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Article

Study of Binary Liquid Mixtures of Cyclohexane with Glycols and Polyglycols at 308.15 K Using Sound Velocities

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ABSTRACT

Binary liquid mixtures of cyclohexane with glycols (ethylene glycol [EG], diethylene glycol [DEG], triethylene glycol [TEG] and polyglycols (polyethylene glycol -200 [PEG-200], PEG-400 and polyethylene-600 [PEG-600]) are used to study the interactions between molecules by measuring the densities and sound velocities at 308.15 K. Functions like excess ultrasonic velocity (u^E), excess Isentropic compressibility (K_S^E), excess Intermolecular free length (L_f^E), and excess acoustic impedance (Z^E) for the binary liquid mixtures under study have been calculated from the measured data. These excess function values were fitted to the Redlich–Kister polynomial equation. The nature and extent of intermolecular interactions between the components are discussed from the results and are found to be in the following order CH + EG < CH + DEG < CH + TEG < CH + PEG-200 < CH + PEG-400 < CH + PEG-600.

Key words: Ultrasonic velocity, Cyclohexane, Ethylene glycols, Poly (ethylene glycols), Isentropic compressibility, Intermolecular free length, Acoustic impedance.

1. INTRODUCTION

Intermolecular interactions between the component molecules were studied using ultrasonic investigations of liquid mixtures consisting of polar and non-polar component as they have a lot of applications in industrial and technological processes [1,2]. Further, these studies as a function of mole fraction are useful in gaining knowledge of the structure and bonding between the associated molecular complexes. The variation of ultrasonic parameters and excess values of the parameters with the mole fraction of one of the components have been studied by many scientists [3,4].

Sound velocities affect the physical properties of the medium and hence can be used to study the molecular interactions of the liquid mixtures. The difference in molecular size and the interaction between the molecules attribute to the non-linear deviation from ideal behavior [5,6]. The nature of the molecular interactions in pure liquids [7] binary liquid mixtures and tertiary liquid mixtures [8-10] can be studied by measuring ultrasonic velocities. The method of studying the molecular interactions from the knowledge of the variation of thermodynamic parameters and their excess values with composition gives an insight into the molecular processes [11,12]. As a part of our research work on thermodynamic properties of liquid-liquid mixtures [13-17], we have also used these data in the present paper.

Cyclohexane has been picked as the dissolvable for the current investigation since its properties have been the subject of significant premium due to its flexibility as a dissolvable solvent. Cyclohexane is non-polar, unassociated, and inert hydrocarbon possessing a globular structure. Due to the non-polar nature of cyclohexane and its inertness towards electron donors [18], cyclohexane behaves as an inert solvent towards an electrophile or nucleophile. A dispersive type of interaction is expected between cyclohexane and other components (glycols and polyglycols). The glycols, on the other hand, have relatively low values of relative permittivity and dipole moments, yet they are self-associated through hydrogen bonding. Poly (ethylene glycol [EG]) comprises a series of linear chain polymers of oxyethylene units with a wide variety of applications in pharmaceuticals, chemical cosmetics, and food industries. Their low toxicity and high water solubility enable their use for the purification of biological materials and as additives in the production of edible films for food coatings.

Therefore thermodynamic properties of cyclohexane-glycols/ polyglycols are of interest whereas glycols and polyglycols are polar and associative in nature. Moreover, glycols and polyglycols are a very good object for the investigations of structural effects due to the presence of hydrogen and etheric bonds that are capable of formatting hydrogen bonds with CH molecules. Thus, cyclohexane and its binary mixtures with EG, diethylene glycol (DEG), triethylene glycol (TEG) and poly(ethylene glycols) like poly(ethylene glycol -200) (PEG-200), poly(ethylene glycol – 400) (PEG - 400), and poly(ethylene glycol -600) (PEG – 600) that are having ethereal and hydroxyl oxygen in the same molecule will be interesting to study the molecular interactions. This paper includes ultrasonic and density behavior of binary mixtures of cyclohexane with glycols and polyglycols over the entire composition range at 308.15 K and the results are presented here.

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2. EXPERIMENTAL

2.1. Materials

Cyclohexane (CH), EG, DEG, TEG, poly (EG-200) (PEG-200), poly (EG-400) (PEG-400), and poly (EG -600) (PEG-600) were purchased from E-Merck, Mumbai and used as purchased. The density and ultrasonic velocity values of the liquids used were measured at 308.15 K and compared with the literature values and are included in Table 1.

2.2. Methods

A weighed amount of pure liquids using Mettler balance with an accuracy of ±0.1 mg was used to prepare mixtures adopting the method of a closed system to avoid evaporation. The single - crystal variable - path ultrasonic interferometer (Mittal Enterprises, New Delhi) operating at a frequency of 2 MHz and these were accurate up to ±0.03% was used to measure the ultrasonic sound speed in pure liquid and binary liquid mixtures. The densities (ρ) of liquids and their mixtures were measured using a bicapillary pycnometer having a capillary diameter of 0.85 mm, which was aligned utilizing double distilled water. The vital lightness adjustments were applied. The necessary buoyancy corrections were applied. Comparing the purity of compounds the measured values of density are those reported in literature and were found to be accurate up to ±0.02 kg/m^3. The temperature was maintained constant during the period of measurement by a water circulation system from a thermostatically controlled and well-stirred constant temperature water bath, whose temperature was controlled to ±0.02K, and was used for all measurements. Mixtures were allowed to stand for some time before every measurement, so as to avoid air bubbles. The purities of the liquids were checked by comparing the values of densities and ultrasonic velocities with literature data (Table 1) and found in good agreement in general. Care was taken to see that there was no evaporation loss and hence the experiment was conducted in A C rooms.

3. RESULTS AND DISCUSSION

From the measured densities (ρ) and ultrasonic velocities (u), the various acoustical parameters such as isentropic compressibility (K_S), acoustic impedance (Z), and intermolecular free-length (L_f) were calculated using the following equations 1-3, respectively, for the binary systems CH+EG, CH+DEG, CH + TEG, CH + PEG-200, CH + PEG-400 and CH + PEG-600 under study and are incorporated in Table 2.

$$K_S = 1/u^2 \rho \quad (1)$$

$$Z = \rho u \quad (2)$$

$$L_f = K (K_s)^{1/2} \quad (3)$$

Table 1: The experimental values of densities and ultrasonic velocities of pure liquids with literature values at 308.15 K.

Liquid	Density (×10^{-3} kg m^{-3})		Ultrasonic velocities u (m/s)	
	Expt	Lit	Expt	Lit
Cyclohexane	0.7644	0.7657[19]	1208.0	1208.0[19]
Ethylene glycol	1.1030	1.1029[20]	1632.2	1632.1[21]
Diethylene glycol	1.1062	1.1062[21]	1557.9	1557.9[22]
Triethylene glycol	1.1128	1.1129[23]	1582.2	1586.0[24]
Poly (ethylene glycol-200)	1.1124	1.1122[25]	1564.7	1585.1[20]
Poly (ethylene glycol-400)	1.1140	1.1142[26]	1591.5	1484.1[20]
Poly (ethylene glycol-600)	1.1143	1.1144[27]	1622.0	1611.2[28]

Where 'K' is Jacobson's constant

The excess functions Y^E have been calculated using the relation:

$$Y^E = Y_{mix}-(X_1Y_1+X_2Y_2) \quad (4)$$

Where, Y denotes u, Z, K_S, and L_f respectively and X is the mole fraction of cyclohexane and suffixes 1 and 2 denote the components 1 and 2 in binary mixtures and the values are given in Table 3.

The dependence of u^E, Z^E, K_S^E, and L_f^E on the mole fraction of cyclohexane (X_{CH}) for all the six systems were fitted to the following Redlich–Kister equation by the least square method, and the values are incorporated in Table 4.

$$Y^E = X(1-X) \Sigma A_i (2\times-1) \quad (5)$$

Where Y^E is u^E, Z^E, K_S^E, and L_f^E parameters.

The parameters A_i is obtained by a non-linear least square polynomial fitting procedure and their values are presented in Table 4, together with standard deviation (σ) values.

The values of u, Z, K_S, and L_f varied with the mole fraction of cyclohexane (X_{CH}) are included in Table 2. The variations in the values of the above parameters indicate the presence of interactions in these liquid mixtures. The variations of u for the mixtures depend on the value of L_f. The observed decrease in u and corresponding increase in L_f with X_{CH} (Table 2) for all the systems are in accordance with the view proposed by Eyring and Kincaid [29]. From Table 2, it is clear that the non-linear behavior of these parameters (u, Z, K_S, and L_f) with the mole fraction of cyclohexane (X_{CH}) which is different from ideal behavior can be attributed to the presence of intermolecular interactions in the systems [6,30,31]. However, the excess functions which are a measure of the deviations from the ideal behavior are relatively more sensitive to the intermolecular interactions between the unlike molecules of the mixture than the pure acoustical parameters as explained above.

With this view in mind, the variations in excess acoustical parameters, such as the excess ultrasonic velocity (u^E), excess acoustic impedance (Z^E), excess isentropic compressibility $\left(K_S^E\right)$ and intermolecular free-length (L_f^E) with mole fraction of CH (X_{CH}) are examined from the Figures 1-4 respectively. It is observed from Figure 1 that the u^E is positive for all the liquid mixtures except for CH + EG and CH + DEG systems under study. In general, if the media is dense the ultrasonic velocity value will be more, and if the media is less dense the ultrasonic velocity value will be less. When we mix two liquids if they condense or compress more, ultrasonic velocity will be more. For these mixtures, since the excess volume (V^E) values are negative [32], it indicates the mixtures compressed more leading to positive excess ultrasonic velocities for these mixtures. Figure 2 shows the variation of Z^E with the composition of liquid mixtures that exhibit positive deviations as expected as per the equation (2) for Z^E calculation.

The positive deviations in u^E and Z^E (Figures 1 and 2) for all the systems except CH + EG and CH + DEG systems under study are observed over the entire range of composition. These trends for these systems again support our view that the interactions between unlike molecules are quite possible, and these values are in the following order: CH + EG < CH +DEG < CH +TEG < CH +PEG - 200 < CH + PEG - 400 < CH + PEG – 600. Bai *et al*. [14] reported a similar observation from their ultrasonic velocity studies of binary liquid mixtures of butoxy ethanol with some amines.

Usually, K_S^E values depend upon two factors, (i) increase in free length, defined by Jacobson [28] due to loss of dipolar association,

Table 2: Values of density (ρ), ultrasonic velocity (u), acoustic impedance (Z), isentropic compressibility (K_S), and intermolecular-free length (L_f) for the binary mixtures of cyclohexane (CH) with glycols and polyglycols at 308.15 K.

Mole fraction (X_{CH})	$\rho\times10^{-3}$ (kg/m)	u (m/s)	$Z\times10^{-4}$ (kg/m/s)	$K_S\times10^{11}$ (m/N)	$L_f\times10^{12}$ (m)
CH+EG					
0.0000	1.1030	1632.2	1.8003	34.03	3.8635
0.0537	1.0692	1589.7	1.6997	37.01	4.0290
0.1133	1.0354	1547.6	1.6024	40.33	4.2056
0.1797	1.0016	1504.3	1.5067	44.12	4.3991
0.2541	0.9678	1462.5	1.4154	48.31	4.6031
0.3382	0.9340	1420.1	1.3264	53.09	4.8256
0.4340	0.9002	1377.8	1.2403	58.52	5.0662
0.5439	0.8664	1335.2	1.1568	64.74	5.3289
0.6715	0.8326	1292.4	1.0761	71.91	5.6160
0.8214	0.7988	1250.6	0.9990	80.04	5.9252
1.0000	0.7644	1208.0	0.9234	89.65	6.2707
CH+DEG					
0.0000	1.1062	1557.9	1.7233	37.25	4.0419
0.0883	1.0720	1522.6	1.6322	40.24	4.2011
0.1789	1.0378	1487.5	1.5437	43.55	4.3705
0.2719	1.0036	1452.4	1.4576	47.24	4.5517
0.3674	0.9694	1417.6	1.3742	51.33	4.7450
0.4656	0.9352	1382.6	1.2930	55.94	4.9533
0.5665	0.9010	1347.4	1.2140	61.13	5.1782
0.6703	0.8668	1312.7	1.1378	66.95	5.4190
0.7770	0.8326	1277.4	1.0636	73.61	5.6819
0.8869	0.7984	1242.8	0.9923	81.09	5.9639
1.0000	0.7644	1208.0	0.9234	89.65	6.2707
CH+TEG					
0.0000	1.1128	1582.2	1.7607	35.90	3.9680
0.1199	1.0780	1544.8	1.6653	38.87	4.1291
0.2346	1.0432	1507.3	1.5724	42.19	4.3019
0.3444	1.0084	1469.9	1.4822	45.90	4.4868
0.4497	0.9736	1432.5	1.3947	50.05	4.6855
0.5507	0.9388	1395.1	1.3097	54.73	4.8995
0.6477	0.9040	1357.6	1.2273	60.02	5.1308
0.7409	0.8692	1320.5	1.1478	65.98	5.3795
0.8306	0.8344	1282.8	1.0704	72.83	5.6519
0.9169	0.7996	1245.6	0.9960	80.61	5.9460
1.0000	0.7644	1208.0	0.9234	89.65	6.2707
CH+PEG-200					
0.0000	1.1124	1564.7	1.7406	36.72	4.0131
0.1536	1.0776	1529.5	1.6482	39.67	4.1712
0.2899	1.0428	1493.4	1.5573	43.00	4.3427
0.4117	1.0080	1457.6	1.4693	46.69	4.5256
0.5212	0.9732	1422.0	1.3839	50.82	4.7211
0.6202	0.9384	1386.1	1.3007	55.47	4.9323
0.7101	0.9036	1350.8	1.2206	60.65	5.1578
0.7921	0.8688	1315.4	1.1428	66.52	5.4016

(Contd...)

Table 2: *(Continued)*.

Mole fraction (X_{CH})	$\rho\times10^{-3}$ (kg/m)	u (m/s)	$Z\times10^{-4}$ (kg/m/s)	$K_S\times10^{11}$ (m/N)	$L_f\times10^{12}$ (m)
0.8672	0.8340	1279.3	1.0669	73.26	5.6687
0.9363	0.7992	1243.5	0.9938	80.92	5.9576
1.0000	0.7644	1208.0	0.9234	89.65	6.2707
CH+PEG-400					
0.0000	1.1140	1591.5	1.7729	35.44	3.9427
0.2660	1.0791	1553.5	1.6764	38.40	4.1039
0.4492	1.0442	1514.0	1.5809	41.78	4.2808
0.5829	1.0093	1476.5	1.4902	45.45	4.4648
0.6850	0.9744	1438.0	1.4012	49.63	4.6657
0.7653	0.9395	1399.5	1.3148	54.34	4.8823
0.8303	0.9046	1361.5	1.2316	59.64	5.1144
0.8839	0.8697	1323.0	1.1506	65.69	5.3678
0.9288	0.8348	1284.5	1.0723	72.60	5.6431
0.9671	0.7999	1246.0	0.9967	80.52	5.9430
1.0000	0.7644	1208.0	0.9234	89.65	6.2707
CH+PEG-600					
0.0000	1.1143	1622.0	1.8074	34.11	3.8680
0.3521	1.0795	1616.5	1.7450	35.45	3.9433
0.5501	1.0443	1571.5	1.6411	38.77	4.1240
0.6770	1.0096	1525.0	1.5396	42.59	4.3221
0.7653	0.9743	1480.0	1.4420	46.86	4.5335
0.8302	0.9393	1435.0	1.3479	51.70	4.7620
0.8800	0.9044	1389.5	1.2567	57.27	5.0119
0.9194	0.8693	1344.0	1.1683	63.68	5.2852
0.9514	0.8342	1298.5	1.0832	71.10	5.5842
0.9778	0.7993	1253.5	1.0019	79.62	5.9097
1.0000	0.7644	1208.0	0.9234	89.65	6.2707

CH: Cyclohexane, EG: Ethylene glycol, DEG: Diethylene glycol, TEG: Triethylene glycol, PEG-200: Polyethylene glycol-200, PEG: Polyethylene glycol-400, PEG-600: Polyethylene glycol-600

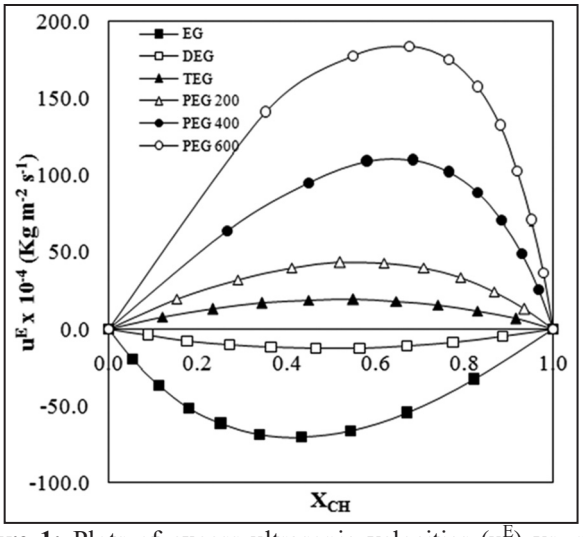

Figure 1: Plots of excess ultrasonic velocities (u^E) vs. mole fraction of cyclohexane (X_{CH}) for the binary mixtures of cyclohexane with glycols and polyglycols at 308.15 K.

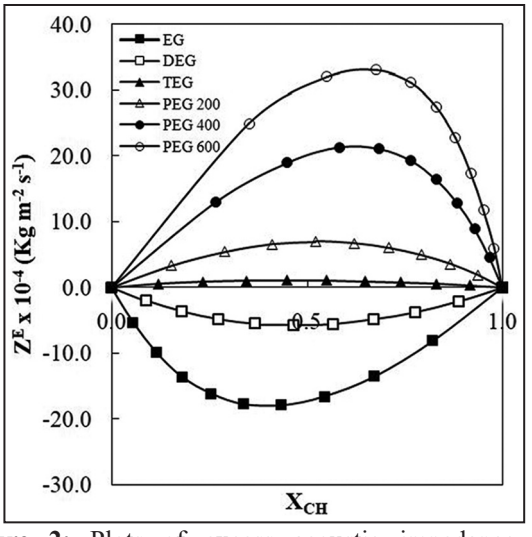

Figure 2: Plots of excess acoustic impedance (Z^E) vs. mole fraction of cyclohexane (X_{CH}) for binary mixtures of cyclohexane with glycols and polyglycols at 308.15 K.

Table 3: Excess ultrasonic velocity (u^E), excess acoustic impedance (ZE), excess isentropic compressibility (K_S^E) excess intermolecular free length (L_f^E), and mole fractions of cyclohexane (X_{CH}) for the binary liquid mixtures of cyclohexane (CH) with glycols and polyglycols at 308.15 K.

Mole fraction (X_{CH})	u^E (m/s)	Z^E10^{-4} (kg m^{-2}/s)	$K_S^E\times10^{11}$ (m^2/N)	$L_f^E\times10^{12}$ (m)
CH+EG				
0.0000	0.0000	0.0000	0.0000	0.0000
0.0537	−19.7044	−5.3486	−0.0107	0.3614
0.1133	−36.5384	−9.8577	−0.0077	0.6938
0.1797	−51.6772	−13.6039	0.0952	1.0303
0.2541	−61.8931	−16.2047	0.1424	1.2787
0.3382	−68.6216	−17.7339	0.2473	1.4789
0.4340	−70.3143	−17.9472	0.3508	1.5813
0.5439	−66.2707	−16.6527	0.4598	1.5608
0.6715	−54.9367	−13.5385	0.5265	1.3600
0.8214	−33.1506	−8.1010	0.3261	0.8440
1.0000	0.0000	0.0000	0.0000	0.0000
CH+DEG				
0.0000	0.0000	0.0000	0.0000	0.0000
0.0883	−4.4157	−2.0513	−1.6343	−0.3757
0.1789	−7.8154	−3.6538	−3.0711	−0.7008
0.2719	−10.3665	−4.8223	−4.2589	−0.9616
0.3674	−11.7342	−5.5196	−5.1690	−1.1583
0.4656	−12.3822	−5.7873	−5.7084	−1.2636
0.5665	−12.2720	−5.6146	−5.8001	−1.2632
0.6703	−10.6630	−4.9294	−5.4219	−1.1687
0.7770	−8.6121	−3.8186	−4.3602	−0.9182
0.8869	−4.7738	−2.1619	−2.6305	−0.5470
1.0000	0.0000	0.0000	0.0000	0.0000
CH+TEG				
0.0000	0.0000	0.0000	0.0000	0.0000
0.1199	7.4532	0.4982	−3.4681	−1.1486
0.2346	12.8692	0.8128	−6.3125	−2.0622
0.3444	16.5708	0.9925	−8.5110	−2.7421
0.4497	18.5708	1.0518	−10.0154	−3.1796
0.5507	18.9727	1.0138	−10.7696	−3.3661
0.6477	17.7718	0.8908	−10.6937	−3.2865
0.7409	15.5558	0.7470	−9.7448	−2.9460
0.8306	11.4061	0.5129	−7.7132	−2.2866
0.9169	6.4977	0.2995	−4.5748	−1.3326
1.0000	0.0000	0.0000	0.0000	0.0000
CH+PEG-200				
0.0000	0.0000	0.0000	0.0000	0.0000
0.1536	19.5801	3.3115	−5.1784	−1.8858
0.2899	32.1048	5.3639	−9.0643	−3.2480
0.4117	39.7563	6.5127	−11.8158	−4.1700
0.5212	43.2186	6.9246	−13.4907	−4.6871
0.6202	42.6247	6.6956	−14.0802	−4.8090

(Contd...)

Table 3: *(Continued)*.

Mole fraction (X_{CH})	$_{u}^{E}$ (m/s)	Z^E10^{-4} (kg m^{-2}/s)	$K_S^E\times10^{11}$ (m^2/N)	$L_f^E\times10^{12}$ (m)
0.7101	39.3916	6.0286	−13.6526	−4.5842
0.7921	33.2454	4.9541	−12.1232	−3.9973
0.8672	23.9409	3.5044	−9.3576	−3.0220
0.9363	12.7753	1.8349	−5.3574	−1.6929
1.0000	0.0000	0.0000	0.0000	0.0000
CH+PEG-400				
0.0000	0.0000	0.0000	0.0000	0.0000
0.2660	64.0093	12.9424	−11.4612	−4.5800
0.4492	94.7491	18.9557	−18.0087	−7.0751
0.5829	108.5610	21.2537	−21.5936	−8.3503
0.6850	109.1874	21.0166	−22.9419	−8.7163
0.7653	101.5084	19.2084	−22.5838	−8.4214
0.8303	88.4146	16.4039	−20.8131	−7.6117
0.8839	70.4597	12.8552	−17.6614	−6.3249
0.9288	49.1969	8.8423	−13.1875	−4.6185
0.9671	25.3656	4.5292	−7.3386	−2.5098
1.0000	0.0000	0.0000	0.0000	0.0000
CH+PEG-600				
0.0000	0.0000	0.0000	0.0000	0.0000
0.3521	140.2677	24.8870	−18.2150	−7.7074
0.5501	177.2431	32.0014	−25.8883	−10.6577
0.6770	183.2842	33.0726	−29.1208	−11.7253
0.7653	174.8313	31.1088	−29.7559	−11.7326
0.8302	156.7226	27.4440	−28.5212	−11.0084
0.8800	131.8384	22.7228	−25.7176	−9.7056
0.9194	102.6457	17.3724	−21.4903	−7.9195
0.9514	70.3675	11.6825	−15.8521	−5.6959
0.9778	36.3038	5.8891	−8.7918	−3.0765
1.0000	0.0000	0.0000	0.0000	0.0000

CH: Cyclohexane, DEG: Diethylene glycol, TEG: Triethylene glycol, PEG-200: Polyethylene glycol-200, PEG: Polyethylene glycol-400, PEG-600: Polyethylene glycol-600

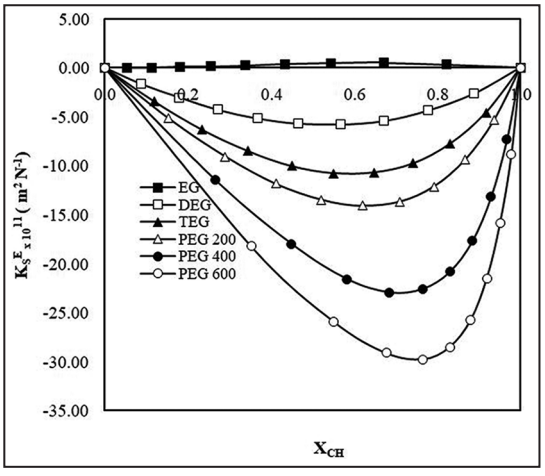

Figure 3: Plots of excess isentropic compressibility (K_S^E) vs. mole fraction of cyclohexane (X_{CH}) for binary mixtures of cyclohexane with glycols and polyglycols at 308.15 K.

breaking up of hydrogen bonding [29], and difference in size and shapes of the component molecules and (ii) decrease in free-length as a result of dipole-dipole interactions, hydrogen bonding association [29] and complex formation between the component molecules [33].

The first effect contributes to an increase in interspace between molecules in mixtures, consequently sound waves cover smaller distances in mixtures than in pure components. This would result in a negative deviation in ultrasonic velocity and positive deviation in isentropic compressibility. The second effect contributes to a decrease in inter-space between molecules in mixtures consequently sound waves cover larger distances in mixtures than in pure components. This would result in positive deviation in ultrasonic velocity and negative deviation in isentropic compressibility. The actual values of K_S^E would depend on the balance between these two opposing effects. The experimental values indicate that the negative contributions predominate in these mixtures.

The behavior of K_S^E and L_f^E with the composition of the mixture can be qualitatively examined by considering the nature of the component molecules in the pure state and the mixture. The molecules of CH are

Table 4: The coefficients of a_i of the Redlich–Kister type polynomial equation (6) and the corresponding standard deviation σ (V^E) for the binary mixtures of cyclohexane with glycols and polyglycols at 308.15 K.

Redlich–Kister equation by the least-squares method						
Excess property	**A_0**	**A_1**	**A_2**	**A_3**	**A_4**	**σ**
CH+EG						
u^E (m/s)	−0.1408	−398.0641	711.3079	−443.3607	130.3475	0.3991
Z^E×10−4 (kg m^{-2}/s)	−0.0613	−108.0424	208.0972	−144.2515	44.2723	0.0803
K_S^E×1011 (m^2/N)	0.0025	−0.6149	6.7983	−9.1839	2.9919	0.0283
L_f^E×1012 (m)	0.9997	7.1542	−8.7122	1.5075	0.0470	0.0121
CH + DEG						
u^E (m/s)	−0.0087	−56.2435	75.5004	−31.6993	12.4839	0.1333
Z^E×10−4 (kg m^{-2}/s)	−0.0345	−26.0839	33.2256	−9.5279	2.3883	0.0109
K_S^E×1011 (m^2/N)	−0.0049	−19.6887	13.0687	5.9100	0.7086	0.0128
L_f^E×1012 (m)	−0.0024	−4.5448	3.2491	1.6526	−0.3573	0.0052
CH+TEG						
u^E (m/s)	0.0014	69.2599	−59.9452	−2.0250	−7.2687	0.1079
Z^E×10−4 (kg m^{-2}/s)	−0.0012	4.9508	−6.7066	2.1006	−0.3365	0.0123
K_S^E×1011 (m^2/N)	0.0158	−32.0352	23.7118	−14.6724	22.9484	0.0402
×1012 (m)	0.0030	−10.5579	7.6282	−1.8289	4.7488	0.0092
CH+PEG-200						
u^E (m/s)	0.0254	145.0332	−124.2024	41.1496	−62.1272	0.1923
Z^E×10^{-4} (kg m^{-2}/s)	0.0048	24.5303	19.9428	−1.7318	−2.8769	0.0212
K_S^E×1011 (m^2/N)	0.0316	−39.8859	42.1939	−58.8521	56.4315	0.0982
L_f^E×Z1012 (m)	0.0062	−14.1450	12.6614	12.7069	14.1705	0.0194
CH+PEG-400						
u^E (m/s^{-1})	−0.0739	338.4864	−543.4408	867.2167	−661.2331	0.9313
Z^E×10^{-4} (kg m^{-2}/s)	−0.0091	63.8185	−77.7968	106.6453	−92.5341	0.1113
K_S^E×1011 (m^2/N)	0.0603	−80.8267	226.5993	−416.4797	269.8056	0.7134
L_f^E×1012 (m)	0.0167	−28.9598	69.5491	−125.2620	84.4291	0.1962
CH+PEG-600						
u^E (m/s)	−0.1035	916.1785	−2544.0092	3870.0640	−2238.3896	0.1863
Z^E×10^{-4} (kg m^{-2}/s)	−0.0120	139.9691	−337.1559	513.9329	−316.3254	0.3667
K_S^E×1011 (m^2/N)	0.0441	−174.9176	655.7436	−1099.9852	617.2252	0.4672
L_f^E×1012 (m)	0.0134	−63.8084	220.7386	−366.7192	209.2272	0.4369

CH: Cyclohexane, DEG: Diethylene glycol, TEG: Triethylene glycol, PEG-200: Polyethylene glycol-200, PEG: Polyethylene glycol-400, PEG-600: Polyethylene glycol-600

non-polar [34] and those of the glycols and polyglycols EG, DEG, TEG, PEG-200, PEG-400, and PEG-600) have large quadrupole moment [35], which causes molecular order in the pure state because of this polar nature.CH on mixing with the gylcols, would induce a decrease in the molecular order in the latter, resulting in an expansion in volume, and hence, may lead to positive K_S^E and L_f^E values. On the other hand, (L_f^E) versus mole fraction of cyclohexane (X_{CH}) for binary mixtures of cyclohexane (CH) with EG there is the possibility of the charge-transfer type of interactions [32,36] between highly electronegative etheric oxygen and –OH groups of glycols and polyglycols (acting as proton acceptor) and H atom of CH molecules (acting as proton donars), resulting in negative K_S^E and L_f^E values.

Thus the observed negative K_S^E and L_f^E values suggest the presence of significant donor-acceptor interactions between CH and glycols & polyglycols –O- and –OH- group molecules in these mixtures. Recently, Yang *et al*. [37], reported a similar type of donor-acceptor interaction between the oxygen atom of sulfolane and ϖ-electrons of the aromatic hydrocarbons (B, MB, EB, o-xylene, m-xylene, and p-xylene) and Ali *et al*. [38], also reported similar interactions between the oxygen atom of dimethyl sulfoxide and ϖ-electrons of the aromatic hydrocarbons (B, MB, EB, o-xylene, m-xylene, p-xylene, and mesitylene) from their physicochemical studies of binary liquid mixtures.

It is observed that K_S^E and L_f^E becomes more negative (Figures 3 and 4) as the number of metheric oxygen and OH groups in the glycols and polyglycols.

This would be responsible for more negative sequence, CH + EG < + DEG < + TEG < + PEG-200 < + PEG- 400 < + PEG-600.

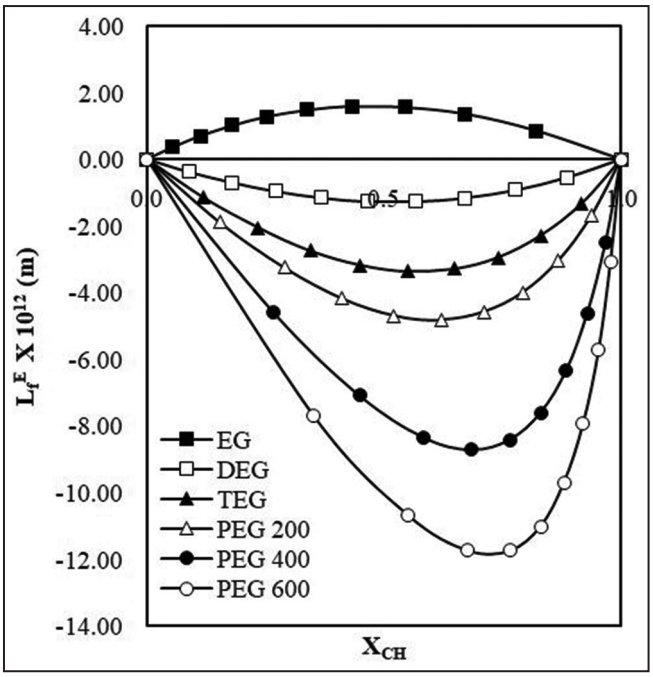

Figure 4: Plots of excess Free length (L_f^E) versus mole fraction of cyclohexane (X_{CH}) for the binary mixtures from the above order it is evident that the molecular interactions increase with increase in chain length of glycols and polyglycols from EG to PEG-600. The order of increase of interactions from EG to PEG is due to the more hydrogen bond formation between electron-rich oxygen atom of etheric oxygen of PEGs and the hydrogen atom of cyclohexane molecules. A similar observation was reported by Ali *et al*. [39] from their ultrasonic velocity studies on DME + Octonal mixtures.

4. CONCLUSION

One of the powerful probes for characterizing the physicochemical properties of liquid mixtures is using sound velocities and is also confirmed by the derived properties of excess acoustical parameters. The interactions and their order of intensity in the binary liquid mixtures depend on the nature of the solvent. This may be attributed to the fact that as molecular weights of glycols increase the ability of hydrogen bond formation that takes place due to the increase in the chain length of glycols and polyglycols which are mainly responsible for molecular interactions with cyclohexane. A similar observation was made by Pal and Das [21] from their ultrasonic velocity studies for the binary liquid mixtures. It is observed from Figures 3 and 4 which show that K_S^E and L_f^E are positive for the system CH + EG and negative for CH + DEG, CH + TEG, CH + PEG-200, PEG - 400, and CH+PEG-600 over the entire composition range. The curves obtained for the systems K_S^E and L_f^E reveals that the structural effects are predominant in these mixtures over the effect of complex formation between unlike molecules. Negative K_S^E and L_f^E values may be attributed due to the increase in the donor-acceptor interaction between the unlike molecules.

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