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Ultrasonic studies of molecular interactions in the solutions of poly (propylene glycol) 400 in N-alkanols

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ABSTRACT

The densities, ρ and ultrasonic speeds, u of Poly (propylene glycol) 400 in ethanol, 1-propanol and 1-butanol have been measured at 30°C. By using the experimental values of ρ and u, the parameters adiabatic compressibility, intermolecular free length, available volume, acoustic impedance and relaxation strength have been computed. The variations of these parameters with composition of the mixture have been used to discuss the nature and extent of intermolecular interactions between the component molecules.

Key Words: Ultrasonic velocity, compressibility, PPG, molecular interactions

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INTRODUCTION

The study of miscibility and molecular interactions present in polymer and solvent in a polymer solution system provide substantial information on the processes involving polymer production and their uses. Further, polymer dissolution also plays a key role in many industrial applications and an understanding of the dissolution process allows the optimization of design and processing conditions as well as selection of suitable solvent[1,2].

In recent years, numerous studies have been carried out on mixtures containing Poly (propylene glycol) 400, PPG. PPG is used in many formulations of polyurethanes. It is used as a rheology modifier, in automobile seats, in foams and in membranes. As PPG is an industrially important polymer and the solvent alcohol is basically a very good solvent for many polymers, it was thought worthwhile to study the molecular interaction of the solutions of PPG in alcohols.

Ultrasonic technique has been widely used to study the molecular interaction in polymer solutions. Adiabatic compressibility, computed from ultrasonic velocity and density of the solution gives direct information's about different interactions involved among the various polymer-solvent systems and of the complex formation, association or dissociation, structural and destructural nature of the solvents. The ultrasonic technique has now been established as a powerful and reliable technique for polymer characterization. In recent years, several workers[3-7] have used such this technique to characterize the polymer and polymer solutions. The present communication describes the ultrasonic studies of Poly (propylene glycol) 400 in alcohols (ethanol, 1-propanol and 1-butanol) at 30°C.

MATERIALS AND METHODS

Experimental details

Poly (propylene glycol**)** having molecular weight 400 was obtained from Fluka Company. The alcohols were obtained from BDH Company. They were used after standard purification[8]. The solutions were stirred under reflux using a magnetic stirrer until a clear solution was obtained.

The ultrasonic velocity measurements in the Poly (propylene glycol**)** 400 and alcohol solutions were made using a single frequency continuous wave ultrasonic interferometer (Model F81, Mittal Enterprises, New Delhi) to an accuracy of ±0.05% at a frequency of 2 MHz by standard procedure. The values of densities were measured using precalibrated specific gravity bottle by standard procedure with an accuracy of 1%. All the measurements were carried out at 303K.

Calculation of acoustical parameter

Using the measured values of density (ρ) and ultrasonic velocity (U) of the polymer solution for various mole fractions, the related acoustical parameters[9,10] were calculated as detailed below.

The adiabatic compressibility (β_{ad}) has been calculated using the relation

$$\beta_{ad} = [U^2\rho]^{-1} \qquad \ldots(1)$$

where, ρ is the density of the solution and U is the ultrasonic velocity of the solution.
The intermolecular free length (L_f) has been calculated using the formula

$$L_f = K_T\,[\beta_{ad}]^{1/2} \qquad \ldots(2)$$

where, K_T is a constant for different temperatures known as Jacobson constant[11]
The Specific acoustic Impedance:

$$Z=U\,\rho \qquad \ldots(3)$$

Rao's number:

$$R=U^{1/3}V \qquad \ldots(4)$$

where, V is the molar volume of the solution.

From the experimental value of ultrasonic velocity, available volume V_a can be calculated from the following relation:

$$V_a= V\,[1-(U_{exp}/\,U_\infty)] \qquad \ldots(5)$$

The relaxation strength[12] :

$$r = 1-[U/U_\infty]^2 \qquad \ldots(6)$$

where U_∞= 1600 m/s
Then these parameters are correlated with mole fraction of PPG.

RESULTS AND DISCUSSION

The measured values of ultrasonic velocity, density and other related parameters of the PPG 400 + alcohols systems, as a function of PPG mole fractions at 303K are shown in Table-1. It can be seen from the table 1, that the ultrasonic velocity increases non-linearly with increase of concentration of PPG 400 in ethanol, propan-1-ol and butan-1-ol systems at the room temperature 303K. Adiabatic compressibility decreases non-linearly with increase of concentration of PPG. Intermolecular free length also behaves in the same fashion as that of adiabatic compressibility. Available volume increases, whereas the relaxation strength decreases with increase of polymer concentration in all the three systems. It is found that Rao's constant and acoustic impedance varies non-linearly with concentration of PPG in all the systems studied.

Table 1. Variation of ultrasonic velocity and related parameters of PPG 400 in alcohols at 303K

Mole Fraction	U	ρ	$\beta_{ad} \times 10^{10}$	$L_f \times 10^{11}$	$Z \times 10^{-3}$	$R \times 10^3$	$V_A \times 10^5$	r
x_1	ms^{-1}	kgm^{-3}	$N^{-1}m^2$	m	$Kgm^{-2}s^{-1}$		$m^3\ mol^{-1}$	
PPG400 + Ethanol								
0.0	1152	783.7	9.614	6.236	902.8	0.616	1.646	0.482
0.1	1226	872.5	7.625	5.553	1069.6	1.000	2.185	0.413
0.2	1273	916.8	6.730	5.217	1167.0	1.383	2.609	0.367
0.3	1299	940.9	6.298	5.047	1222.2	1.769	3.050	0.341
0.4	1321	961.0	5.963	4.911	1269.4	2.147	3.412	0.318
0.5	1326	966.9	5.882	4.877	1282.1	2.539	3.959	0.313
0.6	1335	974.7	5.756	4.825	1301.2	2.926	4.401	0.304
0.7	1342	980.3	5.664	4.786	1315.5	3.313	4.844	0.296
0.8	1344	984.5	5.623	4.769	1323.1	3.699	5.363	0.294
0.9	1347	988.6	5.574	4.748	1331.6	4.083	5.846	0.291
1.0	1350	999.9	5.487	4.711	1349.8	4.432	6.266	0.288
PPG400 + 1-Propanol								
0.0	1190	795.7	8.874	5.991	946.8	0.800	1.935	0.447
0.1	1295	936.3	6.368	5.075	1212.5	1.096	1.917	0.345
0.2	1308	957.6	6.103	4.968	1252.5	1.465	2.444	0.332
0.3	1319	979.9	5.865	4.871	1292.4	1.817	2.910	0.320
0.4	1328	983.3	5.766	4.829	1305.8	2.196	3.396	0.311
0.5	1331	986.7	5.720	4.810	1313.2	2.570	3.928	0.308
0.6	1338	988.8	5.649	4.780	1323.0	2.949	4.382	0.301
0.7	1344	990.6	5.588	4.754	1331.3	3.327	4.825	0.294
0.8	1345	996.7	5.546	4.736	1340.5	3.685	5.321	0.293
0.9	1348	998.6	5.510	4.721	1346.1	4.058	5.786	0.290
1.0	1350	999.9	5.487	4.711	1349.8	4.432	6.266	0.288
PPG400 + 1-Butanol								
0.0	1226	801.9	8.296	5.793	983.1	0.989	2.160	0.412
0.1	1311	967.5	6.013	4.932	1268.3	1.208	1.994	0.328
0.2	1314	976.3	5.932	4.898	1282.8	1.564	2.554	0.325
0.3	1324	980.2	5.819	4.851	1297.7	1.928	3.030	0.315
0.4	1328	987.4	5.742	4.819	1311.2	2.280	3.527	0.311
0.5	1336	989.0	5.664	4.786	1321.3	2.645	3.963	0.302
0.6	1342	991.0	5.603	4.760	1329.9	3.007	4.397	0.296
0.7	1345	996.3	5.548	4.737	1340.0	3.356	4.846	0.293
0.8	1347	998.1	5.521	4.726	1344.4	3.713	5.317	0.291
0.9	1349	999.2	5.499	4.716	1347.9	4.072	5.782	0.289
1.0	1350	999.9	5.487	4.711	1349.8	4.432	6.266	0.288

The increase in ultrasonic velocity with solute concentration is due to the association between solute and solvent molecules. At lower concentration, the interaction is between the polymer and the solvent molecules. As the concentration of polymer increases, one macromolecule may influence another indirectly by way of mutual interaction. In more concentrated solutions and bulk polymers, direct segment-segment interaction will exist. This Vander wall's interaction causes association between the molecules namely PPG and alcohols in the lower concentrations and in the higher concentrations, in addition to polymer-solvent interactions, polymer-polymer interaction exist and may be responsible for an increase in ultrasonic velocity. This observation is in accordance with those reported in the cases of polyvinyl acetate in alcohols[13] and poly (vinylpyrrolidone) and CAB in DMF solutions[14].

It can be seen that, for the whole range of polymer composition, the polymer solution compressibility is less than that of pure alcohol, in conformity with an earlier report[15]. In solvation, the highly polar forces in a strong localized electric field and the solvating molecules form an incompressible region around polymer chains thereby reducing the hydrodynamic volume[16].This effect results in a reduction of adiabatic compressibility of the solution relative to that of pure solvent.

The variation of adiabatic compressibility in polymer solutions is an indicative of an increase in intermolecular forces forming aggregates of solvent molecules around the solute due to which structural arrangement is affected (Polymer – solvent interactions). The addition of PPG's in alcohols tends to break up the molecular clustering of alcohols, releasing dipole for interactions. In view of the greater force of interaction between alcohol on one hand and PPG on the other, there will be an increase in cohesive energy, which manifests itself as a decrease in compressibility.

The variation of ultrasonic velocity in solution also depends on intermolecular free length on mixing. As per the model of Eyring and Kincaid[17] for sound propagation, ultrasonic velocity increases on decrease of free length. Intermolecular free length is predominating factor in determining the variation of ultrasonic velocity in solutions. In the present investigation, the intermolecular free length was found to decrease non-linearly with concentration. This is due to decrease in compressibility with increase in concentration. This shows significant interaction between the solute and solvent molecules in the system.

Since PPG is bulkier than the different alcohols considered in this study, it may be accommodating alcohol molecules in the voids which may results in increasing the magnitude of available volume and velocity.

If the variation of Rao's number with concentration of one of the components is non-linear, it generally indicates a strong association between molecules[18]. As R varies non-linearly with concentration, it is concluded that there may be association between PPG and alcohol molecules.

Acoustic impedance increases with increasing concentration which is an indicative of strong polymer- solvent interaction and is further supported by a decrease in relaxation strength(r) as shown also for poly (vinylpyrrolidone) in N, N-DMF solutions[19].

CONCLUSION

Experimental data at 303K of density and ultrasonic velocity of Poly (Propylene glycol) 400 in alcohols have been reported. The values of adiabatic compressibility, intermolecular free length, available volume, acoustic impedance and relaxation strength have been calculated from the measured data. On the basis of experimental findings, it is concluded that, apart from a polymer-solvent interaction, a strong screening polymer-polymer interaction exists in solutions investigated.

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