Molecular interactions of polymethyl methacrylate and polyethyeleneglycol solutions in tetrahydrofuran

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The ultrasonic velocity, density and viscosities of the polymethylmethacrylate (PMMA) and polyethyleneglycol (PEG) solutions in tetrahydrofuran (THF) have been measured in the temperature range 293-313K. Using these data, free energy of mixing, solvation number and different polymer-solvent interaction parameters for the solution systems have been calculated to know the presence of molecular interactions in the system. The trends in the variation of the solution property parameters indicate the existence of positive molecular interactions between the polymer and the solvent in solutions. The results also show the presence of higher degree of interaction between PEG and THF in solution compared to PMMA and THF.

Keywords: Polymer solutions, Ultrasonic velocity, Viscosity, Interaction parameter, Miscibility, PMMA, PEG, THF

1 Introduction

The study of miscibility and molecular interactions present in polymer and solvent in a polymer solution system is of great significance for engineering applications of polymers. They also provide substantial information on the processes involving polymer production and their uses[1,2]. Further, polymer dissolution also plays a key role in many industrial applications in a variety of areas and an understanding of the dissolution process allows for the optimization of design and processing conditions as well as selection of a suitable solvent[3]. Many researchers have undertaken these studies qualitatively through ultrasonic velocity, adiabatic compressibility and viscosity measurements[4-6]. However, there are very few studies on the quantitative study of the interactions in a polymer solution system[7,8]. Polymethylmethacrylate (PMMA) is a versatile material and has been used in a wide range of fields and applications[9-13]. Polyethyleneglycol (PEG) finds enormous use in the fields of microbiology, biochemistry, drug delivery, gas chromatography and pharmaceutical industry[14,15]. Tetrahydrofuran has been used as a solvent in many polymer miscibility studies because of its interesting features[16-19].

In this paper, molecular interactions and miscibility behaviour of polymethylmethacrylate (PMMA) and polyethyleneglycol(PEG) in tetrahydrofuran(THF) has been studied.

2 Materials and Methods

PMMA (molecular weight, M_w, 75000; Alfa Aesar) and PEG (molecular weight, M_w, 6,000; Alfa Aesar) were used as received. THF (Merck) was distilled before use. Dilute solutions of 2% (w/v) PMMA and PEG in THF were prepared separately in different stoppered conical flasks. Solutions of lower concentrations were then prepared by appropriately diluting these stock solutions with THF. The densities of the polymer solutions in THF were measured with a Mettler Toledo Digital density meter model Densito 30 PX. The temperature of the density measurement was within an uncertainty of ±0.1°C. The instrument was calibrated with standard density water supplied with the instrument. The estimated error in the density measurement was within ±0.05%. Dilute solution viscosities of PMMA, PEG solutions in THF were measured at different temperatures using a Ubbelhode viscometer with an accuracy of ±0.1%. Solution viscosities at different temperatures were determined by equilibrating the viscometer tube in a thermostat maintained at a desired temperature for about 10 min before the flow time measurement. The temperature of the bath was kept constant within an accuracy of ±0.1°C. Ultrasonic velocity measurements were carried out on a fixed frequency continuous wave ultrasonic interferometer (Model F81, Mittal Enterprises, New Delhi) operating at 2 MHz using the standard procedure. The error in the measurement of

ultrasonic velocity was within ± 0.1%. Measurements at different temperatures were carried out by circulating water at required temperatures from a thermostatic bath, inside the double walled jacket covering the interferometer cell. The accuracy of temperature maintenance was within ±0.1°C. The adiabatic compressibility (β) has been calculated using the formula, $\beta = (C^2\rho)^{-1}$, where ρ is the density of the solution and C the ultrasonic velocity of the solution. The intermolecular free length has been calculated using the formula, $L_f = k\beta^{1/2}$ where k is temperature dependent constant, known as the Jakobson constant[20]. The relaxation time (τ) and relaxation amplitude (α/f^2) have been calculated[21,22] using the formulae, $\tau = 4\eta_s/3\rho C^2$ and $\alpha/f^2 = 8\pi^2\ \eta_s/3\rho C^3$ respectively, where η_s is the reduced viscosity of the solution. The uncertainty in all the calculated parameters was found to be within ± 0.1%.

3 Results and Discussion

The solution property parameters namely, density, viscosity, ultrasonic velocity, adiabatic compressibility, relaxation time, relaxation amplitude and intermolecular free lengths for PMMA and PEG in THF at 293, 298, 303, 308 and 313K have been presented in Tables 1 and 2 respectively. All these parameters except adiabatic compressibility and intermolecular free length are found to increase with increase of concentration of polymer at all temperatures. The adiabatic compressibility of polymer solutions decreased with concentration. This observation is in accordance with those reported in the case of PMMA in chlorobenzene and dioxane[23,24]. The ultrasonic velocity and viscosity vary gradually with the concentration in solutions. The motion of PMMA and PEG macromolecule is affected by mutual interaction between the macromolecule and the solvent molecule and the interaction between one macromolecule with another macromolecule. The first type of mutual interaction is termed as hydrodynamic screening which is significant in determining the viscous flow properties of dilute polymer solutions. The interaction gives rise to the association between two types of molecules. At low concentrations PMMA/PEG and solvent interactions dominates whereas at high concentrations PMMA-PMMA/PEG-PEG interaction exists.

The attenuation of ultrasound energy depends on viscosity, thermal conductivity, scattering and intermolecular processes[24]. Since the thermal

condition and scattering effects are known to be negligible as suggested by Pauling[21], the intermolecular processes and viscosity are mainly responsible for the observed changes in the solution properties. The relaxation time and the relaxation amplitude are found to increase with increase in concentration at all temperatures studied. At a fixed concentration, these values decrease with temperature. This trend is quite normal as the variation in these parameters is cumulative effect of the variations in ultrasonic velocity, density and viscosity of the solutions under the given condition.

The variation of ultrasonic velocity in solution also depends on intermolecular free length on mixing. As per the model of Eyring and Kincaid[25] for sound propagation, ultrasonic velocity increases on decrease of free length. Intermolecular free length is predominant factor in determining the variation of ultrasonic velocity in solutions. In the present investigation, the intermolecular free length was found to decrease linearly with concentration at all studied temperatures. This decrease is due to decrease in compressibility with increase in concentration. This shows significant interaction between the solute and solvent molecules in the system. However, at any solute concentration, the ultrasonic velocity decreased with increase of temperature and this may be due to the weakening of intermolecular forces.

The free energy G_{12} of the polymer solution can be expressed[7] in RT units as:

$$G_{12} = \ln\left(\frac{\eta_{12}V_{12}}{hN}\right) \qquad \qquad …(1)$$

where η_{12} and V_{12} are the viscosity and molar volume of the solution, respectively and h and N are the Planck's constant and Avogadro's number respectively.

The Gibbs free energy G_1 of the solvent is

$$G_1 = \ln\left(\frac{\eta_1V_1}{hN}\right) \qquad \qquad …(2)$$

where η_1 and V_1 are the viscosity and molar volume of the solvent alone.

Using viscosity (η), density (ρ) and ultrasonic velocity (C) data, the relaxation time (τ) is obtained through the relation[18]

Table 1 — Solution property parameters for PMMA solutions in THF at different temperatures

K	Φ_2	C (m/s)	ρ (kg/m³)	η (10⁻³Nsm⁻²)	τ (10⁻¹²s)	L_f (Å)	α/f^2 (10⁻¹⁵ s²m⁻¹)	B (10⁻¹¹ N⁻¹ m²)	X From η	X From τ	S_p
293	0	1320	874.2	0.585	0.512	0.5175	8.451	65.65	-	-	-
	0.001	1325	876.1	0.631	0.545	0.5162	9.053	65.01	0.41	0.39	2.3
	0.003	1330	877.2	0.666	0.571	0.5155	9.525	64.46	0.41	0.39	2.1
	0.004	1335	878.3	0.712	0.604	0.5143	10.12	63.88	0.42	0.40	2.0
	0.006	1339	879.1	0.774	0.652	0.5133	10.91	63.44	0.43	0.41	2.0
	0.008	1342	880.1	0.778	0.653	0.5126	11.03	63.09	0.44	0.42	1.8
	0.009	1345	881.2	0.843	0.705	0.5115	11.82	62.73	0.44	0.43	1.8
298	0	1301	870.4	0.547	0.495	0.5149	7.501	67.87	-	-	-
	0.001	1306	871.2	0.578	0.518	0.5127	7.832	67.99	0.39	0.37	2.0
	0.003	1311	872.3	0.606	0.532	0.5104	8.112	66.70	0.39	0.38	1.8
	0.004	1315	873.1	0.661	0.583	0.5086	8.754	66.23	0.40	0.39	1.6
	0.006	1317	874.1	0.704	0.618	0.5072	9.252	65.85	0.41	0.40	1.6
	0.008	1321	875.2	0.722	0.629	0.5053	9.391	65.37	0.42	0.41	1.5
	0.009	1323	876.6	0.775	0.671	0.5034	9.972	65.07	0.43	0.42	1.5
303	0	1277	866.7	0.511	0.482	0.5307	7.441	70.75	-	-	-
	0.001	1283	868.4	0.545	0.508	0.5277	7.813	69.95	0.36	0.33	1.6
	0.003	1287	868.8	0.572	0.529	0.5260	8.124	69.49	0.37	0.34	1.5
	0.004	1293	869.5	0.624	0.572	0.5237	8.752	68.79	0.38	0.35	1.5
	0.006	1296	870.7	0.651	0.593	0.5221	9.051	68.37	0.38	0.35	1.4
	0.008	1300	871.9	0.670	0.606	0.5202	9.225	67.86	0.39	0.36	1.4
	0.009	1304	873.0	0.721	0.647	0.5182	9.822	67.36	0.40	0.37	1.3
308	0	1273	857.3	0.474	0.474	0.5396	7.031	71.77	-	-	-
	0.001	1277	860.7	0.496	0.471	0.5376	7.284	71.24	0.32	0.29	1.3
	0.003	1281	861.7	0.520	0.490	0.5356	7.552	70.72	0.32	0.29	1.2
	0.004	1285	862.2	0.560	0.524	0.5338	8.053	70.24	0.33	0.30	1.2
	0.006	1289	863.1	0.606	0.563	0.5319	8.621	69.73	0.34	0.31	1.2
	0.008	1293	864.3	0.614	0.566	0.5299	8.645	69.20	0.35	0.32	1.1
	0.009	1297	865.1	0.645	0.590	0.5280	8.982	68.71	0.36	0.33	1.1
313	0	1241	853.1	0.400	0.405	0.5601	6.450	76.12	-	-	-
	0.001	1244	854.1	0.454	0.457	0.5584	7.254	75.65	0.27	0.25	1.3
	0.003	1247	855.3	0.477	0.478	0.5566	7.562	75.18	0.28	0.26	1.2
	0.004	1250	856.9	0.513	0.510	0.5548	8.053	74.68	0.29	0.26	1.2
	0.006	1252	857.8	0.542	0.536	0.5536	8.462	74.37	0.30	0.27	1.1
	0.008	1255	858.5	0.556	0.546	0.5521	8.612	73.95	0.31	0.28	1.1
	0.009	1257	859.3	0.596	0.585	0.5509	9.181	73.65	0.32	0.29	1.0

K; temperature in Kelvin, Φ_2; volume fraction of PMMA, C; ultrasonic velocity, ρ; density, η; viscosity, τ; relaxation time, L_f; intermolecular free length, α/f^2; relaxation amplitude, β; adiabatic compressibility, χ; interaction parameter, S_p; solvation number

$$\tau = \frac{4\eta}{3\rho C^2} \qquad \ldots(3)$$

Having known the value of τ, one can also estimate G_{12} through the expression[26]

$$G_{12} = \ln\left(\frac{\tau kT}{h}\right) \qquad \ldots(4)$$

where k and T are the Boltzmanns constant and absolute temperature.

The relaxation time (τ) corresponding to that of the solvent is to be used in the above expression while G_1 is estimated.

The free energy per unit mole of the solution (ΔG_m) will be

$$\Delta G_m = \frac{G_{12}}{n_1 + xn_2} \qquad \ldots(5)$$

where n_1 and xn_2 represent the number of solvent molecules and polymer molecules with x segments respectively.

Table 2 — Solution property parameters for PEG solutions in THF at different temperatures

K	Φ_2	C (m/s)	ρ (kg/m³)	η (10^{-3} Nsm⁻²)	τ (10^{-12} s)	L_f (Å)	α/f^2 (10^{-15} s²m⁻¹)	β (10^{-11} N⁻¹ m²)	X From η	χ From τ	S_p
293	0	1320	874.2	0.585	0.512	0.5007	7.651	65.65	-	-	-
	0.002	1323	875.1	0.593	0.516	0.4993	7.694	65.38	0.043	0.039	6.7
	0.005	1325	876.2	0.611	0.529	0.4982	7.882	65.00	0.043	0.039	6.3
	0.007	1327	877.3	0.616	0.531	0.4972	7.901	64.73	0.044	0.040	6.1
	0.010	1329	878.9	0.628	0.539	0.4960	8.003	64.41	0.045	0.041	5.7
	0.013	1331	879.1	0.639	0.547	0.4952	8.112	64.22	0.046	0.042	5.3
	0.015	1333	880.5	0.649	0.553	0.4940	8.184	63.91	0.047	0.043	5.0
298	0	1301	870.4	0.547	0.495	0.5149	7.501	67.87	-	-	-
	0.002	1304	870.7	0.553	0.498	0.5136	7.532	67.54	0.037	0.035	5.9
	0.005	1306	871.3	0.565	0.506	0.5126	7.652	67.28	0.037	0.035	5.7
	0.007	1307	872.4	0.579	0.518	0.5119	7.825	67.10	0.038	0.036	5.5
	0.010	1309	873.3	0.583	0.519	0.5109	7.831	66.82	0.038	0.036	5.1
	0.013	1310	874.2	0.603	0.535	0.5102	8.072	66.65	0.039	0.037	5.0
	0.015	1312	875.6	0.605	0.535	0.5090	8.043	66.34	0.040	0.038	4.8
303	0	1277	866.7	0.511	0.482	0.5324	6.971	70.75	-	-	-
	0.002	1279	867.3	0.520	0.488	0.5318	7.025	70.48	0.032	0.029	5.7
	0.005	1280	868.2	0.534	0.500	0.5311	7.042	70.30	0.032	0.029	5.6
	0.007	1282	869.3	0.541	0.504	0.5303	7.101	69.99	0.033	0.030	5.6
	0.010	1284	870.3	0.547	0.508	0.5296	7.243	69.69	0.034	0.030	5.0
	0.013	1285	871.5	0.554	0.513	0.5284	7.315	69.49	0.035	0.031	5.0
	0.015	1287	872.3	0.566	0.522	0.5274	7.402	69.21	0.036	0.032	4.9
308	0	1273	857.3	0.474	0.454	0.5404	7.051	71.18	-	-	-
	0.002	1274	858.4	0.479	0.458	0.5396	7.102	71.77	0.028	0.025	5.1
	0.005	1275	859.2	0.482	0.460	0.5389	7.121	71.59	0.028	0.025	5.1
	0.007	1276	860.4	0.488	0.464	0.5381	7.186	71.38	0.029	0.026	4.9
	0.010	1277	861.3	0.499	0.473	0.5374	7.314	71.19	0.029	0.026	4.9
	0.013	1279	862.3	0.507	0.479	0.5363	7.392	70.88	0.031	0.027	4.9
	0.015	1281	862.4	0.516	0.485	0.5351	7.482	70.58	0.032	0.028	4.8
313	0	1241	853.1	0.400	0.405	0.5601	6.451	76.12	-	-	-
	0.002	1242	853.5	0.441	0.446	0.5592	7.084	75.83	0.024	0.021	4.2
	0.005	1244	854.1	0.448	0.451	0.5584	7.162	75.65	0.024	0.021	4.2
	0.007	1245	855.2	0.455	0.457	0.5576	7.253	75.43	0.025	0.022	4.1
	0.010	1246	856.4	0.457	0.458	0.5567	7.252	75.21	0.026	0.023	3.9
	0.013	1247	857.6	0.460	0.459	0.5559	7.271	74.98	0.027	0.024	3.9
	0.015	1248	858.3	0.471	0.469	0.5552	7.422	74.80	0.028	0.025	3.7

K; temperature in Kelvin, Φ_2; volume fraction of PEG, C; ultrasonic velocity, ρ; density, η; viscosity, τ; relaxation time, L_f; intermolecular free length, α/f^2; relaxation amplitude, β; adiabatic compressibility, χ; interaction parameter, S_p; solvation number.

Using the values ΔG_m of a polymer-solvent interaction parameter, χ can be calculated using the expression[7]

$$\chi = \frac{(\Delta G_m - G_1 \phi_1)}{n_1 \phi_2} \qquad \ldots(6)$$

where $\phi_1 = \dfrac{n_1}{n_1 + xn_2}$ and $\phi_2 = \dfrac{xn_2}{n_1 + xn_2}$

The obtained values of χ through the Eq. (6) have been included in both the Tables 1 and 2. It is evident

from the results that there is a fair agreement between the values of χ obtained from the viscosity (Eq. (1)) and the relaxation time (Eq. (4)) routes. Also χ varied slightly with concentration and with temperature. This may indicate the extent of influence of concentration and temperatures on the solution phase interactions.

A linear dependence of the interaction parameter on the volume fractions Φ_2 of the solute can be written as the first approximation[27]:

$$\chi = \chi_0 + \sigma \qquad \ldots(7)$$

Table 3 — The values of χ_o, σ and Sp_o for PMMA and PEG solutions in THF at different temperatures

Polymer	Temperature (K)	χ_o		σ		Sp_o
		from η	from τ	from η	from τ	
PMMA	293	0.40	0.37	4.37	4.73	2.3
	298	0.37	0.36	5.19	5.19	1.9
	303	0.35	0.32	4.48	4.48	1.6
	308	0.30	0.27	5.19	5.19	1.3
	313	0.26	0.24	6.08	6.08	1.3
PEG	293	0.04	0.03	0.32	0.32	7.0
	298	0.03	0.03	0.22	0.22	6.1
	303	0.03	0.02	0.32	0.22	5.9
	308	0.02	0.02	0.31	0.22	5.1
	313	0.02	0.01	0.32	0.32	4.3

Table 4 — Polymer-Solvent Interaction Parameters for PMMA and PEG in THF

Temperature (K)	Polymer	χ_{ps}
293	PMMA	0.02
	PEG	2.92
298	PMMA	0.02
	PEG	2.88
303	PMMA	0.01
	PEG	2.85
308	PMMA	0.01
	PEG	2.84
313	PMMA	0.01
	PEG	2.83

where χ_o is the interaction parameter at infinite dilution and σ denotes the change in the interaction parameter per unit volume fraction of the polymer. This represents the slope in the plot of χ versus ϕ_2. Further, the equation is valid only at low concentrations of the polymer solution. For an accurate determination of χ_o and σ, least square fitting technique is adopted. The values of χ_o obtained from the plots are given in Table 3 ($r = 0.99$). There is an inner agreement between both the values of χ_o obtained through viscosity and relaxation time in the temperature range studied. From the value of χ_o, the type of interaction can be known[8,28] as:

$\chi_o \gg 0.5$: no detectable interaction between the two components;

$\chi_o > 0.5$: some interaction between the two;

$\chi_o = 0.5$: marked degree of interaction between the two;

$\chi_o < 0.5$: strong interaction between the two.

In the present case χ_o obtained by both viscosity and relaxation time routes for the polymers are found to be less than 0.5, indicating the strong interaction between the polymer and the solvent. The comparison of the values between PMMA and PEG shows that the extent of interaction is more between PEG and THF than that in PMMA and THF.

To have further evidence on the polymer-solvent interactions, the polymer-solvent interaction parameter (χ_{ps}) was computed from Flory-Huggins theory[29] with

$$\chi_{ps} = \left(\frac{V_i}{RT} \right)(\delta_2 - \delta_1)^2 \qquad \ldots(8)$$

where δ_1 and δ_2 are the solubility parameter of solvent and polymer, respectively, and V_i, R, and T are the molar volume of the solvent, universal gas constant and temperature (K), respectively. The χ_{ps} values have been given in Table 4. It is evident from the results that the polymer solvent interaction parameter value for PMMA in THF is quite less compared to that of PEG in THF. This may be indicative of higher order of interactions in PEG-THF solution compared to that in PMMA-THF system. This result is also in conformity with the inference obtained from χ_o studies.

In the study of electric properties of macromolecules, O'Konski[30] has given the picture of the solvated water. Solvation signifies a more or less firm attachment of the solvent molecules to polar or polarizable groups. Passynskii[31] has estimated the degree of solvation/hydration by the equation:

$$S_p = \left(\frac{m}{m_0} \right)\left(1 - \left(\frac{\beta}{\beta_0} \right)\right)\left(\left(\frac{100 - x}{x} \right)\right) \qquad \ldots(9)$$

where β and β_o are the adiabatic compressibility of the polymer solution and solvent respectively, m and m_o are the molecular weights of polymer repeat unit and the solvent respectively, x is the weight of polymer in 100 gram of the solution and S_p is the number of solvent molecules taking part in the solvation of a repeat unit.

Solvation numbers computed for the PMMA and PEG solutions have also been included in the Tables 1 and 2. The solvation numbers decreased with increase in polymer concentration indicating the increased solute-solute interaction with concentration. The Sp_o values for both the systems have been determined from the y-intercepts of the Sp versus concentration plots and are included in Table 3. These values are found to decrease like χ with increase of concentrations at all temperatures studied. Higher solvation number obtained in the case of PEG may be due to the presence of stronger molecular interactions between PEG and THF. This observation is again in line with the previous results. When temperature is increased both Sp_o and χ_o decreased showing that solute- solvent interactions also decrease with temperature. On the basis of solvation numbers, the degree of interactions present in PEG-THF system can be considered to be around three times more than that in PMMA-THF system.

From the values of the solubility parameter for the solvent and the polymer, the heat of mixing of solution has been calculated by Scatchard[32]-Hildebrand[33] equation as:

$$\Delta H_m = V((\delta_2 - \delta_1)^2 \, \Phi_1 \, \Phi_2 \qquad \ldots(10)$$

where V is the volume of mixture and Φ_1 and Φ_2 are volume fractions of the solvent and the solute. Fig. 1 presents the plots of ΔH_m versus concentration of polymer solutions of PMMA and PEG. As can be seen from the plots, the heat of mixing of the solutions varies linearly with concentration indicating complete miscibility without any phase separation.
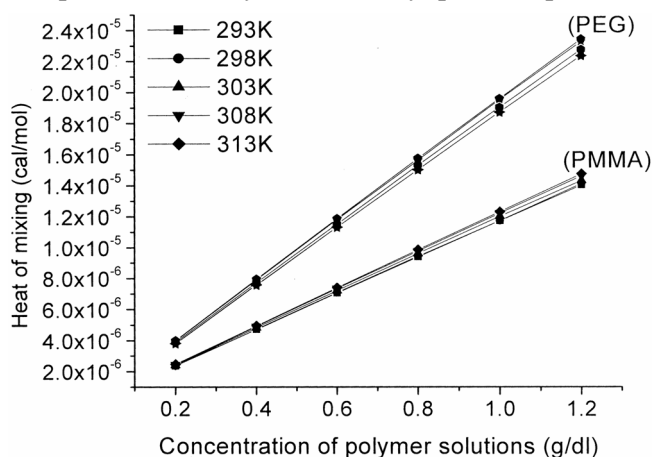
The slightly higher heat of mixing values in the case of PEG may be indicative of higher solute solvent interactions compared to PMMA system. However, the heat of mixing values did not vary appreciably with temperature indicating the insignificant effect of temperature on heat of mixing.

4 Conclusions

The molecular interactions present in PMMA and PEG solutions with THF as solvent have been investigated by viscosity, density and ultrasonic velocity studies. Polymer-solvent interaction parameters for the solution systems have been estimated based on Gibbs' free energy calculations using data on viscosity and ultrasonic velocity of solutions along with heat of mixing and solvation numbers for the solution systems between 293 and 313 K. The results indicate the existence of positive interactions between the polymer and the solvent in their solutions. The results also show the presence of higher degree of interaction between PEG and THF in solution compared to PMMA and THF.

Fig. 1 — Plot of heat of mixing versus concentration of PEG/PMMA solutions

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