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Acoustical and thermodynamical properties of PEG in non-electrolytes at 303, 313 and 323 K

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ABSTRACT

Ultrasonic velocity (U), density (ρ) and viscosity (η) have been measured for polyethylene glycols (PEG 4000 & 6000) in two solvents namely water and chloroform at 303, 313 and 323 K. Using the experimental values, the adiabatic compressibility (β), free length (L_f), acoustic impedance (Z), free volume(V_f), internal pressure (π_i) and cohesive energy were calculated. The variations of these parameters have been discussed in the light of intermolecular interactions.

Key Words: Ultrasonic velocity, adiabatic compressibility, free length, free volume and internal pressure.

INTRODUCTION

Acoustic propagation in liquid, liquid mixtures and solutions has been useful in the study of structure and the interactions among liquid molecules. Ultrasonic studies have been found to be useful in describing the theory of liquid state of matter. The propagation of ultrasonic velocity through polymers and their solutions have been attracted the attention of many researchers in the recent past and is serving as an important tool to understand the nature of polymer solutions. Thus the study of polymer solutions, both dilute and concentrated, gives a wealth of information for both academic curiosity and the end uses of polymers. Thermodynamical properties of polymers are of great interest from the point of view of science and technology and an abundant literature is available on this subject. PEG has a wide variety of industrial applications and hence, a further understanding of its physical properties will widen its area of application.Glycols are widely used low and high molecular weight polymers, drawing the attention of polymer scientists.

Owing to these considerations, an attempt has been made to elucidate the molecular association / molecular interactions of binary liquid mixture of PEG (4000 & 6000) with non-electrolytes such as water and chloroform at the temperatures 303, 313 and 323 K by measuring ultrasonic velocity, density and viscosity. The acoustical and thermodynamical parameters such as adiabatic compressibility, free length, acoustic impedance, free volume, internal pressure and

cohesive energy have been computed from the experimental data with a view to investigate the nature of molecular interactions between the component of a liquid mixtures.

MATERIALS AND METHODS

All the chemicals used in the present study are of analytical reagent (AR) and spectroscopic reagent (SR) without further purification. The purities of the above chemicals were checked by density determination at 303, 313 and 323 \pm 0.1K, which showed an accuracy of \pm 1 \times 10⁻⁴ gcm⁻³ with the earlier values. The density was determined using a specific gravity bottle by relative measurement method with an accuracy of \pm 0.01 kgm⁻³. The weight of the sample was measured using electronic digital balance with an accuracy of \pm 0.1mg (Model: SHIMADZU AX-200). An Ostwald's viscometer (10 ml) was used for the viscosity measurement. Efflux time was determined using a digital chronometer within \pm 0.01s. An ultrasonic interferometer having the frequency of 3 MHz (MITTAL ENTERPRISES, New Delhi, Model: F-81) with an overall accuracy of \pm 0.1% has been used for velocity measurement. An electronically digital operated constant temperature bath (RAAGA Industries) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. The accuracy in the temperature measurement is \pm 0.1K.

Various acoustical and thermodynamical parameters calculated from the measured data are as follows:

Adiabatic compressibility¹

$$\beta = \frac{l}{U^2 \rho} \qquad \dots (1)$$

Intermolecular free length²
 $L_f = K \beta^{\frac{1}{2}} \qquad \dots (2)$

where K is temperature dependent constant. Its value is 631×10^{-6} , 636×10^{-6} and 642×10^{-6} , respectively at 303, 308 and 313K.

Specific acoustic impedance³ $Z=U\rho$... (3) Free volume ⁴⁻⁵ $V_f = \left(\frac{M_{eff} U}{K\eta}\right)^{3/2}$... (4)

where M_{eff} is the effective molecular weight ($M_{eff} = \sum m_i x_i$, in which m_i and x_i are the molecular weight and the mole fraction of the individual constituents, respectively). *K* is a temperature independent constant which is equal to 4.28×10^9 for all liquids. Internal pressure

$$\pi_i = bRT \left(\frac{K\eta}{U}\right)^{1/2} \left(\frac{\rho^{2/3}}{M_{eff}}\right) \qquad \dots (5)$$

where b is the cubic packing which is assumed to be 2 for all liquids and solutions. R is the universal gas constant.

Molar cohesive energy $= \pi_i V_m$... (6)

Where the molar volume of the mixture is given by

$$V_{\rm m} = \frac{M_{\rm eff}}{\rho_{\rm mix}}$$

where M_{eff} is the effective molecular weight $\left(M_{eff} = \sum_{i=1}^{n} M_i X_i\right)$ where M_i and X_i refer to the

molecular weight and mole fraction of the individual components in the mixtures, and ρ_{mix} is the density of the mixture.

RESULTS AND DISCUSSIONS

The values of density, viscosity and ultrasonic velocity of PEG (4000 & 6000) with water and chloroform mixtures at 303, 313 and 323 K are listed in Table1. The acoustical and thermodynamical parameters such as adiabatic compressibility, free length, specific acoustic impedance, free volume, internal pressure and cohesive energy are presented in Tables 2 and 3.

In first two systems, (Table 1) the values of density increases with increase in concentration of PEG but it found to decreases with increase in temperature, whereas in systems III and IV, these values are decreases with increase in concentration as well as rise in temperature. This increasing behaviour suggests, a strong electrolytic nature in which the solute tends to attract the solvent molecules and vice versa. Further from Table 1 it is observed that the values of viscosity increases with increasing of solute content but where as it decreases with rising of temperature. The gradual increase in density and viscosity with solute concentration at all temperatures may be due to association between solute and solvent molecules. A rise in temperature leads to less ordered structure and more spacing between the molecules. The decrease in density and viscosity with temperature indicates decrease in intermolecular forces due to increase in the thermal energy of the systems, which causes increase in volume expansion and hence increase in free path length. The values of ultrasonic velocity (Table 1) are increases with increase in the concentration of PEG (4000 & 6000) as well as with rising of temperature in aqueous medium, whereas in chloroform mixtures these values are decreases with increasing of solute content but however, it found to increases with rising of temperature. Decrease in ultrasonic velocity may be attributed to the solute-solvent interaction and also due to increase in the mobility of solutes. The increase of thermal energy weakens the molecular forces and hence the decrease in velocity is expected.

From the Table 2 it is observed that,

I. The values of adiabatic compressibility are decreases with increasing of PEG, but it found to increases with elevation of temperature in aqueous medium, whereas reverse trend was obtained in chloroform mixtures.

II. The values of L_f are decreases with increasing of PEG as well as temperature in all systems studied except with increasing of PEG in chloroform mixtures.

III. The values of Z, increases with increasing of PEG as well as temperature in all systems studied except with increasing of PEG in chloroform mixtures.

				•					
Concentration of PEG (Wt.%)	ρ/(kg. m ⁻³)			$\eta/(\times 10^{-3} \text{Nsm}^{-1})$			<i>U/</i> (m. s ⁻¹)		
	303 K	313 K	323 K	303 K	313 K	323 K	303 K	313 K	323 K
System-I: PEG 40)00 in aqu	eous medi	um						ı
0.0	995.7	992.3	988.1	0.7982	0.6540	0.5477	1483.00	1490.00	1510.03
1.0	996.5	993.5	989.3	0.8923	0.7116	0.5787	1515.20	1553.80	1584.70
2.0	997.0	994.4	989.7	0.9862	0.7851	0.6224	1521.07	1556.20	1596.94
3.0	997.6	995.4	990.0	1.0757	0.8599	0.6672	1526.53	1558.40	1609.06
4.0	998.4	995.8	990.8	1.1642	0.9305	0.7412	1544.26	1568.14	1648.23
5.0	999.2	996.2	991.6	1.2527	1.0019	0.8117	1560.66	1576.93	1687.20
System-II: PEG 6	5000 in aqu	ueous med	ium			•			
0.0	995.7	992.3	988.1	0.7982	0.6540	0.5477	1483.00	1490.00	1510.03
1.0	997.2	993.5	989.6	0.8784	0.7127	0.5996	1532.53	1533.06	1538.13
2.0	998.1	994.2	990.3	0.9940	0.8091	0.6686	1546.49	1547.00	1551.14
3.0	999.0	995.0	990.8	1.1078	0.9051	0.7363	1555.20	1560.26	1569.06
4.0	999.5	995.6	991.6	1.2764	1.0065	0.8254	1564.01	1571.25	1579.02
5.0	999.9	996.2	992.4	1.4461	1.1057	0.9106	1572.05	1573.40	1597.12
System-III: PEG	4000 in ch	loroform				1			
0.0	1185.1	1175.5	1163.8	0.5299	0.4788	0.4382	912.26	967.00	972.00
1.0	1183.1	1172.0	1163.1	0.6025	0.5150	0.4749	905.06	940.00	964.00
2.0	1182.1	1170.9	1162.5	0.6689	0.5709	0.5229	901.51	917.60	959.41
3.0	1181.2	1170.0	1161.9	0.7339	0.6279	0.5701	890.93	894.93	953.86
4.0	1180.6	1169.2	1161.4	0.7940	0.6924	0.6277	881.29	890.55	904.41
5.0	1180.0	1168.4	1160.8	0.8540	0.7541	0.6842	855.81	867.20	890.21
System-IV: PEG 6000 in chloroform									
0.0	1185.1	1175.5	1163.8	0.5299	0.4788	0.4381	912.26	967.00	972.00
1.0	1183.9	1174.7	1162.6	0.5798	0.5188	0.4721	901.51	946.93	949.86
2.0	1182.8	1173.4	1161.4	0.6584	0.5851	0.5208	891.09	917.04	928.36
3.0	1182.0	1172.0	1160.3	0.7373	0.6491	0.5706	860.26	888.53	907.20
4.0	1181.4	1170.8	1159.7	0.8474	0.7343	0.6367	844.40	877.67	882.33
5.0	1180.8	1169.6	1159.1	0.9609	0.8230	0.7010	828.26	857.33	866.66

Table: 1. Values of density (ρ), viscosity (η) and ultrasonic velocity (U) at 303,313 and 323K for

Concentration of PEG (Wt.%)	β/(×10 ⁻¹⁰ m ² N ⁻¹)			$L_{f'}(\times 10^{-10} \mathrm{m})$			$Z/(\times 10^4 {\rm Kg \ s \ m^{-2}})$			
	303 K	313 K	323 K	303 K	313 K	323 K	303 K	313 K	323 K	
System-I: PEG 4000 in aqueous medium										
0.0	4.5666	4.5393	4.4384	1.3338	1.3298	1.3149	147.662	147.853	149.206	
1.0	4.3710	4.1691	4.0251	1.3049	1.2744	1.2522	150.990	154.370	156.774	
2.0	4.3347	4.1525	3.9620	1.2995	1.2719	1.2424	151.666	154.749	158.049	
3.0	4.3016	4.1366	3.9010	1.2945	1.2694	1.2328	152.287	155.123	159.313	
4.0	4.2001	4.0837	3.7152	1.2791	1.2613	1.2030	154.179	156.155	163.307	
5.0	4.1090	4.0367	3.5427	1.2652	1.2540	1.1748	155.941	157.094	167.303	
System-II: PEG 6000 in aqueous medium										
0.0	4.5666	4.5393	4.4384	1.3338	1.3298	1.3149	147.662	147.853	149.206	
1.0	4.2697	4.2827	4.2712	1.2897	1.2917	1.2899	152.824	152.310	152.213	
2.0	4.1892	4.2029	4.1969	1.2775	1.2796	1.2787	154.355	153.803	153.609	
3.0	4.1387	4.1280	4.0995	1.2698	1.2681	1.2637	155.364	155.261	155.462	
4.0	4.0901	4.0684	4.0447	1.2623	1.2589	1.2553	156.323	156.434	156.576	
5.0	4.0468	4.0549	3.9504	1.2556	1.2568	1.2405	157.189	156.742	158.498	
System-III: PE	System-III: PEG 4000 in chloroform									
0.0	10.139	9.0975	9.0947	1.9874	1.8826	1.8823	108.112	113.671	113.121	
1.0	10.393	9.4937	9.5335	2.0049	1.9395	1.8985	107.087	110.168	112.123	
2.0	10.647	10.134	9.9905	2.0137	1.9878	1.9081	106.567	107.442	111.531	
3.0	11.432	10.808	10.472	2.0384	2.0390	1.9197	105.237	104.707	110.829	
4.0	11.872	11.088	11.076	2.0612	2.0497	2.0251	104.045	104.123	105.038	
5.0	12.345	11.632	11.486	2.1231	2.1056	2.0579	100.986	101.324	103.336	
System-IV: PEG 6000 in chloroform										
0.0	10.139	9.0975	9.0947	1.9874	1.8826	1.8823	108.112	113.671	113.121	
1.0	10.318	9.6564	9.2519	2.0122	1.9231	1.9272	106.730	111.236	110.431	
2.0	10.409	10.143	9.3454	2.0366	1.9869	1.9728	105.398	107.605	107.820	
3.0	10.666	10.672	9.4594	2.1103	2.0519	2.0198	101.683	104.136	105.262	
4.0	10.906	10.784	10.527	2.1505	2.0784	2.0772	99.757	102.758	102.324	
5.0	11.571	11.381	10.871	2.1930	2.1288	2.1154	97.801	100.273	100.455	

Table 2: Values of adiabatic compressibility (β), inter molecular free length (L_f) and specific acoustic impedance (Z) at 303, 313 and 323 K for

Concentration of PEG (Wt.%)	$V_{f}/(\times 10^{-7} \mathrm{m}^{3} \mathrm{mol}^{-1})$			$\pi_{i/(}\times 10^8\mathrm{Nm}^{-2})$			COHESIVE KJ / mol		ENERGY	
	303 K	313 K	323 K	303 K	313 K	323 K	303 K	313 K	323 K	
System-I: PEG 4000 in aqueous medium										
0.0	0.2177	0.2956	0.3935	23.027	21.432	41.6278	41.6278	38.8768	36.5213	
1.0	0.1930	0.2815	0.3953	23.823	21.658	43.4596	43.4596	39.6300	36.5715	
2.0	0.1696	0.2471	0.3639	24.722	22.486	45.5180	45.5180	41.5135	37.7138	
3.0	0.1519	0.2192	0.3365	25.491	23.268	47.3674	47.3674	43.3317	38.8323	
4.0	0.1392	0.1994	0.3023	26.086	23.865	48.9020	48.9020	44.8560	40.3645	
5.0	0.1286	0.1825	0.2770	26.633	24.429	50.3660	50.3660	46.3371	41.6743	
System-II: PEC	G 6000 in a	aqueous m	edium							
0.0	0.2177	0.2956	0.3935	23.027	21.432	20.048	41.6278	38.8768	36.5213	
1.0	0.2010	0.2752	0.3585	23.513	21.821	20.566	42.8656	39.9290	37.7805	
2.0	0.1718	0.2341	0.3129	24.630	22.892	21.390	45.3049	42.2726	39.6543	
3.0	0.1494	0.2033	0.2795	25.652	23.851	22.073	47.6017	44.4338	41.2989	
4.0	0.1236	0.1778	0.2412	27.160	24.792	23.048	50.8627	46.6098	43.5064	
5.0	0.1048	0.1569	0.2148	28.523	25.689	23.818	53.9064	48.7308	45.3543	
System-III: PEG 4000 in chloroform										
0.0	3.3170	4.2142	4.8520	2.955	2.803	2.742	29.7703	28.4701	28.1245	
1.0	2.7428	3.6744	4.3085	3.125	2.910	2.833	31.2853	29.9061	29.4959	
2.0	2.3647	3.0795	3.7567	3.261	3.065	2.946	33.4894	32.2330	31.2970	
3.0	2.0503	2.6085	3.3176	3.396	3.217	3.050	36.0194	34.4467	33.0968	
4.0	1.8178	2.2679	2.6890	3.512	3.348	3.250	38.9213	36.8210	35.4008	
5.0	1.5816	1.9442	2.3395	3.655	3.501	3.382	41.7897	39.3931	37.4277	
System-IV: PEG 6000 in chloroform										
0.0	3.3170	4.2147	4.8529	2.955	2.803	2.742	29.7704	28.4714	28.1264	
1.0	2.8890	3.6745	4.2526	3.072	2.914	2.845	31.8369	29.9282	29.3627	
2.0	2.3804	2.9665	3.5981	3.254	3.107	2.986	33.5677	31.8543	30.8385	
3.0	1.9329	2.4568	3.0746	3.465	3.285	3.125	35.3227	33.7816	32.2501	
4.0	1.5473	2.0327	2.5377	3.707	3.475	3.309	36.8900	35.5133	34.7025	
5.0	1.2625	1.6773	2.1687	3.941	3.679	3.464	38.7683	37.5081	36.4695	

Table 3 : Values of free volume (V_f) internal pressure (π_i) and cohesive energy for at 303, 313 and 323 K for

The decrease in velocity and increase in compressibility were attributed to the formation of hydrogen bonds between solute and solvent molecules. The compressibility appears to be increasing with increase in hydrogen bond strength formed by solute and solvent molecules in chloroform mixtures. The increase in free length and compressibility imply that there is enhanced molecular association in these systems with increase in solute content⁶, as the new entities (formed due to molecular association) become compact and less compressible. The acoustic impedance behaviour can be explained on the basis of lyophilic interaction between solute and solvent molecules, which increases the intermolecular distance, making relatively wider gap between the molecules, with elevations of temperatures and becoming responsible for the propagation of ultrasonic waves.

The following observations have been made on the variation of free volume, internal pressure and cohesive energy (Table 3).

I. The values of V_f , decreases with increasing concentration of solute and increases with increase in temperature in all systems.

II. The magnitude of free volume is in order PEG 4000 + chloroform > PEG 6000 + chloroform > PEG 4000 + water > PEG 6000 + water.

III. The values of π_i and $\pi_i V_m$ are increases with increase of PEG and decreases with elevation of temperature for all the four systems.

The continuous decrease in free volume leads to a closer packing of the molecule inside a shield which may be brought about by the increase in the magnitude of interaction⁷. The increase in internal pressure with increase of PEG may be due to the strengthening of cohesive forces perhaps due to making up the structure of the solvent⁸. When the temperature is increased, there is a tendency for the solute molecules to move away from each other, reducing the possibility for interaction, which may further reduce the cohesive forces and ultimately leads to an increase in the free volume.

CONCLUSION

The present study reveals that water has better interaction with PEG than chloroform mixtures for both molecular weights. Though the polymer and the solvents are polar in nature, the variations in the properties studied (in particular π_i and V_f which are indicators of interactions) show that the tightly coiled configuration of PEG having spherical symmetry with the ethyl groups buried inside the coil would probably have led to existence of interactions with the solvents. In the solution, hydrogen bonding and dispersive forces have played a major role in defining the polymer-solvent interactions. The existence of polymer-solvent interactions is taking place through hydrogen bonding with increase of polymer concentration whereas dispersive type of interactions dominates with raising of temperature. From the magnitude of V_f it can be concluded that the strength of interaction is in order: PEG 6000 + water > PEG 4000 + water > PEG 6000 + chloroform > PEG 4000 + chloroform.

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