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Estimation of the compatibility of poly(ethylene glycol)/poly(ethylene oxide) blends from dilute solution viscosity measurements

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The intrinsic viscosities of poly(ethylene glycol)/poly(ethylene oxide) (PEG/PEO) blends have been measured in benzene as a function of blend composition for various molecular weights of PEO at two different temperatures (293.15 K and 303.15 K). In order to predict the compatibility of polymer pairs in solution, the interaction parameter term, Δb, and the difference between the intrinsic viscosities of the polymer blends and the weight average intrinsic viscosities, $\Delta[\eta]$, of the two polymer solutions taken separately are used. The effects of both temperatures and molecular weight of the blend components on the extent of compatibility was elucidated. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: intrinsic viscosity; single point measurement)

INTRODUCTION

Modern technology needs new types of polymer materials, properties of which are fitted to the particular use and may be even tuned in a sensitive way. However, the number of available monomers is limited; they do not provide a way to finely adjust the properties of the polymer. Frequently, a polymer is needed which would combine properties of two known polymers. Under such circumstances, it is often possible to copolymerize two or more monomers and prepare copolymers which do not only combine the properties of the homopolymers but sometimes exhibit valuable new properties. However, preparation of some copolymers may be difficult or outright impossible. In such cases, blending of polymers may be the answer. Technically, blending is an easy operation: the popularity of blends is ever increasing, as is the amount of literature devoted to the subject[1].

The key problem for the evaluation of polymer blends is the compatibility of the components on the molecular level: are the polymers miscible, partially miscible, or totally immiscible? As for all mixtures, the answer is provided by an analysis of the thermodynamic behaviour of the mixture. Different techniques are used for the evaluation of the compatibility of polymer blends. These techniques involve thermal and mechanical methods[2,3], NMR studies[4], scattering technique such as light scattering technique and neutron scattering which provide a valuable information about the thermodynamic behaviour of blends[5,6], calorimetric data for concentrated solutions in low molecular weight solvents[7,8], measurement of vapour sorption[4], inverse gas chromatography[9,10] and viscometry[11–17].

Due to its simplicity, viscometry becomes an attractive method for studying the compatibility of polymers in solution[11–17]. The basis for using dilute solution viscosity as a parameter for compatibility determination of polymer blends lies in the fact that while in solution the repulsive interaction may cause shrinkage of the polymer coils resulting in a lower value of the viscosity of the polymer blend than the value calculated from viscosities of both pure blend components on the assumption of the additivity law. On the other hand, the attractive interaction increases the viscosity of the system.

The present work discusses in detail an extensive investigation of compatibility in solutions of PEG/PEO blends in benzene at 293.15 K and 303.15 K by viscometric technique. Accordingly, the main objective of this article is to examine the regions of miscibility for PEG/PEO blends in terms of the interspecific interaction coefficient and the difference in the intrinsic viscosities of the polymer blends and the weight average intrinsic viscosities, $\Delta[\eta]$.

EXPERIMENTAL

Materials

Benzene was dried over anhydrous $MgSO_4$ and filtered to be dried additionally over sodium wire before it was distilled at atmospheric pressure. Three poly(ethylene oxide) samples were obtained from Aldrich Chemical Co. Ltd. (UK). their quoted relative molar masses M were 1.0×10^5, 3.0×10^5 and 6.0×10^5. These samples designated here as PEO1, PEO2 and PEO3, respectively. The nominal ratio of weight- to number-average molecular weights $\frac{M_w}{M_n}$ for the samples PEO1–PEO3 was less than 1.09. Poly(ethylene glycol) sample was obtained from Aldrich Chemical Co. Ltd. (UK). The quoted relative molar mass, M, was 1.0×10^5.

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Density and viscosity

The density of pure benzene was measured at different temperatures dilatometrically as described before[18,19]. The dilatometer was calibrated with mercury to determine their volumes up to a fixed mark and capillary radii. Details of the preparation of solutions as well as measurements of $[\eta]$ have been described elsewhere[20–22]. Viscosities of each polymer and polymer blends, cover the whole range of composition, were measured at 293.15 K and 303.15 K in benzene by using dilution Ubbelohde viscometer having flow time of 85 s for pure benzene at 293.15 K and the results are quoted on the basis of Huggins[23] and Kraemer[24] equations.

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2 c \qquad (1)$$

$$\frac{\ln\eta_r}{c} = [\eta] - k_k[\eta]^2 c \qquad (2)$$

where η_{sp}, η_r, k_H, k_k are the specific viscosity, relative viscosity, Huggins viscosity slope constant and Kraemer's viscosity slope constant, respectively.

The viscometer was calibrated with water and the obtained data indicate that no need for applying end correction to the length of the capillary and kinetic energy correction for this particular viscometer.

RESULTS AND DISCUSSION

During the last two decades, viscometry methods have been successfully used to investigate and characterize compatibility of different pairs of polymers by Shih and Beatty[25], Lizymol and Thomas[26], and other research groups[27–29]. Kulshreshtha et al.[30], applied the viscosity method to the poly (vinyl chloride) / poly (acrylonitrile–co–butadiene–co–styrene) (PVC/ABS) poly blend system to study the compatibility. They found that the plot of absolute viscosity versus composition deviates from linearity according to the degree of compatibility.

Basically the dilute solution viscometry based on the classical Huggins equation[23] that expresses the specific viscosity (η_{sp}) of the polymer as a function of concentration, c, when one of the components is alone in the solution (equation (1)). Krigbaum and Wall[31] modified Huggins equation and derived an expression of the viscosity $\eta(c_1,c_2)$ of a dilute solution containing two polymers (1,2) at concentrations (c_1,c_2):

$$\frac{\eta_{(c_1,c_2)}}{\eta_0} - 1 = c_1[\eta_1] + c_2[\eta_2] + c_1^2 b_1 + c_2^2 b_2 + 2c_1c_2b_{12} + \ldots \qquad (3)$$

where $[\eta_i]$ is the intrinsic viscosity of polymer 'i' in pure solvent; η_0, the solvent viscosity; and b_{12}, the interaction coefficient between the two polymers.

The specific viscosity, $\eta_{sp.m}$, of a mixed polymer solution can be expressed as follows if b_1,b_2 are replaced by b_{11},b_{22} and five terms only are considered:

$$\eta_{sp.m} = [\eta_1]c_1 + [\eta_2]c_2 + b_{11}c_1^2 = b_{22}c_2^2 + 2b_{12}c_1c_2 \qquad (4)$$

For mathematical convenience Krigbaum and Wall[31] define the interspecific interaction coefficient b_{12} as

$$b_{12} = \sqrt{b_{11}b_{22}} \qquad (5)$$

The values of b_{11} and b_{22} are the slopes of the plots according to Huggins equation, for polymer (1) and polymer (2), respectively. The definition of b_{12} according to equation (5) is not valid for systems that have negative values for b_{11} or b_{22}. Therefore the modification by Williamson and Wright[32] is used to evaluate b_{12}, which can be expressed as

$$b_{12} = \frac{[b_{11} + b_{22}]}{2} \qquad (6)$$

The value of b_{12} can be obtained from equation (4) be determining the specific viscosity of the mixture, $\eta_{sp.m}$, the intrinsic viscosity of the pure components, $[\eta_i]$, and the value of b_{11} and b_{22}. Also, parameter b_{12} can be theoretically calculated from equation (5) or equation (6). The parameter b_{12} computed from any of these equations is defined as b_{12}^*. Krigbaum and Wall[31] suggested that information about the interaction between two polymers should be obtained from the difference of experimental b_{12} and theoretical b_{12}^*. The difference was defined as Δb and expressed as

$$\Delta b = b_{12} - b_{12}^* \qquad (7)$$

Negative values of Δb are found for solutions to incompatible polymer systems while positive values of Δb refer to attractive interaction.

Equation (4) can be simplified to the form of equation (8) at infinite dilution of the solution (i.e., when c approaches zero).

$$\left[\frac{\eta_{sp.m}}{c}\right]_{c\to 0} = \left[\frac{[\eta_1]c_1}{c}\right]_{c\to 0} + \left[\frac{[\eta_2]c_2}{c}\right]_{c\to 0} \qquad (8)$$

This means that the intrinsic viscosity of a mixture of two polymers can be expressed as the weight-average of the intrinsic viscosities of the two polymers. For compatible systems the observed intrinsic viscosities are reported to be higher than the calculated values[32].

Recently, the compatibility of solutions of PVC/poly(-ethylene-co-vinyl acetate), PVC/poly(styrene-co-acrylonitrile), and poly(ethylene-co-vinyl acetate)/poly(styrene-co-acrylonitrile) has been characterized by a viscometry technique using the Krigbaum and Wall parameter, Δb, by Lizymol and Thomas[26]. Using the same technique, Chen et al.[33], and Shih and Beatty[25], respectively, determined the compatibility of poly(ethylene oxide)/poly(vinyl acetate) and polycarbonate/poly(hexamethylene sebacate) polymer pairs.

Hereinafter we discuss in detail the compatibility in solutions of PEG/PEO blends in benzene at 293.15 K and 303.15 K by viscometric technique. The calculation in the present context, is based on the theoretical consideration suggested by Krigbaum and Wall[31] (equation (4)) in which b_{12} parameter corresponds to the geometric mean of each polymer–solvent interaction parameter, b_{12} (equation (5)), is used instead of the arithmetic mean of b_{12} (equation (6)). However, in some publications, equation (6) is used because the definition of b_{12} according to equation (5) is not valid for

Table 1 Intrinsic viscosity, interaction coefficient (b) and viscosity slope constant (k_H) at 293.15 K and 303.15 K derived from Huggins equation for different polymer–benzene systems

Temp. (/K)	Polymer	$[\eta]$ (/(dm^3 kg^{-1}))	b_{11} or b_{22} × 10^{-4} (/(dm^3 kg^{-1})^2))	k_H
293.15	PEG	67.78	0.1657	0.3606
	PEO1	94.60	0.3226	0.3605
	PEO2	208.90	1.5589	0.3572
	PEO3	357.10	4.6447	0.3642
303.15	PEG	70.10	0.1767	0.3596
	PEO1	98.30	0.3473	0.3594
	PEO2	221.40	1.7685	0.3608
	PEO3	363.00	4.7525	0.3607

systems that have negative values for b_{11} or b_{22}. According to the approach of Krigbaum and Wall[31], comparison of experimental values of b_{12} with the theoretical values of $b_{12}(b_{12}^*)$ could give information on interactions of the polymer pairs. A positive difference between the experimental and the theoretical viscosity interaction coefficients, Δb, is evidence of a compatible polymer pair. The higher the value of Δb, the higher the extent of compatibility. Negative value refer to repulsive interaction and incompatible mixes.

The values of $[\eta]$ for pure polymers and their blends were derived from Huggins and Kraemer plots. These plots are not presented here for brevity. The values of $[\eta]$, b obtained by the linear least-squares analysis and k_H for pure polymers are grouped in *Table 1* while the specific viscosity data and Δb of all polymer blends having different compositions are tabulated in *Tables 2, 3* and *4*.

The variation of Δb with the concentration of PEG/PEO blends of varying molecular weights of PEO as a function of weight % of both components and concentration of the polymer blend at 293.15 K and 303.15 K are shown in *Figures 1–3*. However, for PEO having the lowest molecular weight (*Figure 1*), it can be seen that the values of Δb, at 293.15 K, are positive when the ratio of PEG/PEO1 is either 10/90 or 75/25 meanwhile, they are negative for other two ratios. The lowest compatibility is detected for the ratio 50/50. This finding may be attributed to the similarity of the molecular weights of PEO1 and PEG (1.0×10^5). It may be assumed that PEO1 is dissolved in PEG or vice versa at low percentage of PEO1 or PEG. In other words the component in excess is considered as a solvent while the other component is considered as a solute. On the other hand *Figure 1* shows that all PEG/PEO1 blends are incompatible at 303.15 K and the incompatibility at this temperature increases with decreasing the content of PEG in the blend. The above mentioned figures (*Figures 1–3*) reveal also that there is a different influence of the total concentration of the mixture on Δb values. For incompatible blends values Δb increase with the concentrations of the blends while values of Δb decrease with increasing concentrations of the mixtures in case of miscible blends.

Table 2 Viscosity data, interaction coefficient, b_{12} and Δb at 293.15 K and 303.15 K for different concentrations and compositions of PEG–PEO1

PEG:PEORatio	At 293.15 K				At 303.15 K			
	Conc. $\times 10^3$	η_{SP}	$b_{12} \times 10^{-4}$	$\Delta b \times 10^{-4}$	Conc. $\times 10^3$	η_{SP}	$-b_{12} \times 10^{-4}$	$-\Delta b \times 10^{-4}$
75:25	9.37	0.9125	0.349	0.118	9.65	0.8702	−0.037	0.211
	8.33	0.7920	0.357	0.126	8.57	0.7559	−0.21	0.227
	7.50	0.6993	0.365	0.134	7.72	0.6677	0.0003	0.248
	6.82	0.6255	0.371	0.140	6.43	0.5408	0.034	0.282
	5.77	0.5162	0.390	0.159	5.51	0.4541	0.068	0.316
	5.00	0.4393	0.411	0.180	4.82	0.3912	0.101	0.349
	4.41	0.3819	0.430	0.199	3.86	0.3061	0.174	0.422
	3.57	0.3030	0.474	0.243	3.09	0.2406	0.261	0.509
	2.88	0.2406	0.536	0.305				
50:50	9.38	0.9387	0.159	−0.072	9.22	0.9073	−0.046	0.202
	8.33	0.8143	0.154	−0.077	8.20	0.7876	−0.027	0.221
	7.50	0.7184	0.145	−0.086	7.38	0.6952	−0.009	0.239
	6.82	0.6427	0.138	−0.093	6.15	0.5627	0.025	0.273
	5.77	0.5301	0.126	−0.105	5.27	0.4721	0.058	0.306
	5.00	0.4509	0.115	−0.116	4.10	0.3568	0.124	0.372
	4.41	0.3920	0.105	−0.126	3035	0.2866	0.181	0.429
	3.57	0.3108	0.085	−0.416	2.73	0.2299	0.261	0.509
	3.00	0.2573	0.061	−0.170				
25:75	8.33	0.9115	0.178	−0.053	8.26	0.8580	0.143	0.391
	7.50	0.8029	0.170	−0.061	7.43	0.7565	0.171	0.419
	6.82	0.7171	0.163	−0.068	6.76	0.6762	0.204	0.452
	5.77	0.5902	0.154	−0.077	5.72	0.5572	0.263	0.511
	5.00	0.5011	0.146	−0.085	4.95	0.4736	0.312	0.560
	4.41	0.4352	0.141	−0.090	3.91	0.3638	0.428	0.676
	3.57	0.3433	0.127	−0.104	3.10	0.2819	0.577	0.825
	3.00	0.2847	0.111	−0.120	2.56	0.2299	0.701	0.949
	2.50	0.2339	0.093	−0.138				
10:90	7.50	0.9091	0.709	0.478				
	6.82	0.8105	0.732	0.501				
	5.77	0.6654	0.792	0.561				
	5.00	0.5637	0.853	0.622				
	4.41	0.4888	0.923	0.692				
	3.75	0.4073	1.012	0.781				
	3.00	0.3185	1.178	0.947				
	2.50	0.2613	1.339	1.108				

$\Delta b = b^{12} - \sqrt{b_{11}b_{22}} = b_{12} - b_{12}^*$ ($b_{12}^* = 0.231$ at 293.15 K and 0.248 at 303.15 K)

Table 3 Viscosity data, interaction coefficient, b_{12} and Δb at 293.15 K and 303.15 K for different concentrations and compositions of PEG–PEO2

PEG:PEORatio	At 293.15 K				At 303.15 K			
	Conc. × 10^3	η_{SP}	$b_{12} \times 10^{-4}$	$\Delta b \times 10^{-4}$	Conc. × 10^3	η_{SP}	$-b_{12} \times 10^{-4}$	$-\Delta b \times 10^{-4}$
75:25	7.50	0.9367	−0.268	0.240	7.33	0.9023	0.008	0.567
	6.67	0.8125	−0.241	0.267	6.66	0.8047	0.043	0.602
	6.00	0.7174	−0.225	0.283	6.11	0.7257	0.086	0.645
	5.00	0.5798	−0.180	0.328	5.23	0.6060	0.155	0.714
	4.29	0.4864	−0.133	0.375	4.58	0.5200	0.233	0.792
	4.00	0.4499	−0.119	0.389	3.66	0.4045	0.371	0.930
	3.73	0.4160	−0.097	0.411	2.93	0.3163	0.557	1.116
	3.00	0.3271	−0.023	0.485	2.44	0.2596	0.727	1.286
	2.50	0.2683	0.054	0.562				
50:50	5.45	0.9106	−0.192	0.316	5.12	0.8421	0.241	0.800
	5.00	0.8199	−0.163	0.345	4.51	0.7256	0.301	0.860
	4.62	0.7455	−0.134	0.374	3.65	0.5673	0.442	1.001
	4.00	0.6302	−0.098	0.410	3.07	0.4653	0.594	1.153
	3.73	0.5812	−0.075	0.433	2.65	0.3942	0.746	1.305
	3.00	0.4538	0.0005	0.509	2.25	0.3307	0.863	1.422
	2.50	0.3704	0.077	0.585	1.87	0.2698	1.130	1.689
	2.00	0.2902	0.186	0.694				
25:75	4.29	0.9023	0.084	0.592	4.29	0.8665	1.538	2.097
	4.00	0.8302	0.104	0.612	3.84	0.7587	1.709	2.268
	3.53	0.7155	0.170	0.678	3.47	0.6742	1.858	2.417
	3.00	0.5920	0.258	0.766	2.92	0.5511	2.211	2.770
	2.40	0.4592	0.398	0.906	2.51	0.4655	2.482	3.041
	2.00	0.3746	0.542	1.050	2.14	0.3897	2.866	3.425
	1.71	0.3163	0.596	1.104	1.78	0.3172	3.487	4.046
	1.50	0.2736	0.805	1.313	1.43	0.2504	4.262	4.821

$\Delta b = b_{12} - \sqrt{b_{11}b_{22}} = b_{12} - b^*_{12}$ ($b^*_{12} = 0.508$ at 293.15 K and 0.559 at 303.15 K)

This may be due to the increase in polymer–solvent interaction at high solvent concentration. In other words, the polymer solvent interaction exceeds the polymer–polymer interaction at very high dilution. This may lead to the speculation that Δb values of the above studied polymer blends may approach zero or become positive values at very high concentrations which in turn leads to the assumption that these blends are compatible at solid state.

These *Figures 1–3* demonstrate also the effect of temperature on the compatibility with PEG. Careful inspection of these figures divulge that the compatibility decreases with increasing the temperature.

The effect of molecular weight of PEO on its compatibility with PEG can be also detected from *Figures 1–3* and from the data listed in *Tables 2–4*. For instance, values ranging from −0.17 to −0.072, −0.694 to −0.316 and −4.683 to −2.280 for Δb are assigned for (50/50 wt%) PEG/PEO1, PEG/PEO2 and PEG/PEO3, respectively. This reveals that as the molecular weight of PEO increases from 1.0×10^5 to 6.0×10^5 the negative value of Δb increases which indicates the increase of incompatibility of PEO with PEG. This behaviour is shown more obviously in *Figure 4* at which the variation of Δb with the concentration of PEG/PEO (25/75) blends is demonstrated. This finding indicates that the compatibility of PEO and PEG is strongly dependent upon the molecular weight of PEO.

The derived values of $[\eta]$ obtained by the linear least-squares analysis and $\Delta[\eta]$ for polymer blends having different compositions measured at different temperatures are tabulated in *Table 5*. The values of $\Delta[\eta]$ are used here as an alternative mean for determining the compatibility of polymer blends. In this respect, the viscosity of a binary polymer solution (a single polymer dissolved in a solvent) expressed by Huggins equation (equation (1)) can be extended to a ternary polymer system [solvent/polymer (A)/polymer (B)] following the method proposed by Krigbaum and Wall[31] and discussed in detail by Kragg and Bigelow[34]:

$$\left(\frac{\eta_{sp}}{c}\right)_m = [\eta]_m + b_m c = \sum_i [\eta]_i \frac{c_i}{c} + \left(\frac{\sum_i b_{ii}^{1/2} c_i}{c^{1/2}}\right)^2 \tag{9}$$

where subscript m refers to the ternary system, i = A, B to each of the polymer components, and $c = c_A + c_B$ is the total concentration of the polymer blend. The parameter b_m summarizes the global interactions between all the segments in a polymer chain, no interactions between unlike i–j segments are included.

In equation (9), the intrinsic viscosity of the mixture of polymers in a common solvent for non-interacting system is expressed by equation (10):

$$[\eta]_m = \sum_i [\eta]_i \frac{c_i}{c} = [\eta]_A w_A + [\eta]_B w_B \tag{10}$$

where $w_i = c_i/c$ (i = A, B) being the weight fraction of polymer A or B.

Most viscometric studies of polymer–polymer compatibility are based on the deviation of the experimental intrinsic viscosity, $[\eta]^E_m$, from the theoretical intrinsic viscosity, $[\eta]^T_m$, values of the polymer mixture. In the

Table 4 Viscosity data, interaction coefficient, b_{12} and Δb at 293.15 K and 303.15 K for different concentrations and compositions of PEG–PEO3

PEG:PEORatio	At 293.15 K				At 303.15 K			
	Conc. $\times 10^3$	η_{SP}	$b_{12} \times 10^{-4}$	$\Delta b \times 10^{-4}$	Conc. $\times 10^3$	η_{SP}	$-b_{12} \times 10^{-4}$	$-\Delta b \times 10^{-4}$
90:10	7.50	0.8616	−0.342	0.535				
	6.67	0.7486	−0.289	0.588				
	6.00	0.6613	−0.247	0.630				
	5.00	0.5358	−0.157	0.720				
	4.00	0.4166	−0.029	0.848				
	3.53	0.3625	0.063	0.940				
	3.00	0.3034	0.185	1.062				
	2.50	0.2491	0.353	1.230				
75:25	5.45	0.8941	0.149	0.728	5.65	0.9242	0.101	1.017
	5.00	0.8053	0.095	0.782	4.71	0.7427	0.244	1.160
	4.29	0.6711	0.008	0.885	4.03	0.6199	0.363	1.279
	3.75	0.5749	0.084	0.961	3.14	0.4653	0.644	1.560
	3.33	0.5025	0.159	1.036	5.57	0.3719	0.914	1.830
	3.00	0.4462	0.256	1.133	2.09	0.2973	1.194	2.110
	2.50	0.3642	0.429	1.306	1.77	0.2474	1.592	2.508
	2.00	0.2854	0.677	1.554				
	1.71	0.2417	0.830	1.707				
50:50	4.00	0.9299	1.403	2.280	3.87	0.8859	1.826	2.742
	3.75	0.8601	1.503	2.380	3.35	0.7465	2.089	3.005
	3.33	0.7472	1.688	2.565	2.96	0.6445	2.384	3.300
	3.00	0.6602	1.897	2.774	2.40	0.5055	2.958	3.874
	2.73	0.5909	2.112	2.989	2.01	0.4154	3.448	4.364
	2.31	0.4884	2.493	3.370	1.68	0.3396	4.179	5.095
	2.00	0.4158	2.859	3.736	1.36	0.2703	5.082	5.998
	1.71	0.3506	3.272	4.149	1.14	0.2245	5.907	6.823
	1.50	0.3029	3.806	4.683				
25:75	3.00	0.9575	3.937	4.814	2.83	0.8587	5.872	6.788
	2.73	0.8531	4.287	5.164	2.59	0.7737	6.237	7.153
	2.50	0.7687	4.572	5.449	2.15	0.6196	7.355	8.271
	2.31	0.6994	4.917	5.794	1.83	0.5161	8.288	9.204
	2.00	0.5920	5.497	6.374	1.52	0.4179	9.762	10.678
	1.71	0.4963	6.143	7.020	1.22	0.3284	11.659	12.575
	1.50	0.4271	7.001	7.878	1.02	0.2704	13.609	14.525
	1.33	0.3746	7.619	8.496				
	1.09	0.3007	9.172	10.049				

$\Delta b = b^{12} - \sqrt{b_{11} b_{22}} = b_{12} - b_{12}^{*}$ ($b_{12}^{*} = 0.877$ at 293.15 K and 0.916 at 303.15 K)

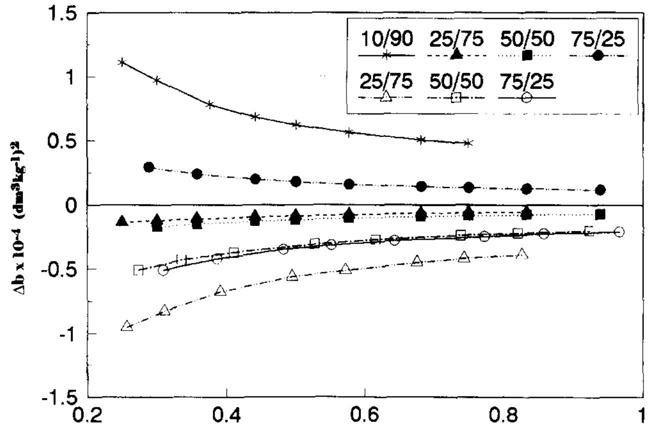

Figure 1 Variation of Δb with concentration for different PEG/PEO1 ratios at 293.15 K (*and solid symbols) and 303.15 K (open symbols)

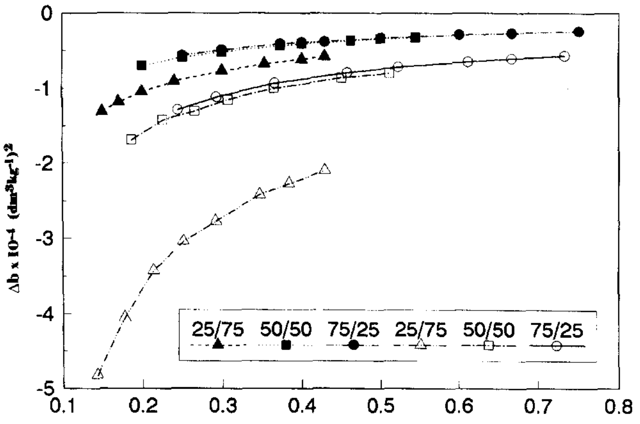

Figure 2 Variation of Δb with concentration for different PEG/PEO2 ratios at 293.15 K (*and solid symbols) and 303.15 K (open symbols)

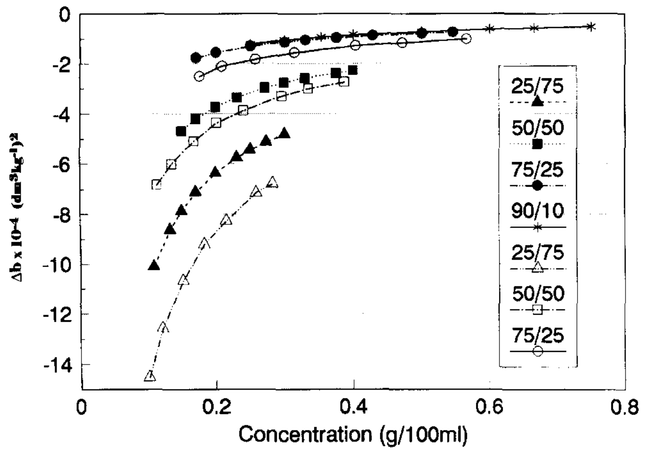

Figure 3 Variation of Δb with concentration for different PEG/PEO3 ratios at 293.15 K (*and solid symbols) and 303.15 K (open symbols)

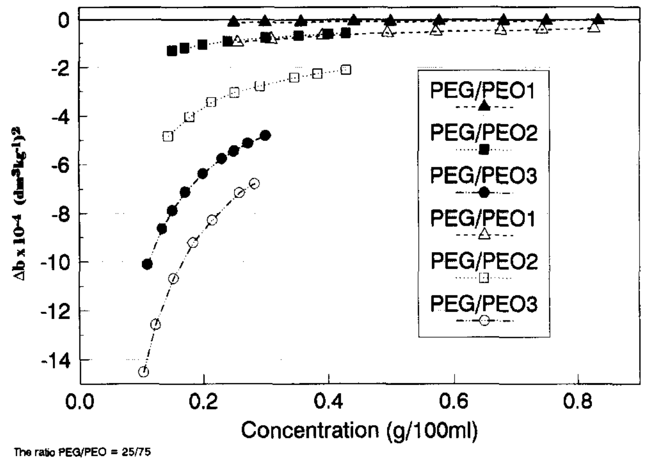

Figure 4 Variation of Δb with concentration for different mixtures of PEG with PEO having different molecular weights at 293.15 K (solid symbols) and 303.15 K (open symbols)

present context $\Delta[\eta]$ corresponds to the difference between $[\eta]^E_m$ and $[\eta]^T_m$. Hence,

$$\Delta[\eta] = [\eta]^E_m - [\eta]^T_m \tag{11}$$

The sign and magnitude of $\Delta[\eta]$ refers to the compatibility and incompatibility of the polymer pairs. The ideal behaviour is attained when the value of $\Delta[\eta]$ equals zero, i.e., $[\eta]^E_m$ and $[\eta]^T_m$ are equal. Under this condition no interaction between the unlike polymers is present. The positive value of $\Delta[\eta]$ reflects an increase of the effective hydrodynamic specific volume which suggests expansion of the coil due to favourable polymer (A)/polymer (B) interaction. The negative value of $\Delta[\eta]$ means a repulsive interaction between the two polymers and hence they are not likely to be compatible in the solid state. The experimental intrinsic viscosity, $[\eta]^E_m$, theoretical intrinsic viscosity, $[\eta]^T_m$, and $\Delta[\eta]$, calculated using equation (11), are given in *Table 5*. For the blends of PEG/PEO1, the data show positive deviations from ideal behaviour, as manifested by the positive values of $\Delta[\eta]$, when the composition of PEG/PEO blend being 75/25 and 10/90 only at 293.15 K. All other compositions at 293.15 K show negative deviation from ideal behaviour. The Δb values of PEG/PEO1 75/25 and 10/90 compositions at 293.15 K, as announced in *Table 2*, are positive at all concentrations indicating attractive interactions. This indicates that there is no definite influence of the amount of the proportion of functional group (OH) in the blend on the compatibility of its components. This finding contradicts the conclusion drawn by Lizymol and Thomas[26] and Walsh et al.[35] who stated that blends containing a higher proportion of functional group are more compatible.

With respect to the effect of molecular weight of PEO on its compatibility with PEG it can be seen from the data listed in *Table 5* that the compatibility decreases with increasing the molecular weight of the PEO. For instance, the values of $\Delta[\eta]$ at 293.15 K for PEG/PEO 50/50 blends are (−2.24),

Table 5 Intrinsic viscosity and $\Delta[\eta]$ at 293.15 K and 303.15 K derived from Huggins equation for different PEG–PEO–benzene systems

Blend	Temp. (/K)	PEG–PEORatio	$[\eta]^T_m$ (/(dm^3 kg^{-1}))	$[\eta]^E_m$ (/(dm^3 kg^{-1}))	$-\Delta[\eta]$ (/(dm^3 kg^{-1}))
PEG–PEO1	293.15	75:25	74.49	77.19	−2.70
		50:50	81.19	78.95	2.24
		25:75	87.90	86.74	1.16
		10:90	91.92	96.30	−4.38
	303.15	75:25	77.15	72.10	5.05
		50:50	84.20	78.10	6.10
		25:75	91.25	83.30	7.95
PEG–PEO2	293.15	75:25	103.06	98.47	4.59
		50:50	138.34	132.33	6.01
		25:75	173.62	167.17	6.45
	303.15	75:25	107.93	97.80	10.13
		50:50	145.75	132.30	13.45
		25:75	183.58	161.7	21.88
PEG–PEO3	293.13	90:10	96.71	91.99	4.72
		75:25	140.11	130.40	9.71
		50:50	212.44	183.51	28.93
		25:75	284.77	250.56	34.21
	303.15	75:25	143.33	129.50	13.83
		50:50	216.55	182.50	34.05
		25:75	289.78	243.00	46.78

(-6.01) and (-28.93) for PEO1, PEO2 and PEO3, respectively. This increase in the negative deviation indicates that the compatibility of blends reduces with increasing the molecular weight of PEO counterpart. On the other hand, the effect of temperature on the compatibility of polymer pairs can be noticed from the data listed in *Table 5*. It can be seen that the deviation from the ideal behaviour, i.e. $\Delta[\eta]$, for any blend increases with increasing the temperature.

Table 5 shows that the only mixtures possess positive $\Delta[\eta]$ values are those that possess positive Δb. Accordingly, this leads to the conclusion that both types of analysis, $\Delta[\eta]$ and Δb, are completely consistent.

It has been reported[26] that compatibility studies by viscometry are in agreement with the solid-state miscibility analysis. Since the data of Δb reveal that the compatibility increases with increasing the blend concentration in the solution, an assumption that these blends are compatible at solid state may be established.

CONCLUSIONS

On the basis of positive difference between the experimental and the theoretical viscosity interaction coefficients, Δb, the compatibility of the blends was estimated. It was found that the only compatible blends were achieved when the molecular weight of PEG and PEO are nearly equal. The compatibility is detected only in case of the blends PEG (75%)/PEO1 (25%) and PEG (10%)/PEO1 (90%).

The studied systems revealed that the values of Δb, in all immiscible blends, increase with increasing the total concentration of the blend. This was attributed to the increase in polymer–polymer interaction at concentrated polymer solutions. This finding leads to the speculation that Δb values of the studied polymer blends may approach zero or become positive values at very high concentrations. This may lead to the assumption that these blends are compatible when they are mixed and melted to be fabricated as solid articles. The derived values of $[\eta]$ obtained by the linear least-squares analysis and $\Delta[\eta]$ for polymer blends having different compositions measured at different temperatures were used as an alternative mean for determining the compatibility of polymer blends. The compatibility data obtained by $\Delta[\eta]$ were found in a good accord with that obtained by Δb.

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