Journal of Molecular Liquids 157 (2010) 57–60

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Viscometric and volumetric study of dilute aqueous solutions of binary and ternary poly(ethylene glycol)/poly(vinyl alcohol) systems at different temperatures

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ARTICLE INFO

Article history:
Received 14 January 2010
Received in revised form 17 August 2010
Accepted 19 August 2010
Available online 20 September 2010

Keywords:
Poly (ethylene glycol)
Poly (vinyl alcohol)
Viscosity of polymer mixtures
Density of polymer mixtures

ABSTRACT

Densities and viscosities of binary and ternary systems of poly(ethylene glycol) (PEG) + H_2O, poly(vinyl alcohol) (PVA) + H_2O and PVA + PEG + H_2O in the concentration range of 0.5–5 wt.% at different temperatures of 298.15, 308.15, 318.15 K, have been measured. The molecular weight of PVA and PEG were 67,000 and 3000, respectively. The mass ratio of PVA to PEG was selected as 75:25, 50:50, 25:75 in the ternary solutions. From density data the apparent specific volumes were obtained and correlated using a semi empirical equation. From viscosity data, the relative, specific and intrinsic viscosities for binary and ternary mixtures were obtained. The compatibility or incompatibility of two different polymer chains was concluded by using densimetric and viscometric method at different temperatures.

1. Introduction

Knowledge of thermodynamic and transport properties of polymer solutions is important for practical purposes. Furthermore, the dependence of these properties on composition and temperature is of great interest from a theoretical standpoint because it may lead to a better understanding of the fundamental behavior of polymer solutions [1–3]. When two polymer solutions with the same solvent are mixed, the two different polymers are dissolved each other or cause a liquid–liquid phase separation according to the interaction between two different polymers [4,5]. This intermolecular interaction is one of significant factors for polymer blending. When the attractive interaction is dominant, the different polymers in blend sample are highly compatible. Contrary, when the repulsive interaction is dominant, the blend sample causes a micro phase separation which characterizes generally the physical properties of samples. Inamura et al. have reported the temperature and composition dependence of the intrinsic viscosity $[\eta]$, the Huggins constant and the interaction parameter between two different polymers in some ternary systems in high polymer-concentration region [6]. They proposed also a relation between Huggins constant and compatibility of binary polymer mixtures in the aqueous ternary systems [7].

In this research work, density and viscosity of two component systems PVA + H_2O and PEG + H_2O and three component system PVA + PEG + H_2O with PVA/PEG mass ratio of 75:25, 50:50, 25:75, were measured in the concentration range of 0.5–5 (W/W) and three different tempratures 298.15, 308.15, 318.15 K. The measured values of densities were used to obtain apparent specific volumes at different temperatures. A new criteria, same as excess property, was proposed to analyse the polymer–polymer compatibility by using apparent specific volumes results. On the other hand, by using relative viscosity data the intrinsic viscosity of polymers were achieved. The same criteria was used to determine the polymer–polymer compatibility in ternary systems by using intrinsic viscosity data.

2. Experimental

PVA (average molar mass of 67,000 g/mol) was obtained from Fluka and PEG (average molar mass of 3000 g/mol) was obtained from Merck and used as received. Binary polymer solutions were prepared by dissolving the appropriate mass of polymers in water, followed by dilution to a measured volume. Ternary polymer solutions were prepared by mixing the two corresponding binary solutions.

All solution density values were measured with a vibrating-tube densimeter (Mettler Toledo DE51) with proportional temperature control that kept the samples at working temperature with temperature stability of ±0.01 K. The densimeter was calibrated with distilled water and dry air. The uncertainty in the density measurements was found to be 5×10^{-5} g cm^{-3}.

Viscosities were measured with an Ubbelohde-type viscometer immersed in a constant temperature bath [8]. The temperature in the water bath was controlled to within ±0.05 K. The flow time of

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doi:10.1016/j.molliq.2010.08.009

Table 1
Density of PVA (1) + H_2O (2) binary system at different temperatures.

$100w_1$	298.15 K	308.15 K	318.15 K
0.00	0.99704	0.99406	0.99024
0.50	0.99890	0.99507	0.99121
1.0	0.99931	0.99633	0.99232
1.50	1.00047	0.99741	0.99343
2.00	1.00167	0.99871	0.99454
2.50	1.00275	0.99993	0.99562
3.00	1.00338	1.00109	0.99681
3.50	1.00521	1.00227	0.99786
4.00	1.00642	1.00348	0.99917
4.50	1.00781	1.00471	1.00038
5.00	1.00898	1.00601	1.00161

investigated solution was measured with accuracy better than ±0.1s. For each solution, the flow time was measured at least three times. The uncertainty for the viscosity measurements was estimated to be ±0.5%.

3. Result and discussion

3.1. Volumetric results

Density data of the binary PEG + water and PVA + water and ternary PVA + PEG + water systems at different temperatures are reported in Tables 1–3. From these data the apparent specific volumes of the binary and ternary polymer solutions were calculated using the following equation:

$$v_{2\phi} = \frac{1}{w}\left(\frac{1}{\rho} - \frac{1-w}{\rho_1}\right) \tag{1}$$

where ρ and ρ_1 are, respectively, density of the solution and pure water and w is the mass fraction of the polymer. The $v_{2\phi}$ values were fitted to the following equation [9]:

$$v_{2\phi} = v_{2\phi}^{\infty} + b_v w \tag{2}$$

where $v_{2\phi}^{\infty}$ (the apparent specific volume of the polymer at infinite dilution) and b_v are empirical parameters which depend on polymer, solvent and temperature. The interaction between polymer and water can be concluded from the apparent specific volume of the polymer at infinite dilution. The calculated $v_{2\phi}^{\infty}$ and b_v values for different systems are reported in Table 4. The average RMSD of the parameters $v_{2\phi}^{\infty}$ and b_v are as: $\delta v_{2\phi}^{\infty} = \pm 0.003$ and $\delta_{bv} = \pm 0.08$. As can be seen from these data, the apparent specific volume at infinite dilution is increased with increasing temperature for both PVA and PEG aqueous binary systems. It means with increasing temperature the segment–solvent interaction is decreased and segment–segment interaction is increased.

Table 2
Density of PEG(1) + H_2O(2) binary system at different temperatures.

$100w_1$	298.15 K	308.15 K	318.15 K
0.00	0.99704	0.99406	0.99024
0.50	0.99782	0.99478	0.99077
1.0	0.99859	0.99553	0.99137
1.50	0.99937	0.99633	0.99206
2.00	1.00016	0.99714	0.99278
2.50	1.00093	0.99789	0.99359
3.00	1.00174	0.99871	0.99426
3.50	1.00253	0.99951	0.99497
4.00	1.00334	1.00033	0.99573
4.50	1.00417	1.00113	0.99655
5.00	1.00497	1.00199	0.99731

Table 3
Density of PVA + PEG + H_2O ternary system at different temperatures and different mass ratios.

$100w_1$	298.15 K	308.15 K	318.15 K
PVA/PEG = 75:25			
0.50	0.99796	0.99514	0.99112
1.0	0.99901	0.99621	0.99232
1.50	1.00001	0.99725	0.99327
2.00	1.00089	0.99828	0.99428
2.50	1.00189	0.99927	0.99512
3.00	1.00304	1.00033	0.99617
3.50	1.00398	1.00151	0.99717
4.00	1.00518	1.00255	0.99799
4.50	1.00615	1.00354	0.99891
5.00	1.00736	1.00501	1.00003
PVA/PEG = 50:50			
0.50	0.99794	0.99540	0.99144
1.0	0.99890	0.99619	0.99221
1.50	0.99977	0.99686	0.99308
2.00	1.00083	0.99814	0.99410
2.50	1.00171	0.99880	0.99499
3.00	1.00281	0.99992	0.99589
3.50	1.00378	1.00102	0.99688
4.00	1.00475	1.00192	0.99771
4.50	1.00577	1.00282	0.99869
5.00	1.00663	1.00372	0.99951
PVA/PEG = 25:75			
0.50	0.99788	0.99529	0.99108
1.0	0.99873	0.99602	0.99192
1.50	0.99959	0.99687	0.99287
2.00	1.00046	0.99784	0.99366
2.50	1.00138	0.99863	0.99457
3.00	1.00231	0.99951	0.99535
3.50	1.00319	1.00036	0.99624
4.00	1.00407	1.00112	0.99713
4.50	1.00505	1.00206	0.99790

For ternary systems we define $\Delta v_{2\phi}^{\infty}$, as difference between the experimental and ideal values of apparent molar volume at infinite dilution, same as excess property:

$$\Delta v_{2\phi}^{\infty} = v_{2\phi\,\mathrm{exp}}^{\infty} - v_{2\phi id}^{\infty} \tag{3}$$

where $v_{2\phi\,\mathrm{exp}}^{\infty}$ is determined from Eq. (2) for ternary systems and reported in Table 4, and $v_{2\phi id}^{\infty}$ is calculated from the apparent molar volumes at infinite dilution of binary systems as follows:

$$v_{2\phi id}^{\infty} = w_1 v_{2\phi PEG}^{\infty} + w_2 v_{2\phi PVA}^{\infty} \tag{4}$$

Using this criteria if $\Delta v_{2\phi}^{\infty} < 0$, the compatibility of two different polymer chains can be concluded or segment–segment interaction is important. If $\Delta v_{2\phi}^{\infty} > 0$, the incompatibility of two different polymer chains can be concluded or segment–solvent interaction is important. The values of $\Delta v_{2\phi}^{\infty}$ for ternary systems at different temperatures are

Table 4
The apparent specific volume at infinit dillution ($v_{2\phi}^{\infty}$/cm^3 g^{-1}) and constant b_v of Eq. (2) at different temperatures.

	298.15 K		308.15 K		318.15 K	
	$v_{2\phi}^{\infty}$	b_v	$v_{2\phi}^{\infty}$	b_v	$v_{2\phi}^{\infty}$	b_v
PVA	0.784	−0.41	0.786	−0.46	0.803	−0.49
PEG	0.848	−0.05	0.856	−0.20	0.901	−0.74
PVA/PEG:75/25	0.814	−0.31	0.788	0.11	0.808	0.07
PVA/PEG:50/50	0.821	−0.24	0.771	1.03	0.789	0.81
PVA/PEG:25/75	0.835	−0.22	0.784	1.08	0.823	0.05

Average RMSD for all systems is as: $\delta v_{2\phi}^{\infty} = \pm 0.003$; $\delta_{bv} = \pm 0.08$.