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Excess compressibility and excess volume studies in the binary mixtures of methyl and ethyl acetate in O-chlorophenol at different temperatures

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Ultrasonic velocity and density measurements have been carried out in the binary mixtures of methyl acetate (MA) and ethyl acetate (EA) in O-chlorophenol (OCP) at 303.15, 308.15, 313.15, 318.15 and 323.15 K. From the experimental data, the excess thermodynamical parameters such as excess adiabatic compressibility (β_S^E), excess intermolecular free length (L_f^E) and excess molar volume (V^E) have been calculated. The results have been interpreted in terms of intermolecular interactions leading to complex formation through the formation of hydrogen bonds between the component molecules of the mixture.

Keywords: Ultrasonic velocity, Excess adiabatic compressibility, Excess freelength, Excess molar volume, Complex formation, Hydrogen bond

1 Introduction

Ultrasonic technique has been considered to be one of the most useful tools for understanding the molecular behavior of liquid mixtures. This is mainly because of its ability to characterize physico-chemical behavior of liquid medium. It has been a long time since; ultrasonic studies have been employed to investigate the nature of molecular interactions in pure liquids and liquid mixtures[1-7]. Measurements of ultrasonic velocity and density of liquid mixtures have been used to calculate various other parameters which can be used to understand different types of molecular interactions present in liquid mixtures. The non-linear behavior of ultrasonic velocity, compressibility and other thermodynamic parameters of liquid mixtures reveal the strength of molecular interactions. Additional information regarding the nature and strength of molecular interactions can also be derived from excess thermodynamical functions such as excess compressibility (β_S^E), excess free length (L_f^E) and excess molar volume[8-10] (V^E). This is because, the deviation of excess thermodynamical functions with composition from its ideal behaviour gives a deep insight into the various molecular processes[11-14] taking place in the mixture. In recent years, a number of studies on the thermodynamical properties of multi-component liquid mixtures[15-22] have been reported in the literature due to their diversified applications in industry and theoretical interest in studying the nature of molecular interactions and packing phenomena in these mixtures.

In the present work, an attempt has been made to investigate the behavior of binary mixtures of methyl acetate (MA) and ethyl acetate (EA) in o-chlorophenol (OCP) using excess thermodynamic functions such as excess adiabatic compressibility (β_S^E), excess intermolecular free length (L_f^E) and excess molar volume (V^E) at different temperatures. The variation of these excess parameters with composition and temperature is useful in understanding the nature and extend of interaction between unlike molecules in these liquid mixtures.

2 Materials and Methods

The chemicals used in the present work are spectroscopic (SR) grade with a minimum assay of 99.9%. These chemicals were purchased from SD Fine chemicals, India and were used as such without further purification. In all systems, the various concentrations of the binary liquid mixtures were prepared in terms of mole fraction. The density values of pure liquids and their liquid mixtures are

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determined using a specific gravity bottle by relative measurement method with a reproducibility of ±0.01 kgm^{-3} at 303.15, 308.15, 313.15, 318.15 and 323.15 K, respectively.

The ultrasonic velocity of the liquid mixtures has been measured using an ultrasonic interferometer (Model F81) supplied by Mittal Enterprises, New Delhi at an RF frequency of 2 MHz with an accuracy of ±0.1 ms^{-1} at different temperatures. The temperature was controlled by circulating water around the liquid cell from a thermostatically controlled water bath (accuracy ±0.1 °C).

Using the measured values of ultrasonic velocity and density, various excess thermodynamical parameters such as excess adiabatic compressibility (β_S^E), excess free length (L_f^E) and excess molar volume (V^E) have been calculated using the equations:

$$\beta_S^E = \beta_{S12} - \beta_{cal} \quad \ldots (1)$$

where

$$(\beta_S)_{cal} = X_1\beta s_1 + X_2\beta s_2$$

$$L_f^E = L_{f12} - (L_f)_{cal} \quad \ldots (2)$$

where

$$(L_f)_{cal} = X_1 L_{f1} + X_2 L_{f2}$$

$$V^E = V_{obs} - V_{cal} \quad \ldots (3)$$

where

$$V_{obs} = \left[\frac{X_1M_1 + X_2M_2}{\rho_{12}}\right]$$

$$V_{cal} = \left[\frac{X_1M_1}{\rho_1} + \frac{X_2M_2}{\rho_2}\right]$$

where M_1, M_2, X_1, X_2, ρ_1, ρ_2, ρ_{12}, βs_1, βs_2, βs_{12}, L_{f1}, L_{f2}, L_{f12} are the molecular weight, mole fraction, density, adiabatic compressibility and intermolecular free length of the components 1 and 2 and their mixtures, respectively.

All the excess thermo-dynamical parameters were fitted to Redlich-Kister type equation:

$$Y^E = X_1 X_2 \sum_{j=1}^{N} A_{j-1}(2X_1 - 1)^{j-1} \quad \ldots (4)$$

and the parameters A_{j-1} were computed using least square fit method.

3 Results and Discussion

The ultrasonic velocity measurements are carried out in the binary mixtures of methyl acetate-orthochlorophenol (MA-OCP) and ethyl acetate-orthochloro phenol (EA-OCP) at different temperatures. The experiment was carried out in the composition range of X_1=0 to 1 mole fraction of methyl and ethyl acetates. The density values of pure methyl acetate, ethyl acetate and O-chlorophenol are given in Table 1.

Using the measured values of ultrasonic velocity and density, various excess thermodynamical parameters such as excess adiabatic compressibility (β_S^E), excess freelength (L_f^E) and excess molar volume (V^E) for the binary mixtures of MA-OCP and EA-OCP are calculated and are presented in Tables 2-5. The constants of Eq. (4), viz., A_0 to A_3

Table 1 — Density values of the pure liquids of O-chlorophenol, methyl acetate and ethyl acetate at 298.15 K

Liquids	Density (g cm^{-3})
O-chlorophenol	1.2573
Methyl acetate	0.9342
Ethyl acetate	0.9006

Table 2 — Ultrasonic velocity (U) and density (ρ) of MA-OCP system at temperatures between 303.15 and 313.15 K

X_1 Mole fraction	Velocity (U) (ms^{-1})			Density (ρ) (kg m^{-3})		
	303.15 K	308.15 K	313.15 K	303.15 K	308.15 K	313.15 K
0.0000	1398.30	1381.20	1370.60	1253.10	1237.10	1213.20
0.1250	1379.44	1367.32	1351.13	1227.52	1210.31	1187.44
0.2440	1366.15	1344.42	1330.25	1202.14	1189.33	1166.53
0.3560	1350.11	1326.54	1307.76	1174.13	1157.52	1134.42
0.4618	1324.73	1301.25	1288.43	1144.12	1125.62	1103.12
0.5628	1293.22	1269.35	1256.34	1112.63	1097.22	1074.73
0.6587	1260.46	1239.35	1223.12	1076.35	1059.45	1037.64
0.7504	1229.23	1214.63	1190.43	1042.54	1024.51	1002.72
0.8372	1197.88	1174.55	1151.12	1007.72	0987.67	0966.93
0.9209	1164.43	1143.83	1121.57	0970.24	0947.86	0928.82
1.0000	1124.50	1101.50	1078.50	0929.20	0904.20	0882.60

X_1-Mole fraction of methyl acetate

Table 3 — Excess thermodynamical functions such as excess compressibility (β_S^E), excess free length (L_f^E) and excess molar volume (V^E) of MA-OCP system at temperatures between 303.15 and 313.15 K

X_1 Mole fraction	Excess compressibility (β_S^E) 10^{-10} m^2N^{-1}			Excess free length (L_f^E) 10^{-12} m			Excess molar volume (V^E) 10^{-6} m^3mol^{-1}		
	303.15 K	308.15 K	313.15 K	303.15 K	308.15 K	313.15 K	303.15 K	308.15 K	313.15 K
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1250	-0.3539	-0.4275	-0.4438	-1.3134	-1.5980	-1.5885	-0.5512	-0.5774	-0.6819
0.2440	-0.7051	-0.7755	-0.8495	-2.6559	-2.8491	-3.0455	-1.1287	-1.6370	-1.7796
0.3560	-0.9858	-1.0643	-1.1391	-3.6949	-3.8689	-4.0097	-1.4768	-1.7819	-1.8937
0.4618	-1.1464	-1.2431	-1.3990	-4.2095	-4.4300	-4.8985	-1.6565	-1.9032	-2.0572
0.5628	-1.2002	-1.3240	-1.5054	-4.2946	-4.6151	-5.1631	-1.7343	-2.3192	-2.4756
0.6587	-1.1513	-1.3052	-1.4719	-4.0046	-4.4465	-4.9159	-1.4294	-1.9608	-2.1416
0.7504	-1.0572	-1.2816	-1.3673	-3.6089	-4.3392	-4.4806	-1.3320	-1.8372	-1.9931
0.8372	-0.8740	-0.9819	-1.0645	-2.9373	-3.2197	-3.3857	-1.1337	-1.5241	-1.7346
0.9209	-0.5590	-0.6656	-0.7585	-1.8535	-2.1673	-2.4151	-0.7396	-0.9668	-1.2799
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

X_1-Mole fraction of methyl acetate

Table 4 — Ultrasonic velocity (U) and density (ρ) of EA-OCP system at temperatures between 303.15 and 323.15 K

X_1 Mole fraction	Velocity (U) (m s^{-1})					Density (ρ) (kg m^{-3})				
	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K	303.15K	308.15 K	313.15 K	318.15 K	323.15 K
0.0000	1398.50	1385.30	1370.30	1349.40	1336.60	1253.10	1232.60	1213.40	1208.40	1203.70
0.1040	1370.23	1358.51	1344.12	1324.63	1307.11	1223.63	1203.31	1187.42	1183.63	1178.12
0.2070	1356.01	1338.76	1323.31	1305.25	1288.45	1194.67	1179.34	1160.54	1156.35	1151.23
0.3090	1345.11	1325.57	1309.56	1295.15	1275.56	1162.24	1145.52	1127.13	1123.01	1117.74
0.4120	1324.83	1307.11	1285.54	1264.86	1246.81	1128.17	1109.86	1091.31	1087.75	1082.54
0.5110	1294.35	1276.23	1255.43	1236.45	1218.53	1093.33	1079.84	1060.83	1057.22	1051.52
0.6100	1263.11	1243.41	1230.62	1210.34	1188.23	1054.12	1041.01	1026.15	1022.76	1017.01
0.7090	1220.65	1206.01	1179.15	1164.94	1147.61	1016.61	1003.42	0985.31	0982.21	0976.51
0.8070	1190.45	1170.32	1147.31	1130.39	1110.97	0978.13	0964.63	0946.85	0943.55	0938.43
0.9040	1152.21	1132.81	1115.78	1093.81	1073.56	0938.91	0924.11	0908.24	0904.91	0899.85
1.0000	1117.40	1094.30	1073.10	1050.60	1029.10	0896.40	0880.20	0862.40	0858.90	0854.30

X_1-Mole fraction of ethyl acetate

computed for β_S^E, L_f^E and V^E determined by least square fit method along with the standard deviations σ are given in Tables 6 and 7. The variation of excess adiabatic compressibility (β_S^E), excess freelength (L_f^E) and excess molar volume (V^E) with increasing concentration of methyl and ethyl acetates (X_1 = 0 to 1 mole fraction) are shown in Figs 1-6.

3.1 Methyl acetate – Ortho chlorophenol system (MA-OCP)

The variation of excess adiabatic compressibility with increasing mole fraction of MA at 303.15, 308.15 and 313.15 K is shown in Fig. 1. Figure 1 shows that the excess adiabatic compressibility at 303.15 K has a negative deviation for the entire concentration range of methyl acetate. The magnitude of negative deviation reaches a maximum at X_1= 0.5628 mole fraction of MA and then becoming less and less negative with further increase in concentration of MA in OCP. The excess free length and excess molar volume also exhibits a similar behaviour as that of excess adiabatic compressibility at 303.15 K. Negative deviation of β_S^E, L_f^E and V^E at 303.15 K has been observed from the ideal behaviour.

Generally, liquid mixtures which show non-linearity in ultrasonic velocity with concentration are analyzed in terms of excess thermodynamical parameters. This is due to the fact that the excess thermodynamical functions are found to be sensitive

Table 5 — Excess thermodynamical functions such as excess compressibility(β_S^E), excess free length(L_f^E) and excess molar volume (V^E) of EA-OCP system at temperatures between 303.15 and 323.15 K

X_1 Mole fraction	Excess compressibility (β_S^E) 10^{-10} m^2N^{-1}					Excess free length (L_f^E) 10^{-12} m					Excess molar volume (V^E) 10^{-6} m^3mol^{-1}				
	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0.1040	-0.2323	-0.2716	-0.3189	-0.3254	-0.3481	-0.7147	-0.8501	-1.0195	-1.1424	-1.0542	-0.5198	-0.5206	-0.8470	-0.9321	-0.8704
0.2070	-0.5328	-0.5853	-0.6448	-0.7114	-0.7432	-1.8052	-1.9475	-2.1148	-2.3416	-2.3829	-1.1008	-1.5206	-1.6200	-1.6648	-1.6463
0.3090	-0.8248	-0.8847	-0.9714	-1.0912	-1.1300	-2.8795	-3.0076	-3.2494	-3.6804	-3.7092	-1.4050	-1.6855	-1.8233	-1.8651	-1.8355
0.4120	-1.0301	-1.1210	-1.1850	-1.2713	-1.3458	-3.5697	-3.8028	-3.9008	-4.1459	-4.3017	-1.6394	-1.7517	-1.8700	-1.9534	-1.9302
0.5110	-1.1014	-1.2296	-1.3112	-1.4255	-1.5171	-3.7080	-4.0823	-4.2360	-4.5776	-4.7866	-1.7158	-2.2418	-2.3228	-2.3941	-2.3263
0.6100	-1.0954	-1.2228	-1.4195	-1.5325	-1.5916	-3.5842	-3.9402	-4.5660	-4.8839	-4.9467	-1.4184	-1.9463	-2.4119	-2.4945	-2.4192
0.7090	-0.9202	-1.1048	-1.1173	-1.2990	-1.4141	-2.8576	-3.4457	-3.3340	-3.9235	-4.2188	-1.2955	-1.7832	-1.9038	-2.0016	-1.9205
0.8070	-0.7837	-0.9033	-0.9500	-1.0953	-1.1835	-2.4107	-2.7510	-2.8024	-3.2499	-3.4586	-1.0616	-1.4785	-1.6006	-1.6635	-1.6348
0.9040	-0.4461	-0.5498	-0.6804	-0.7353	-0.7960	-1.3211	-1.6325	-2.0262	-2.1639	-2.3064	-0.7272	-0.9573	-1.2457	-1.2898	-1.2573
1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

X_1-Mole fraction of ethyl acetate

Table 6 — The constants of Redlich-Kister type equation computed for β_S^E, L_f^E and V^E determined by least square fit method along with the standard deviations (σ) for MA-OCP system at temperatures between 303.15 and 313.15 K coefficients × 10^{10} of Eq. (4) for excess adiabatic compressibility (β_S^E) in m^2N^{-1}

Temperature (K)	A_0	A_1	A_2	A_3	σ 10^{-10} m^2N^{-1}
303.15	- 4.6317	- 1.0931	- 0.7704	-2.5292	0.0917
308.15	- 5.0651	- 1.7307	- 1.6773	-2.0701	0.2471
313.15	- 5.6238	- 1.6856	- 1.6005	-3.1447	0.3820
Coefficients × 10^{12} of Eq. (4) for excess free length (L_f^E) in m					
Temperature (K)	A_0	A_1	A_2	A_3	σ 10^{-12} m
303.15	- 16.8686	- 2.0097	- 1.1134	-9.8987	0.3012
308.15	-17.9192	- 4.4720	- 4.7273	-6.7925	0.9218
313.15	-19.4880	-3.9689	-3.7356	-10.7139	1.3801
Coefficients × 10^6 of Eq. (4) for excess molar volume (V^E) in m^3mol^{-1}					
Temperature (K)	A_0	A_1	A_2	A_3	σ 10^{-6} m^3mol^{-1}
303.15	-6.5639	0.4524	-0.7520	-5.6337	0.2998
308.15	-8.5621	-0.1746	-0.5432	-7.1747	0.8462
313.15	-8.9494	0.7745	-3.1021	-11.3254	0.9190

towards the mutual interactions between the component molecules of the liquid mixture. In ideal mixtures, the physical property of the mixture may be evaluated as a sum of fractional contribution from the individual components. But, non-ideal mixtures show considerable deviation from linearity in their physical property with respect to concentration and these have been interpreted as arising due to strong or weak interactions. The sign and the extent of deviation of these functions from ideality depend on the nature of constituents and composition of the mixtures[23,24].

Excess adiabatic compressibility at 303.15 K shows a negative deviation for the entire composition range of methyl acetate. The deviation becomes

Table 7 — The constants of Redlich-Kister type equation computed for β_S^E, L_f^E and V^E determined by least square fit method along with the standard deviations (σ) for EA-OCP system at temperatures between 303.15 and 323.15 K coefficients × 10^{10} of Eq. (4) for excess adiabatic compressibility (β_S^E) in m^2N^{-1}

Temperature (K)	A_0	A_1	A_2	A_3	σ 10^{-10} m^2N^{-1}
303.15	- 4.3864	-0.8227	0.9230	-1.3904	0.1303
308.15	- 4.8359	-1.3783	0.4269	-1.2180	0.0628
313.15	-5.1146	-0.9807	-0.4011	-2.6661	0.4000
318.15	-5.6771	-1.4043	-0.2568	-2.5863	0.2523
323.15	-5.9789	-1.7272	-0.5094	-2.5318	0.1958
Coefficients × 10^{12} of Eq. (4) for excess freelength (L_f^E) in m					
Temperature (K)	A_0	A_1	A_2	A_3	σ 10^{-12} m
303.15	-14.8598	-0.6488	5.4373	-6.7818	0.5266
308.15	-16.0847	-2.7196	3.6510	-5.4048	0.2448
313.15	-16.5767	-1.0813	0.5832	-10.0741	1.5247
318.15	-18.2622	-2.6708	0.3665	-8.0303	1.0431
323.15	-18.9678	-3.2394	0.77083	-9.6404	0.7087
Coefficients × 10^6 of Eq. (4) for excess molar volume (V^E) in m^3mol^{-1}					
Temperature (K)	A_0	A_1	A_2	A_3	σ 10^{-6} m^3mol^{-1}
303.15	-6.4710	1.6454	-0.6239	-5.2380	0.2711
308.15	-8.3097	0.7946	-0.4655	-6.0502	0.9949
313.15	-8.6231	-0.0113	-4.3879	-4.3572	1.0254
318.15	-8.8762	-0.4483	-5.0093	-3.2844	1.0114
323.15	-8.7041	0.0154	-4.5852	-4.3232	0.9600

increasingly negative with increasing strength of interaction between the components of liquid mixture. The greater negative deviation of β_S^E for MA-OCP system suggests that a specific molecular interaction is likely to operate between OCP and MA molecules leading to the formation of a complex. In MA-OCP system, OCP is a highly associated liquid and MA is highly polar and also a proton acceptor. Hence, in the present binary mixture MA-OCP, the specific interaction responsible for association is likely to be through hydrogen bonding, dipole-dipole interactions or formation of complexes due to charge transfer. In MA-OCP system, the complex formation may be through hydrogen bonding between OCP and MA molecules. From the structure of the molecules of the constituents, it can be inferred that the oxygen atom of carbonyl group (C=O) of MA may be involved in O-H---O bonding with the hydroxyl group (OH) of OCP molecule. This study is supported by the ultrasonic studies carried in the binary mixtures of dimethylsulphoxide-acetone carried out by Syal *et al.*[25] and in some monohydric alcohols+dimethylsulphoxide systems carried out by Palani *et al.*[20].

L_f^E at 303.15 K also shows negative deviation for the entire composition range of MA showing maximum negative deviation at X_1 =0.5628 mole fraction of MA (Fig. 2). The negative deviation in L_f^E indicates that ultrasonic waves cover a longer distance due to decrease in intermolecular free length describing the dominant nature of hydrogen bonding between unlike molecules of the binary mixture. A similar type of studies was reported by Rajagopal and Chenthilnath[26] in the binary mixtures of 2- methyl-2 propanol in acetophenone where hydrogen bonding between oxygen atom of acetophenone and the hydrogen of 2 methyl-2 propanol leads to a negative deviation in L_f^E.

The excess molar volume (V^E) for MA-OCP system also shows a negative deviation for the entire composition range of MA with the maximum negative deviation occurring at X_1= 0.5628 mole fraction

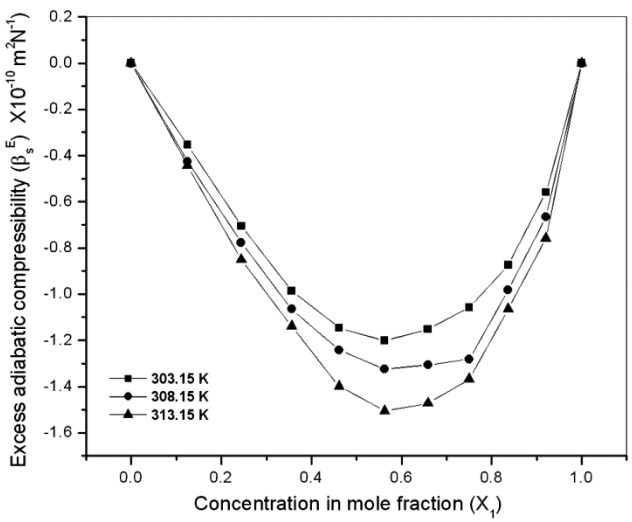

Fig. 1 — Variation of excess adiabatic compressibility (β_S^E) with concentration in mole fraction (X_1) for MA-OCP system at temperatures between 303.15 and 313.15 K (303.15 K: ■, 308.15 K: ● and 313.15 K: ▲).

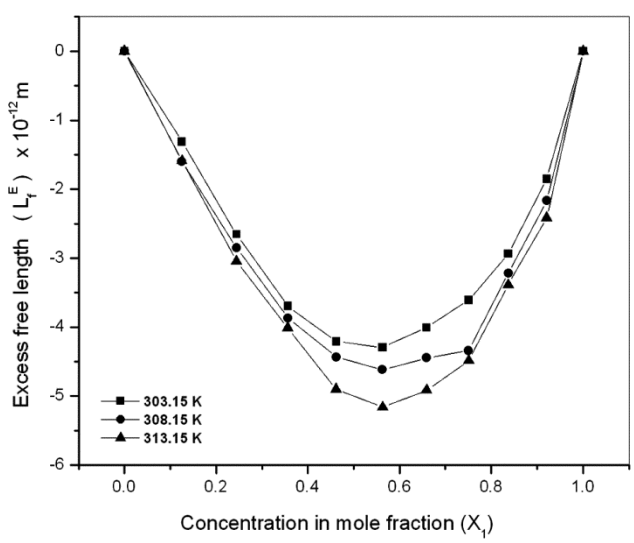

Fig. 2 — Variation of excess free length (L_f^E) with concentration in mole fraction (X_1) for MA-OCP system at temperatures between 303.15 and 313.15 K (303.15 K: ■, 308.15 K: ● and 313.15 K: ▲).

(Fig. 3). The changes in V^E is influenced by two factors namely:

(i) Loss of dipolar association and differences in size and shape and

(ii) Dipole-dipole, dipole-induced dipole interaction, charge transfer complexation and hydrogen bonding between unlike molecules.

The former effect leads to expansion in volume and the latter contributes a contraction in volume. The actual value of V^E depends on the balance between

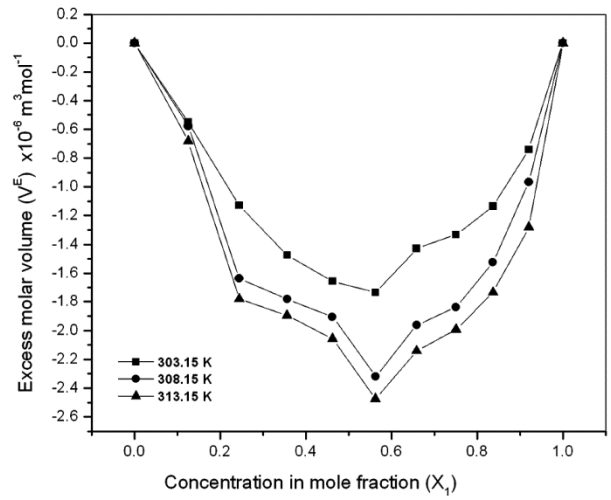

Fig. 3 — Variation of excess molar volume (V^E) with concentration in mole fraction (X_1) for MA-OCP system at temperatures between 303.15 and 313.15 K (303.15 K: ■, 308.15 K: ● and 313.15 K: ▲).

these two opposing contributions[27]. Large negative values of V^E indicate strong interaction between unlike molecules[10]. Such a large negative deviation in V^E is observed in the present MA-OCP system. The greater negative deviation is due to the formation of hydrogen bonding between OCP and MA molecules.

As the temperature is increased to 308.15 K and 313.15 K, the maximum negative deviation of β_S^E, L_f^E and V^E further increases and is more pronounced at 313.15 K compared to their values at 303.15 and 308.15 K, respectively. This indicates that the formation of complexes is more favoured at 313.15 K rather than at 303.15 and 308.15 K, respectively.

At 303.15 K, OCP is self associated through intra-molecular hydrogen bonding. At higher temperature due to thermal agitation, self associated OCP molecules are disrupted, and this facilitates the interaction between OCP and MA molecules through the formation of intermolecular hydrogen bonding. Thus at a higher temperature of 313.15 K, probably the interaction is stronger than at 303.15 K. This supports the conclusion drawn by Chauhan *et al.*[28] in the ultrasonic velocity and viscosity studies of the binary mixture acetonitrile- propylene carbonate between 25 °C and 45 °C. The interaction between acetonitrile and propylene carbonate molecules becoming stronger at 45 °C than at 25 °C.

3.2 Ethyl acetate – Ortho chlorophenol system (EA-OCP)

In EA-OCP system, the variation of excess thermodynamical functions β_S^E, L_f^E and V^E at all

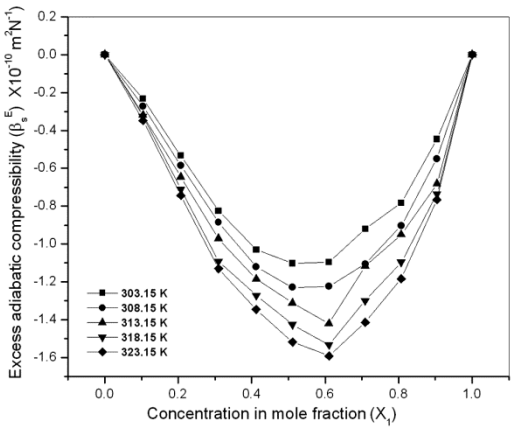

Fig. 4 — Variation of excess adiabatic compressibility (β_S^E) with concentration in mole fraction (X_1) for EA-OCP system at temperatures between 303.15 and 323.15 K (303.15 K: ■, 308.15 K: ● 313.15 K: ▲, 318.15 K: ▼ and 323.15 K: ♦).

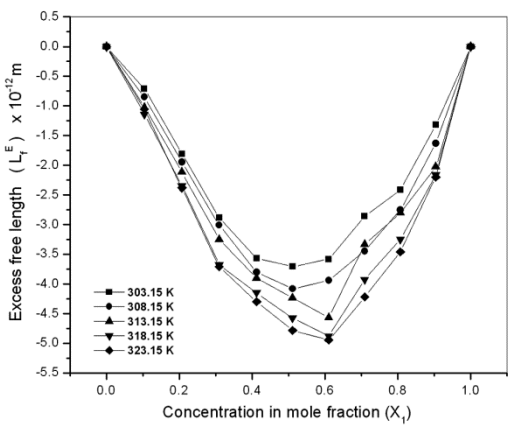

Fig. 5 — Variation of excess free length (L_f^E) with concentration in mole fraction (X_1) for EA-OCP system at temperatures between 303.15 and 323.15 K (303.15 K: ■, 308.15 K: ● , 313.15 K: ▲, 318.15 K: ▼and 323.15 K : ♦).

temperatures studied are shown in Figs 4-6. All these excess parameters show a negative deviation for the entire composition range of EA (X_1=0-1 mole fraction) and for the temperature range studied. The negative deviation of β_S^E and L_f^E increases with increase of temperature showing maximum deviation at 323.15 K but for V^E, the negative deviation increases with temperature showing a maximum deviation at 318.15 K. At 323.15 K the calculated values of negative deviation is found to be less than that at 318.15 K. At 303.15 and 308.15 K, the negative deviation of β_S^E, L_f^E and V^E reach a maximum at X_1= 0.511 mole fraction of EA. But at 313.15, 318.15 and 323.15 K, the negative deviation reach a maximum at a higher concentration of EA

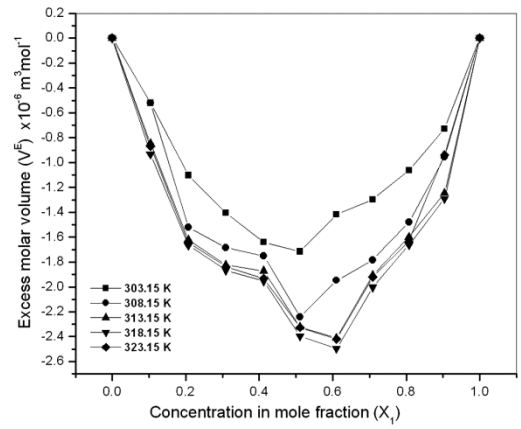

Fig. 6 — Variation of excess molar volume (V^E) with concentration in mole fraction (X_1) for EA-OCP system at temperatures between 303.15 and 323.15 K (303.15 K: ■, 308.15 K: ●, 313.15 K: ▲, 318.15 K: ▼ and 323.15K: ♦).

(X_1=0.610 mole fraction) or at a lower concentration of OCP (X_2 = 0.390 mole fraction).

The negative deviation of β_S^E, L_f^E and V^E observed in EA-OCP system at all the temperatures studied is similar to that in MA-OCP system, so the explanation offered for MA-OCP system is too applicable to EA-OCP system. At 313.15, 318.15 and 323.15 K, the maximum in the negative deviation shifts to a lower composition X_2 = 0.390 mole fraction of OCP. This may be due to the fact that the increase of temperature increases the thermal energy which disrupts the self associated OCP molecules releasing more and more OCP molecules for the formation of intermolecular hydrogen bonding with EA molecules.

The negative deviation of β_S^E increases with the increase of temperature reaching to a maximum at 323.15 K. This indicates that the complex formation is much stronger at this temperature. But the negative deviation of V^E reaches a maximum at 318.15 K. This difference in the behaviour of β_S^E and V^E may be due to the fact that, since β_S^E represents the bulk property of the mixture may be less temperature sensitive compared to V^E. With increase of temperature, the observed molar volume increases which in turn leads to a less negative deviation of V^E at 323.15 K than at 318.15 K. Thus, the increase in observed volume due to increased thermal energy may be dominating over the shrinkage in volume due to complex formation at 323.15 K.

3.3 IR studies

IR spectra are recorded for MA and EA in OCP systems at 303.15 K which are shown in Figs 7 and 8.

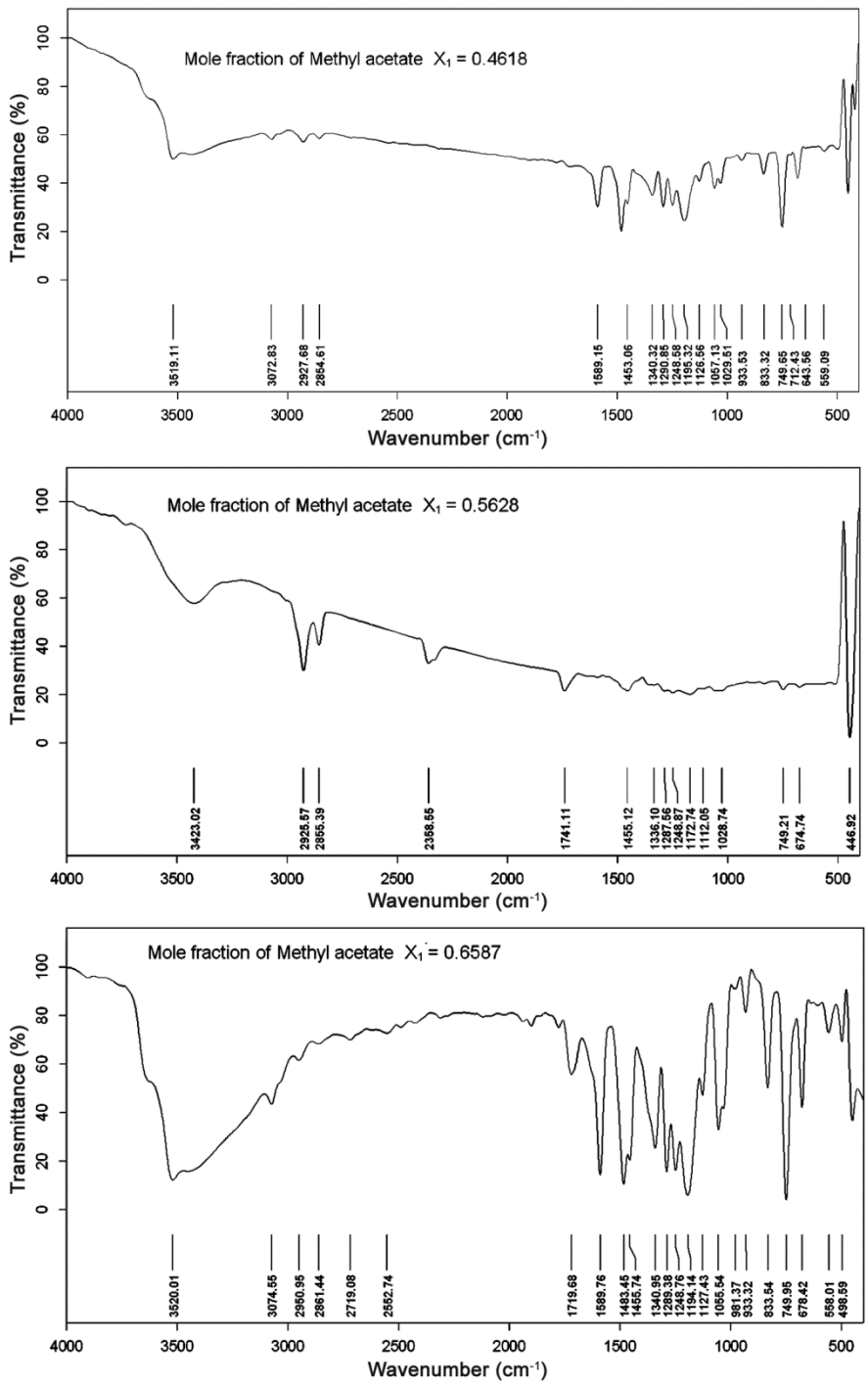

Fig. 7 — IR spectra for MA-OCP system at 303.15 K.

In MA-OCP system, the spectra were recorded at X_1 = 0.4618, 0.5528 and 0.6587 mole fractions of MA. In all the spectra recorded, a broad absorption band centered around 3500 cm^{-1} is observed. This indicates the presence of intermolecular hydrogen bonding between MA and OCP molecules of this system[29].

In MA-OCP system, a broad absorption band is occurs at 3519 cm^{-1}, 3423 cm^{-1} and 3520 cm^{-1}, respectively, corresponding to X_1= 0.4618, 0.5628 and 0.6587 mole fractions of MA. The broad band observed at 3519 cm^{-1} for X_1= 0.4618 mole fraction of MA shifts towards the lower frequency side by 96 cm^{-1},

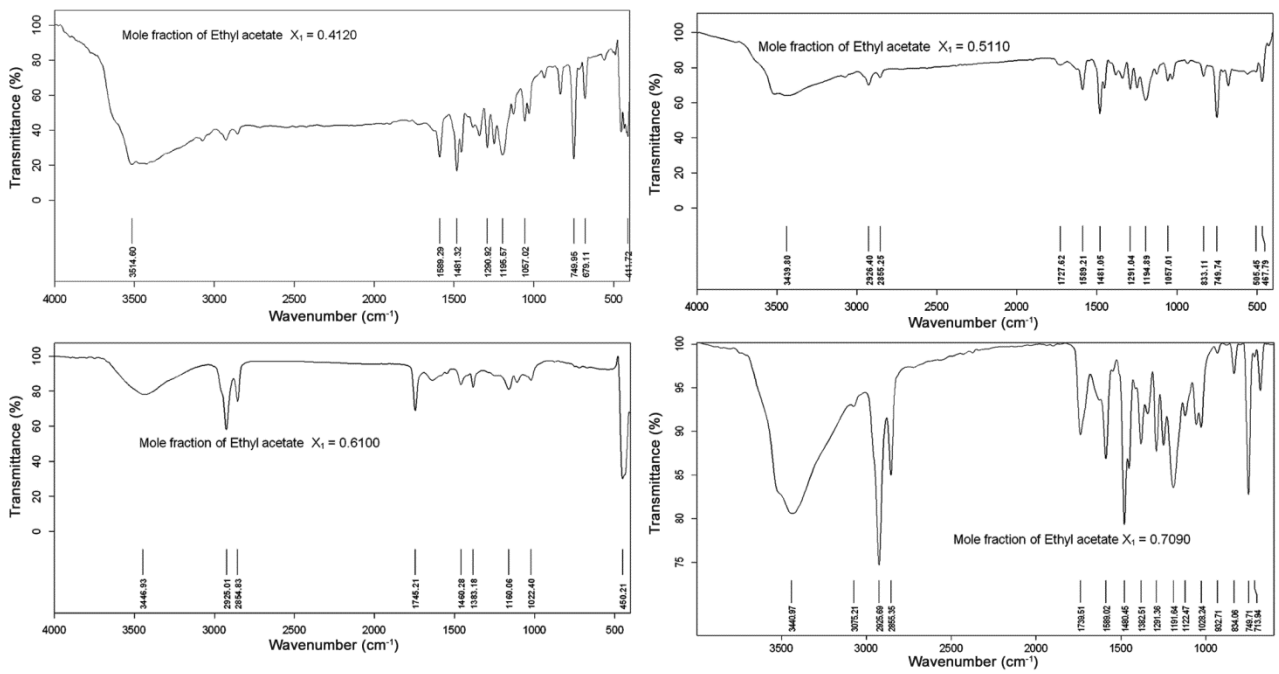

Fig. 8 — IR spectra for EA-OCP system at 303.15 K.

when X_1 is increased to 0.5628 mole fraction. But for X_1 = 0.6587 mole fraction, the broad absorption band shifts towards higher frequency side and occurs at 3520 cm^{-1}. Among the three concentrations of MA, the maximum lower frequency shift is observed at X_1= 0.5628 mole fraction of MA, thus showing that the association through intermolecular hydrogen bonding is stronger at this concentration[29]. This confirms our excess compressibility and excess volume studies carried out in OCP-MA system. The IR spectra recorded for OCP-EA system also exhibit a similar behaviour as that of OCP-MA system. Hence the explanation offered for the IR spectra of OCP-MA systems also holds good for OCP-EA system.

4 Conclusions

The excess thermodynamical functions such as β_S^E, L_f^E and V^E are calculated for the binary mixtures of methyl acetate-orthochloro phenol and ethyl acetate-orthochloro phenol in the temperature range 303.15 K-323.15 K. All these parameters show negative deviation in the composition range X_1= 0-1 mole fraction of methyl acetate and ethyl acetate in O-chlorophenol and at all the temperatures studied. Both the binary mixtures show a maximum negative deviation at 323.15 K indicating that the formation of complexes is much stronger at this temperature. In the binary mixtures studied, the formation of complexes is due to the formation of hydrogen bonds between the oxygen of carbonyl group (C=O) of methyl acetate, ethyl acetate with the hydroxyl group (OH) of O-chlorophenol. The formation of intermolecular hydrogen bonds between the components of liquid mixtures has been confirmed by recording of IR spectra at different compositions.

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