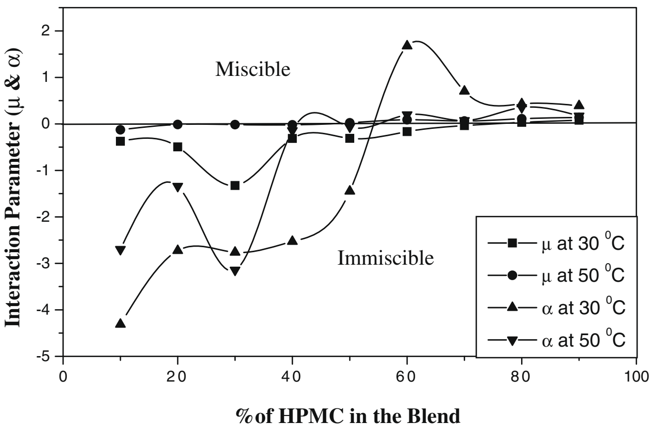


Fig. 3. Effect of temperature on the interaction parameter μ and α of 1% w/v of HPMC/PEG blend in water at 30 and 50 °C.

Table 3
Interaction parameters, density, refractive index, ultrasonic velocity and adiabatic compressibility of HPMC/PEG blend at 30 and 50 °C

Composition HPMC/PEG	Interaction parameter				Ultrasonic velocity (m/s)		Density (g/cm^3)		Refractive index (n)		Adiabatic compressibility (kg/ms^2) × 10^{-11}	
	μ	α	μ	α								
	30 °C		50 °C		30 °C	50 °C	30 °C	50 °C	30 °C	50 °C	30 °C	50 °C
10/90	−0.3736	−4.3120	−0.1275	−2.6998	9950	13990	1.0337	1.0312	1.341	1.339	0.9990	0.4960
20/80	−0.4942	−2.7278	−0.0140	−1.3419	11803	12923	1.0379	1.0305	1.342	1.347	0.6650	0.5810
30/70	−1.3249	−2.7632	−0.0162	−3.1464	11956	11876	1.0349	1.0313	1.340	1.338	0.6760	0.6870
40/60	−0.3138	−2.5312	−0.0205	−0.1469	8336	15987	1.0348	1.0290	1.341	1.339	1.3906	0.3816
50/50	−0.3095	−1.4488	0.0233	−0.0660	11940	12818	1.0364	1.0308	1.340	1.337	0.6777	0.5909
60/40	−0.1652	1.6743	0.0879	0.1948	9918	11886	1.0353	1.0300	1.341	1.339	0.9699	0.6878
70/30	−0.0368	0.7001	0.0616	0.0715	9831	11920	1.0355	1.0305	1.341	1.339	0.9990	0.6876
80/20	0.0320	0.4302	0.1105	0.3506	9865	11875	1.0359	1.0311	1.341	1.339	0.9920	0.6871
90/10	0.0781	0.3880	0.1372	0.1691	9870	11899	1.0361	1.0316	1.341	1.339	0.9890	0.6830

observation was made by Jayaraju, Raviprakash, Keshavayya, and Rai (2006), Varada Rajulu, Reddy, et al. (1998), and Varada Rajulu, Siddaramaiah, et al. (1998) in case of polyvinyl pyrrolidone/polystyrene and chitosan/hydroxypropyl methyl cellulose blends, where μ was found to be negative and α was found to be positive. They confirmed the miscibility of such blends by other methods. To confirm this further, we have measured the ultrasonic velocity (v), density (ρ) and refractive index (n) of the blend under consideration at various compositions, at 30 and 50 °C. These values are presented in Table 3. The variation of the ultrasonic velocity in Fig. 4, density and refractive index with the blend composition is shown in Fig. 5, respectively. The adiabatic compressibility β_{ad} (Varada Rajulu, Rao, & Naidu, 1990) of different blend compositions was evaluated by using the equation.

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

where v is the velocity of sound and ρ is the density of blend solutions, and the values are given in Table 3. The variation of adiabatic compressibility at 30 and 50 °C is shown in Fig. 5. The graphs show both linear and non-linear regions. It was already established (Cabanclas et al. and Sun et al.) that the variation is linear for miscible blend and non-linear for immiscible blend. In the present case, the variation is found to be linear when the HPMC content is more than 60% at 30 and 50 °C, respectively. This observation is in confirmation with μ and α value. So the present study indicates the existence of miscibility windows when the HPMC content is more than 60% in the blend. This is because, the specific interaction between the polymer segments is more when the HPMC content is more than 60%, there by, leading to miscibility of the blend. And below this composition there will not be much interaction between the polymer segments, which leads to immiscibility of the polymer blend. Here, the miscibility of the blend may be due to some specific interaction like H-bonding between HPMC/PEG.

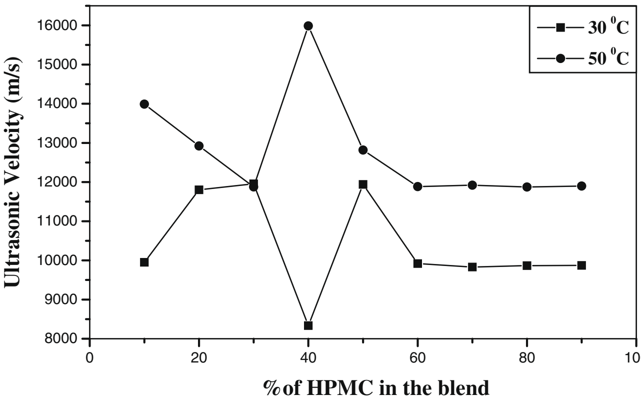


Fig. 4. Effect of temperature on the variation of ultrasonic velocity of 1% w/v of HPMC/PEG blend in water at 30 and 50 °C.

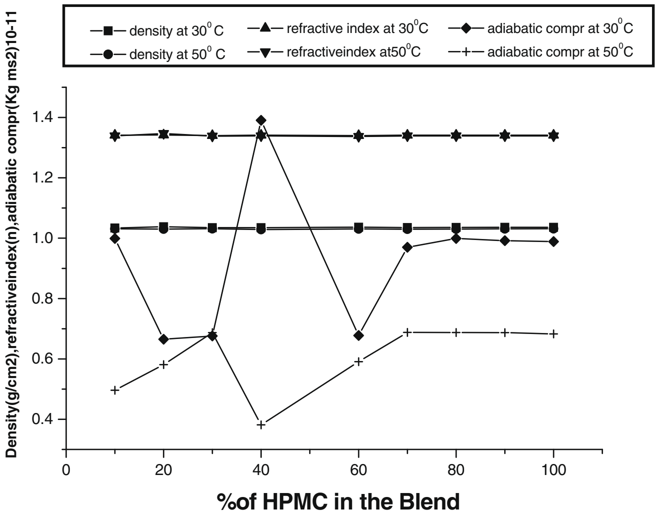


Fig. 5. Effect of temperature on the variation of density, refractive index and adiabatic compressibility of 1% w/v of HPMC/PEG blend in water at 30 and 50 °C.

4. Conclusion

Using viscosity, Ultrasonic velocity, density and refractive index methods, it is concluded that the polymer blend of HPMC/PEG is found to be miscible, when the HPMC content is more than 60% in the blend at 30 and 50 °C, respectively. Below this HPMC concentration, the blends were found to be immiscible. It is also observed that temperature has no significant effect on the miscibility of these blends even though the reduced viscosity, density, refractive index and adiabatic compressibility decreases and the ultrasonic velocity increases as the temperature increases. Thus afore mentioned techniques are simple, low cost, rapid and efficient methods in exploring the miscibility windows of HPMC/PEG blend in solution.

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