Ultrasonic Studies in the Binary Mixtures of O-Chlorophenol with Salicylates at Different Temperatures

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ABSTRACT

The ultrasonic velocities (U), densities (ρ) and viscosities (η) of Binary mixture O-Chlorophenol +methyl salicylate, +ethyl salicylate and +benzyl salicylate from 303.15 to 318.15K. Excess molar volume (V^E), deviation in adiabatic compressibility ($\Delta\beta_{ad}$) and excess inter molecular free length (L_f^E) have been calculated from the measured experimental data. The values of V^E, $\Delta\beta_{ad}$, L_f^E and $\Delta\eta$ have been fitted to Redlich–Kister polynomial equation to estimate binary coefficients and standard deviation between the experimental and computed values. Using Nomoto's relation (U_{NR}), impedance relation (U_{IR}), ideal mixing relation (U_{imx}), Junjie's relation (U_J), Rao's specific velocity relation (U_R) and Kudriavtsev relation (U_K), the theoretical ultrasonic velocities were evaluated. The computed estimations of ratio in velocity (U^2/U^2_{imx}) from measured estimations of (U) are graphically shown. The molecular interaction parameter (α) has been evaluated. The validity of the theories were checked by calculating standard deviation and chi square test.

Keywords: Ultrasonic velocity, Density, Viscosity, Excess parameters, Theoretical velocities.

INTRODUCTION

Molecular studies lie in the ability to assess the information stored in the structure of the molecule as a function of their physical and chemical properties. There had been many developments in Chemistry and Physics during the past two centuries particularly, in the fields of statistical mechanics, thermodynamics and the nature of the chemical bond. The ensuing atomistic view shall be presented and discussed in the context of molecular interactions. Molecular interactions are generally electrostatic in nature. The strength of these interactions and the forces among atoms can be analyzed according to their thermodynamic and kinetic behaviour[1,2].

Ultrasonic velocities have been adequately employed in understanding the nature of molecular interaction in pure liquids and binary mixtures[3,4]. The

method of studying the molecular interaction from the knowledge of the variation of thermodynamic parameters and their excess values with composition gives an insight into the molecular process[5,6]. The present paper is part of our research work on the thermodynamic properties of liquid-liquid mixtures[7-9]. This paper includes the density and ultrasonic behaviour of binary mixtures of O–chlorophenol with methyl salicylate, ethyl salicylate and benzyl salicylate over the entire composition range at 308.15 K.

As the studied compounds have a plenty of industrial and other applications, the author made an attempt to study the thermodynamic behaviour of the binary mixtures of the compound.

A literature survey[10,11] reveals that molecular interactions in O–chlorophenol with various compounds were studied over the entire range of composition at different temperatures.

Study of molecular interactions for the binary mixtures of salicylates was done by many researchers[12,13].

Keeping these important aspects in mind, the present study deals with the ultrasonic and thermodynamic study of O–chlorophenol (OCP) with higher salicylates (methyl salicylate. Ethyl salicylate and benzyl salicylate) over the entire mole fraction range from 303.15 to 318.15K. The liquids under investigation have been chosen based on their multifold applications. Ultrasonic velocities, densities and viscosities of the studied binary mixtures are measured and using the experimental data, excess molar volume, deviation in adiabatic compressibility, excess inter-molecular free length and deviation in viscosity are reported in this paper. The results have been used to estimate the molecular interactions in the constituent molecules.

Experimental techniques

Ultrasonic velocities(U) and densities (ρ) of pure liquids and all liquid mixtures in the present study were measured by employing a pulse-echo interferometer (MODEL M-81) supplied by the Mittal Enterprises, New Delhi and a 10–5 m^3 double-arm pycnometer respectively at (303.15, 308.15, 313.15 and 318.15)K as described by Nikam *et al.,*[14]. The Double-arm pycnometer is calibrated using conductivity water with 995.61 kgm^{-3} as its density at 303.15 K. To maintain the constant temperature, a thermostat is employed with an accuracy of±0.01K. The weighing is carried out using METTLER TOLEDO (Switzerland make) ABB5-S/F ACT digital balance with an accuracy of ±0.01mg. The viscosity was measured using a commercial Ubbelohde capillary viscometer of 0.55mm diameter calibrated with double distilled water at temperatures of 303.15, 308.15, 313.15 and 318.15K. The experimental samples, O-chlorophenol, salicylates such as methyl salicylate, ethyl salicylate and benzyl salicylate used in the present study are of AR grade quality, obtained from S.D. Fine chemicals, India with purity>99%. Experimental values are compared with literature values and are shown in Table 111 & 15. It is evident from Table1, that there is good agreement between the experimental and reported values.

Table 1: Comparison of Experimental Values with Literature Data11, 15 at 303.15K

Liquid	Density kg/m^3		Ultrasonic velocity m/s		Viscosity η cP	
	Exptl	Lit	Exptl	Lit	Exptl	Lit
1-OCP	1.1423	1.2550[a]	1365.2	1381.4[a]	2.823	2.821[a]
Methyl salicylate	1.1752	1.1750[b]	1389.5	1390.4[b]	2.443	2.44[b]
Ethyl salicylate	1.1181	1.118[b]	1355.5	1354.4[b]	3.175	3.117[b]
Benzyl Salicylate	1.1063	1.1065[b]	1498.3	1498.4[b]	6.733	6.722[b]

- Mean molar volume (V) evaluated by the equation $V = \frac{M}{\rho}$
- Excess volume (V^E): $V^E = V - (V_1 X_1 + V_2 X_2)$
- Adiabatic compressibility (β_{ad}): $\beta_a = 1/\rho U^2$
- Deviation in adiabatic compressibility ($\Delta\beta_{ad}$): $(\Delta\beta_{ad}) = \beta_{ad} - (\beta_{ad1} X_1 + \beta_{ad2} X_2)$
- Inter molecular free length (L$_f$): $L_f = K (\beta_{ad})^{1/2}$
- Excess inter molecular free length (L$_f^E$):

$$L_f^E = L_f - (L_{f1} X_1 + L_{f2} X_2)$$

Where, L$_{f1}$ and L$_{f2}$ are the individual inter molecular free length values of pure liquids in the binary mixtures.

Redlich-Kister equation: $Y^E = Y^M_{real} - Y^M_{ideal}$

The standard deviations $\sigma(Y^E)$ were

calculated by using the relation

$$\sigma\,(Y^E) \;=\; \Sigma\left[\frac{(Y_{exp}{}^{E}-Y_{cal}{}^{E})^2}{(m-n)}\right]^{1/2}$$

Where, m is the number of experimental data points and n is the number of coefficients considered and (n=5 in the present calculation).

$Y_{cal}{}^{E}$ has been obtained from the above equation using the best-fit values of A_i.

Theoretical Velocities
Nomoto Equation

Following relation established by Nomoto17 for a liquid mixture

$R = M/\rho U^{1/3}$

Where U and ρ are experimentally determined values of Ultrasonic velocity and density respectively and M indicates the mean molar mass in a binary liquid mixture

$M = (X_1 M_1 + X_2 M_2)$

Where M_1 and M_2 are molecular weights of molecules of constituent components.

On simplification, we get the following relation.

$$U_{Nomoto} = \left[\frac{(X_1 R_1 + X_2 R_2)}{(X_1 V_1 + X_2 V_2)}\right]^3$$

The Van Dael and Vangeel Equation

The ideal mixing theory advanced by Van Dael and Vangeel[18] through light of assumptions of Blandamer and Waddington[19] Van Dael obtained the relation for ultrasonic velocity in liquid mixtures as

$$\frac{1}{(X_1 M_1 + X_2 + M_2)}\times\frac{1}{U^2{}_{imx}} = \frac{X_1}{M_1 U_1^2}+\frac{X_2}{M_2 U_2^2}$$

Where U_{imx} is the ideal mixing ultrasonic velocity in binary liquid mixture. U_1 and U_2 are ultrasonic velocities of main compound and sub compound.

The Impedance relation

Impedance relation[20] $U = \dfrac{\sum X_i Z_i}{\sum X_i \rho_i}$

Where X_i, ρ_t and Z_i are mole fraction, density and acoustic impedance of the mixture respectively.

The Rao's specific velocity method relation

Rao developed the following equation namely specific velocity method[21]

$U = (\Sigma\, X_i\, \rho_i\, r_i)^3]$

Where X_i, U_i, and r_i are the mole fraction, ultrasonic velocity, density and Rao's specific sound velocity of the mixture.

Where Rao's specific sound velocity = $U_i^{1/3}/\rho_i$ and Z_i is the acoustic impedance.

The Junjie equation
Junjie equation[22]

$U_J = (\,X_1 M_1 / \rho_1 + X_2 M_2 / \rho_2\,) / [\,\{\,X_1 M_1 + X_2 M_2\,\}^{1/2} \{X_1 M_1/\rho_1 U_1^2 + X_2 M_2/\rho_2 U_2^2)\}^{1/2}]$

Where M_1, M_2 and ρ_1, ρ_2 are molecular weights and densities of constituent components.

Kudriavtsev equation

Kudriavtsev Relation[23] for the ultrasonic relation between experimental and theoretical values are calculated

$$U_{KUD} = \left[\frac{X_1 M_1 U_1^2}{M_{eff}}\right]+\left[\frac{X_2 M_2 U_2^2}{M_{eff}}\right]^{1/2}$$

Chi square test

As indicated by Karl Pearson[24], Chi-square value is evaluated for the binary liquid mixtures under study utilizing the formula

$$\chi2 = \sum_{i=1}^{n}\left(\frac{(Uobs - Ucal)^2}{Ucal}\right)$$

Where n is the number of data used, and U (obs) = experimental values of ultrasonic velocities U(cal) = computed values of ultrasonic velocities.

Average Percentage Error

The Average percentage error[25] is calculated by utilizing the relation

$$\sigma = \frac{1}{N}\sum_{i=1}^{n}\left(\frac{(Uobs - Ucal)}{Uobs}\right)\times 100$$

Where n is the number of data used. U (obs) =experimental values of ultrasonic velocities

The degree of intermolecular interaction or molecular association is given by

$$\alpha = \left[\frac{U_{exp}^2}{U_{imx}^2} - 1 \right]$$

RESULTS

The experimentally measured values of ultrasonic velocities (U), densities (ρ) and viscosities are presented in the Table 2. From the table it is clear that experimental values are in good agreement with the literature values.

In order to support the presence of interaction between the molecules, it is necessary to study the excess parameters. Excess parameters, associated with a liquid mixture, are a quantitative measure of deviation in the behaviour of the liquid mixture from ideality. The nature and excess functions' sign can be explained in terms of the molecular interactions considering both the positive and negative contributions. The excess values of molar volume (V^E) and inter molecular free length (L_f^E) and deviation in adiabatic compressibility ($\Delta\beta_{ad}$) and viscosity ($\Delta\eta$) are also showed in Table 2. Redlich-Kister coefficients along with the standard deviations for all the excess and deviation properties at all the experimental temperatures are presented in Table 3. The non-rectilinear behaviour of ultrasonic velocity, compressibility and other thermo-dynamical parameters of liquid mixtures with changing mole fractions are attributed to the difference in the size of the molecules and strength of interactions.

Table 2: Ultrasonic velocity, density, viscosity and excess molar volume, Excess intermolecular free length, deviations in viscosity and adiabatic compressibility of binary mixtures of OCP with mehyl salicylate, ethyl salicylate and benzyle salyicilate at 303.15, 308.15, 313.15 and 318.15K

OCP+Methyl salicylate 303.15K										
0.0000	1389.50	1.1752	2.4404	44.0728	129.4673	1.3175	0.0000	0.0000	0.0000	0.0000
0.1231	1395.80	1.1848	2.875	43.3227	125.9686	1.3063	-0.4599	-0.1692	-0.0069	0.387
0.2401	1405.20	1.1939	3.2177	42.4169	122.6905	1.2925	-1.0901	-0.2848	-0.0164	0.685
0.3514	1411.90	1.2027	3.4816	41.7087	119.6131	1.2817	-1.5361	-0.3543	-0.0233	0.907
0.4573	1417.80	1.2111	3.6333	41.0750	116.7188	1.2719	-1.9202	-0.3844	-0.0293	1.018
0.5583	1423.00	1.2192	3.6814	40.5054	113.992	1.2631	-2.2518	-0.3806	-0.0345	1.027
0.6547	1417.50	1.2270	3.6200	40.5625	111.4186	1.2640	-1.9676	-0.3477	-0.0302	0.929
0.7468	1410.00	1.2344	3.5052	40.7478	108.9864	1.2669	-1.5652	-0.2899	-0.024	0.779
0.8349	1400.00	1.2416	3.3138	41.0935	106.684	1.2722	-1.0119	-0.2107	-0.0155	0.554
0.9192	1390.00	1.2485	3.0821	41.4568	104.5016	1.2778	-0.4499	-0.1132	-0.0069	0.290
1.0000	1382.00	1.2551	2.8230	41.7163	102.4301	1.2818	0.0000	0.0000	0.0000	0.0000

308.15K										
0.0000	1374.40	1.1685	2.2284	45.3049	130.2097	1.3358	0.0000	0.0000	0.0000	0.0000
0.1231	1383.00	1.1782	2.57.00	44.3767	126.6774	1.3221	-0.6742	-0.1821	-0.0100	0.309
0.2401	1392.00	1.1873	2.91.00	43.4664	123.3751	1.3084	-1.3432	-0.3022	-0.0200	0.618
0.3514	1397.20	1.196	3.1497	42.8296	120.2834	1.2988	-1.7505	-0.3674	-0.0262	0.828
0.4573	1403.10	1.2044	3.2831	42.1759	117.3749	1.2889	-2.1857	-0.3939	-0.0329	0.933
0.5583	1407.10	1.2124	3.3130	41.6582	114.631	1.2809	-2.495	-0.3902	-0.0377	0.936
0.6547	1401.00	1.2201	3.2608	41.7559	112.0421	1.2824	-2.1985	-0.3567	-0.0332	0.858
0.7468	1393.00	1.2276	3.1210	41.9795	109.5896	1.2859	-1.7849	-0.3037	-0.0270	0.694
0.8349	1383.00	1.2348	2.9381	42.3415	107.2705	1.2914	-1.2412	-0.2265	-0.0187	0.487
0.9192	1373.50	1.2417	2.6999	42.6896	105.0698	1.2967	-0.7191	-0.1331	-0.0108	0.226
1.0000	1361.20	1.2481	2.4950	43.2421	103.0046	1.3051	0.0000	0.0000	0.0000	0.0000

313.15K										
0.0000	1358.00	1.1678	2.2284	46.4336	130.2877	1.3524	0.0000	0.0000	0.0000	0.0000
0.1231	1369.50	1.177	2.48.00	45.3021	126.8066	1.3358	-0.8958	-0.1908	-0.01	0.248

0.2401	1379.00	1.1856	2.7548	44.3540	123.554	1.3217	-1.6199	-0.3181	-0.02	0.520
0.3514	1384.00	1.1937	2.9858	43.7354	120.5172	1.3125	-2.0257	-0.3825	-0.0262	0.747
0.4573	1390.00	1.2014	3.0737	43.0814	117.6666	1.3026	-2.4768	-0.4026	-0.0329	0.832
0.5583	1394.00	1.2088	3.081.0	42.5702	114.9696	1.2949	-2.7947	-0.4011	-0.0377	0.837
0.6547	1388.80	1.216	2.9982	42.6374	112.4235	1.2959	-2.543	-0.3716	-0.0332	0.751
0.7468	1379.70	1.2229	2.8416	42.9583	110.0135	1.3008	-2.0458	-0.3209	-0.027	0.592
0.8349	1369.50	1.2295	2.6591	43.3665	107.7329	1.3069	-1.469	-0.2481	-0.0187	0.407
0.9192	1359.50	1.2357	2.4200	43.7857	105.5816	1.3132	-0.8884	-0.1462	-0.0108	0.165
1.0000	1345.20	1.2413	2.2570	44.5194	103.5688	1.3242	0.0000	0.0000	0.0000	0.0000

318.15K

0.0000	1343.40	1.1645	2.0650	47.5828	130.6569	1.3690	0.0000	0.0000	0.0000	0.0000
0.1231	1355.80	1.1733	2.2579	46.3672	127.2043	1.3514	-1.0526	-0.2027	-0.0131	0.196
0.2401	1365.50	1.1814	2.4806	45.3951	123.9901	1.3372	-1.8698	-0.3299	-0.0239	0.422
0.3514	1371.30	1.1890	2.7147	44.7253	120.9936	1.3273	-2.3923	-0.3905	-0.0300	0.659
0.4573	1377.00	1.1962	2.7938	44.0888	118.1762	1.3178	-2.8885	-0.4121	-0.0368	0.741
0.5583	1381.10	1.2032	2.8003	43.5732	115.5104	1.3100	-3.2705	-0.4126	-0.0418	0.750
0.6547	1374.50	1.2099	2.6972	43.7501	112.9941	1.3127	-2.966	-0.385	-0.0380	0.649
0.7468	1365.00	1.2162	2.5497	44.1285	110.6150	1.3184	-2.4656	-0.335,	-0.0306	0.504
0.8349	1354.00	1.2223	2.3496	44.6257	108.3657	1.3258	-1.8518	-0.2582	-0.0219	0.306
0.9192	1341.00	1.2281	2.1683	45.2802	106.2340	1.3355	-1.0857	-0.1645	-0.0132	0.127
1.0000	1324.10	1.2330	2.0390	46.2589	104.2660	1.3498	0.0000	0.0000	0.0000	0.0000

OCP+Ethyl salicylate
303.15K

0.0000	1355.50	1.11810	3.1770	48.677	148.618	1.385	0.0000	0.0000	0.0000	0.0000
0.1280	1365.90	1.13170	3.4951	47.362	142.580	1.366	-0.4239	-0.1284	-0.0057	0.363
0.2482	1378.30	1.14560	3.7207	45.951	136.908	1.345	-0.9977	-0.2462	-0.0138	0.632
0.3614	1389.50	1.15940	3.8873	44.675	131.606	1.327	-1.4857	-0.3195	-0.0210	0.838
0.4682	139900	1.17300	3.9448	43.558	126.651	1.310	-1.8600	-0.3427	-0.0267	0.934
0.5691	1406.90	1.1868	3.8917	42.569	121.981	1.295	-2.1465	-0.3528	-0.0313	0.916
0.6645	1405.00	1.2003	3.7910	42.204	117.618	1.289	-1.84700	-0.3069	-0.0270	0.849
0.7550	1402.50	1.2138	3.5871	41.884	113.507	1.284	-1.53720	-0.2398	-0.0226	0.677
0.8408	1395.60	1.2275	3.3759	41.827	109.610	1.284	-0.99730	-0.172	-0.0147	0.497
0.9224	1387.70	1.2410	3.1020	41.845	105.947	1.284	-0.4118	-0.068	-0.0080	0.252
1.0000	1382.00	1.2551	2.8230	41.716	102.430	1.282	0.0000	0.0000	0.0000	0.0000

308.15K

0.0000	1338.60	1.1153	2.2530	50.039	148.991	1.404	0.0000	0.0000	0.0000	0.0000
0.1280	1350.00	1.1286	2.5270	48.617	142.969	1.384	-0.5525	-0.1382	-0.0074	0.243
0.2482	1362.00	1.1422	2.7480	47.196	137.31	1.363	-1.1560	-0.2677	-0.0159	0.435
0.3614	1373.00	1.1556	2.9190	45.904	132.033	1.345	-1.6783	-0.3383	-0.0235	0.579
0.4682	1382.00	1.1689	3.0287	44.793	127.095	1.328	-2.0640	-0.3658	-0.0294	0.662
0.5691	1389.00	1.1823	3.0753	43.84	122.446	1.314	-2.3313	-0.3763	-0.0336	0.685
0.6645	1387.00	1.1954	3.0610	43.484	118.101	1.309	-2.0378	-0.3317	-0.0295	0.647
0.7550	1383.50	1.2085	2.9570	43.231	114.005	1.305	-1.6765	-0.2672	-0.0244	0.521
0.8408	1378.00	1.2217	2.8080	43.107	110.134	1.303	-1.2167	-0.1904	-0.0178	0.352
0.9224	1368.40	1.2347	2.6571	43.253	106.487	1.305	-0.5170	-0.0871	-0.0075	0.181
1.0000	1361.20	1.2481	2.4950	43.242	103.005	1.305	0.0000	0.0000	0.0000	0.0000

313.15K

0.0000	1324.00	1.1080	2.2530	51.485	149.973	1.424	0.0000	0.0000	0.0000	0.0000
0.1280	1336.00	1.1215	2.4699	49.956	143.875	1.403	-0.6385	-0.1600	0.0074,	0.216
0.2482	1348.50	1.1352	2.6507	48.445	138.163	1.381	-1.3120	-0.2930	-0.0159	0.397
0.3614	1359.50	1.1486	2.7695	47.106	132.838	1.362	-1.8622	-0.3644	-0.0235	0.515
0.4682	1368.00	1.162	2.8562	45.986	127.850	1.346	-2.2385	-0.3974	-0.0294	0.601
0.5691	1374.60	1.1754	2.879	45.026	123.164	1.332	-2.4955	-0.4016	-0.0336	0.624

0.6645	1373.00	1.1886	2.8279	44.63	118.776	1.326	-2.2268	-0.3603	-0.0295	0.572
0.7550	1369.00	1.2017	2.7028	44.401	114.650	1.322	-1.8248	-0.2886	-0.0244	0.447
0.8408	1364.00	1.2150	2.5586	44.238	110.738	1.320	-1.3903	-0.2174	-0.0178	0.302
0.9224	1353.70	1.2281	2.3894	44.435	107.059	1.323	-0.6254	-0.1115	-0.0075	0.133
1.0000	1345.20	1.2413	2.2570	44.519	103.569	1.324	0.0000	0.0000	0.0000	0.0000

318.15K

0.0000	1306.80	1.1050	2.0060	52.993	150.380	1.445	0.0000	0.0000	0.0000	0.0000
0.1280	1324.00	1.1183	2.1800	51.012	144.290	1.417	-0.7379	-0.1900	-0.0085	0.170
0.2482	1341.50	1.1315	2.3459	49.112	138.615	1.391	-1.4695	-0.3203	-0.0179	0.332
0.3614	1357.00	1.1444	2.4585	47.455	133.331	1.367	-2.0257	-0.383	-0.0258	0.441
0.4682	1370.00	1.1572	2.5366	46.041	128.379	1.347	-2.4016	-0.4109	-0.0315	0.515
0.5691	1380.50	1.1702	2.5607	44.840	123.712	1.329	-2.6223	-0.4265	-0.0355	0.536
0.6645	1383.90	1.1829	2.5160	44.141	119.349	1.319	-2.3937	-0.3878	-0.0319	0.488
0.7550	1384.00	1.1955	2.4105	43.670	115.245	1.311	-1.9861	-0.3201	-0.0262	0.380
0.8408	1382.00	1.2082	2.2793	43.336	111.361	1.306	-1.4857	-0.2452	-0.0201	0.246
0.9224	1376.00	1.2207	2.1279	43.267	107.708	1.305	-0.7618	-0.1372	-0.009	0.091
1.0000	1369.00	1.2330	2.0390	43.274	104.266	1.306	0.0000	0.0000	0.0000	0.0000

OCP+Benzyl salicylate
303.15K

0.0000	1498.40	1.1063	6.7322	40.26	206.309	1.259	0.0000	0.0000	0.0000	0.0000
0.1692	1489.00	1.1206	6.3449	40.249	188.625	1.259	-0.2568	-0.1069	-0.004	0.274
0.3143	1484.00	1.1354	5.9339	39.993	173.432	1.255	-0.7246	-0.2323	-0.0113	0.430
0.4400	1479.00	1.1502	5.6019	39.746	160.306	1.251	-1.1549	-0.2997	-0.018	0.590
0.5500	1474.00	1.1651	5.2100	39.504	148.845	1.247	-1.5568	-0.3341	-0.0243	0.628
0.6470	1468.00	1.1801	4.7990	39.321	138.754	1.244	-1.8808	-0.3419	-0.0294	0.596
0.7333	1451.00	1.1949	4.3900	39.749	129.836	1.251	-1.5788	-0.2976	-0.0246	0.524
0.8105	1435.00	1.2097	3.9700	40.144	121.888	1.257	-1.2965	-0.2258	-0.0201	0.406
0.8800	1415.00	1.2246	3.5600	40.784	114.750	1.267	-0.7572	-0.1469	-0.0117	0.268
0.9429	1396.00	1.2395	3.1500	41.398	108.315	1.277	-0.2347	-0.0515	-0.0036	0.104
1.0000	1382.00	1.2551	2.8230	41.716	102.430	1.282	0.0000	0.0000	0.0000	0.0000\

308.15K

0.0000	1485.90	1.1030	6.0800	41.062	206.927	1.272	0.0000	0.0000	0.0000	0.0000
0.1692	1477.00	1.1171	5.7069	41.034	189.215	1.271	-0.3970	-0.1259	-0.0061	0.234
0.3143	1470.00	1.1316	5.2898	40.897	174.022	1.269	-0.85040	-0.2460	-0.013	0.336
0.4400	1465.10	1.1461	4.8980	40.648	160.879	1.265	-1.3731	-0.3246	-0.0211	0.395
0.5500	1458.30	1.1606	4.5561	40.515	149.419	1.263	-1.7462	-0.3533	-0.0268	0.448
0.6470	1450.00	1.1752	4.2092	40.470	139.328	1.263	-2.0024	-0.3577	-0.0308	0.449
0.7333	1434.40	1.1897	3.8480	40.853	130.406	1.268	-1.8080	-0.3138	-0.0277	0.397
0.8105	1415.60	1.2041	3.4592	41.444	122.456	1.278	-1.3852	-0.2405	-0.0211	0.285
0.8800	1398.10	1.2186	3.1001	41.982	115.315	1.286	-0.9986	-0.1615	-0.0152	0.175
0.9429	1377.00	1.2331	2.7500	42.769	108.875	1.298	-0.349	-0.0687	-0.0053	0.050
1.0000	1361.20	1.2481	2.4950	43.242	103.005	1.305	0.0000	0.0000	0.0000	0.0000

313.15K

0.0000	1471.80	1.0995	5.3748	41.986	207.585	1.286	0.0000	0.0000	0.0000	0.0000
0.1692	1463.00	1.1134	5.0681	41.962	189.844	1.286	-0.4525	-0.1398	-0.0061	0.221
0.3143	1456.70	1.1276	4.7269	41.793	174.631	1.283	-0.9892	-0.2655	-0.013	0.332
0.4400	1452.20	1.1419	4.3950	41.528	161.478	1.279	-1.5731	-0.343	-0.0211	0.392
0.5500	1444.10	1.1561	4.0800	41.477	150.001	1.278	-1.9029	-0.3785	-0.0268	0.420
0.6470	1435.20	1.1704	3.7700	41.48	139.904	1.278	-2.1451	-0.3791	-0.0308	0.413
0.7333	1419.50	1.1845	3.4350	41.899	130.980	1.285	-1.9451	-0.3286	-0.0277	0.347
0.8105	1402.00	1.1986	3.1002	42.446	123.018	1.293	-1.5937	-0.2607	-0.0211	0.252
0.8800	1383.60	1.2128	2.7650	43.072	115.8670	1.302	-1.1436	-0.1847	-0.0152	0.134
0.9429	1361.70	1.2269	2.4957	43.957	109.427	1.316	-0.4177	-0.0858	-0.0053	0.061
1.0000	1345.20	1.2413	2.2570	44.519	103.569	1.324	0.0000	0.0000	0.0000	0.0000

318.15K										
0.0000	1457.00	1.0950	5.4540	43.02	208.438	1.302	0.0000	0.0000	0.0000	0.0000
0.1692	1447.00	1.1088	5.0082	43.073	190.632	1.303	-0.4943	-0.1789	-0.0068	0.132
0.3143	1441.10	1.1227	4.5800	42.889	175.394	1.300	-1.1484	-0.3074	-0.0150	0.199
0.4400	1432.50	1.1365	4.1792	42.879	162.238	1.300	-1.5662	-0.3673	-0.0239	0.228
0.5500	1425.50	1.1504	3.8280	42.779	150.753	1.298	-2.0217	-0.3934	-0.0289	0.252
0.6470	1415.20	1.1644	3.4908	42.881	140.625	1.300	-2.2348	-0.4104	-0.0325	0.246
0.7333	1398.00	1.1782	3.1520	43.428	131.678	1.308	-1.9674	-0.3692	-0.0294	0.202
0.8105	1381.10	1.1919	2.8470	43.986	123.709	1.316	-1.6596	-0.297	-0.0240	0.161
0.8800	1363.00	1.2057	2.5350	44.645	116.549	1.326	-1.2255	-0.2192	-0.0171	0.086
0.9429	1342.50	1.2194	2.2581	45.501	110.101	1.339	-0.5723	-0.1188	-0.0062	0.024
1.0000	1324.10	1.2330	2.0390	46.259	104.266	1.350	0.0000	0.0000	0.0000	0.0000

Table 3: Values of Redlich - Kister coefficients and standard deviation (σ) for for the binary systems OCP+Methyl Salicylate, OCP+Ethyl Salicylate and OCP+Benzyl Salicylate

	A_0	A_1	A_2	A_3	A_4	
			OCP+Methyl salicylate			
			Deviation in Adiabatic Compressibility			
303.15K	-8.7652	4.3983	10.3075	-5.0538	-7.7485	0.1014
308.15K	-9.7692	4.3597	11.4484	-4.2453	-13.7768	0.1163
313.15K	-10.9699	4.4680	11.3003	-4.5802	-15.9644	0.1224
318.15K	-12.8104	5.2435	11.4075	-4.7023	-16.5977	0.1244
			Excess molar volume			
303.15K	-1.5466	-0.0272	0.0007	0.0003	-0.0013	0.00003
308.15K	-1.5887	-0.0657	-0.0686	0.1575	-0.2374	0.0023
313.15K	-1.6328	-0.0914	-0.286	0.2892	-0.0825	0.0026
318.15K	-1.6781	-0.0723	-0.2083	0.3299	-0.519	0.0053
			Excess Int. mole free length			
303.15K	-0.1341	0.0699	0.1612	-0.0800	-0.1222	0.0016
308.15K	-0.1474	0.0682	0.1766	-0.0662	-0.2116	0.0018
313.15K	-0.1637	0.0692	0.1729	-0.0703	-0.2418	0.0019
318.15K	-0.1888	0.0797	0.1732	-0.0718	-0.2482	0.0019
			Deviation in Viscosity			
303.15K	4.1358	-0.3309	-0.7031	0.1311	0.1268	0.0065
308.15K	3.7776	-0.2402	-0.7305	-0.0539	-0.9200	0.0055
313.15K	3.4005	-0.0632	-1.0153	-0.1731	-1.2557	0.0138
318.15K	3.0576	-0.0475	-1.6123	-0.1533	-0.6975	0.0175
			OCP+Ethyl salicylate			
303.15K	-8.2366	4.8777	7.5927	-5.3047	-3.9493	0.0824
308.15K	-9.0287	4.6353	7.9376	-4.9068	-5.6939	0.0865
313.15K	-9.7323	4.3177	7.5847	-3.7933	-6.0017	0.0901
318.15K	-10.2698	3.9598	6.2431	-2.3928	-5.7436	0.0618
			Excess molar volume			
303.15K	-1.4414	0.0624	0.5701	-0.1989	0.0343	0.0099
308.15K	-1.5294	0.1054	0.4799	-0.1149	-0.0197	0.0085
313.15K	-1.6390	0.0685	0.5761	-0.0018	-0.5358	0.0086
318.15K	-1.7271	0.1493	0.4490	-0.1348	-0.9130	0.0108

			Excess Int. mole free length			
303.15K	-0.1191	0.0780	0.1137	-0.0835	-0.0597	0.0013
308.15K	-0.1293	0.0735	0.1178	-0.0759	-0.0852	0.0013
313.15K	-0.1376	0.0682	0.1114	-0.0584	-0.0890	0.0013
318.15K	-0.1419	0.0652	0.0911	-0.038	-0.0852	0.0009

			Deviation in Viscosity			
303.15K	3.7254	-0.1582	-0.6422	-0.0912	0.1265	0.0136
308.15K	2.7184	-0.6357	-0.602	0.5741	0.0954	0.0072
313.15K	2.4773	-0.6623	-1.1356	1.0349	0.5015	0.0096
318.15K	2.1222	-0.5968	-0.8493	0.9893	-0.2997	0.0068

			OCP+Benzyl salicylate Deviation in Ad Comp			
303.15K	-5.8022	9.3881	0.3822	-10.5721	3.4375	0.095
308.15K	-6.6350	8.7182	2.2434	-9.5756	-0.8669	0.0802
313.15K	-7.2381	7.3829	-1.7824	-4.7367	6.7160	0.0717
318.15K	-7.5019	9.2987	3.1449	-8.6334	-5.4434	0.1175

			Excess molar volume			
303.15K	-1.3058	0.7426	0.0737	-0.5413	0.9325	0.0072
308.15K	-1.4024	0.6818	0.2631	-0.4406	0.3555	0.0052
313.15K	-1.4876	0.7518	0.4300	-0.5181	-0.2214	0.007
318.15K	-1.6007	0.8638	0.5500	-0.7906	-1.3322	0.0168

			Excess Int. mole free length			
303.15K	-0.0907	0.1479	0.0103	-0.1693	0.0472	0.0015
308.15K	-0.1021	0.1349	0.0389	-0.1512	-0.0190	0.0013
313.15K	-0.1099	0.1126	-0.0227	-0.0755	0.0971	0.0011
318.15K	-0.1118	0.1391	0.0510	-0.1328	-0.0848	0.0018

			Deviation in Viscosity			
303.15K	2.4355	-0.4243	0.7484	-0.1506	-2.5559	0.03
308.15K	1.7053	-0.9368	0.4909	1.9457	-1.0406	0.0086
313.15K	1.6755	-0.6835	-0.3652	1.5361	0.3330	0.0108
318.15K	0.9522	-0.3125	0.6860	0.6023	-1.4678	0.0074

The variations of excess molar volume, inter molecular free length, deviation in adiabatic compressibility and viscosity with the mole fraction of OCP for the studied systems are given in figures 1.1 to 3.4 respectively.

Using Nomoto's relation (U_{NR}), impedance relation (U_{IR}), ideal mixing relation (U_{imx}), Junjie's relation (U_J), Rao's specific velocity relation (U_R) and Kudriavtsev relation (U_K), the theoretical values of ultrasonic velocity were evaluated. The computed estimations of ratio in velocity (U^2/U^2_{imx}) from measured estimations of ultrasonic velocity (U) are graphically shown. From the values of experimental and theoretical velocities the molecular interaction parameter (α) has been evaluated and discussed its variation with the composition mixture has been conferred in terms of molecular interactions. The validity of the theories were checked by calculating standard deviation and chi square test.

The experimentally measured velocities and percentages of deviation using various theories are represented in Table 4. Average percentage deviations and Chi square test are results are also given in Table 4.

Table 4: Percentage deviations, interaction parameters (α) alongwith average percentage deviation and Chi square test values for the systems OCP+Methyl Salicylate, OCP+Ethyl Salicylate and OCP+Benzyl Salicylate

X_1	U_{EXP}	$\%U_N$	$\%U_{imp}$	$\%U_{VDV}$	$\%U_{JUN}$	$\%U_{RAO}$	U^2/U^2_{imx}	
				OCP + Methyl salicylate				
				303.15K				
0.0000	1389.5	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
0.1231	1395.8	-0.5023	-0.5252	-0.6809	-0.565	-1.0655	1.0138	0.0138
0.2401	1405.2	-1.2191	-1.2581	-1.5187	-1.3308	-2.0941	1.0311	0.0311
0.3514	1411.9	-1.7394	-1.7887	-2.1119	-1.8868	-2.8237	1.0436	0.0436
0.4573	1417.8	-2.2002	-2.2546	-2.6045	-2.3697	-3.3750	1.0542	0.0542
0.5583	1423.0	-2.6100	-2.6647	-3.0107	-2.7877	-3.7658	1.0630	0.0630
0.6547	1417.5	-2.2853	-2.3365	-2.6548	-2.4583	-3.3957	1.0553	0.0553
0.7468	1410.0	-1.8196	-1.8634	-2.131	-1.9735	-2.8204	1.0440	0.0440
0.8349	1400.0	-1.1735	-1.2062	-1.4027	-1.2929	-1.9653	1.0287	0.0287
0.9192	1390.0	-0.5187	-0.5367	-0.6434	-0.5871	-1.032	1.013	0.0130
1.0000	1382.0	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	σ	-0.1434	-0.1472	-0.1714	-0.1557	-0.2299		
	$\chi2$	3.7643	3.9509	5.2425	4.3857	8.9782		
				308.15K				
0.0000	1374.4	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
0.1231	1383.0	-0.7127	-0.7527	-0.9116	-0.769	-1.2377	1.0185	0.0185
0.2401	1392.0	-1.4459	-1.5141	-1.7798	-1.5462	-2.2836	1.0366	0.0366
0.3514	1397.2	-1.9045	-1.9909	-2.3203	-2.0368	-2.9262	1.0481	0.0481
0.4573	1403.1	-2.4095	-2.5047	-2.8609	-2.5613	-3.5272	1.0598	0.0598
0.5583	1407.1	-2.7802	-2.8760	-3.2283	-2.9391	-3.8835	1.0678	0.0678
0.6547	1401.0	-2.4515	-2.5413	-2.8651	-2.6062	-3.507	1.0599	0.0599
0.7468	1393.0	-1.9876	-2.0644	-2.3365	-2.1249	-2.9366	1.0484	0.0484
0.8349	1383.0	-1.3769	-1.4343	-1.634	-1.4833	-2.1182	1.0335	0.0335
0.9192	1373.5	-0.7946	-0.8262	-0.9346	-0.8554	-1.2528	1.019	0.0190
1.0000	1361.2	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	σ	-0.1619	-0.1686	-0.1934	-0.173	-0.2439		
	$\chi2$	4.5115	4.872	6.3228	5.1155	9.7624		
				313.15K				
0.0000	1358.0	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
0.1231	1369.5	-0.9289	-0.9676	-1.1263	-0.9831	-1.4191	1.0229	0.0229
0.2401	1379.0	-1.7008	-1.7669	-2.0321	-1.7973	-2.4831	1.0419	0.0419
0.3514	1384.0	-2.1460	-2.2296	-2.5584	-2.2732	-3.1055	1.0532	0.0532
0.4573	1390.0	-2.6590	-2.7511	-3.1067	-2.8049	-3.6953	1.0652	0.0652
0.5583	1394.0	-3.0296	-3.1224	-3.4740	-3.1824	-4.0552	1.0733	0.0733
0.6547	1388.8	-2.7591	-2.8459	-3.1690	-2.9075	-3.7492	1.0665	0.0665
0.7468	1379.7	-2.2119	-2.2863	-2.5580	-2.3438	-3.0849	1.0532	0.0532
0.8349	1369.5	-1.5795	-1.6350	-1.8345	-1.6816	-2.2406	1.0377	0.0377
0.9192	1359.5	-0.9532	-0.9838	-1.0921	-1.0116	-1.353	1.0222	0.0222
1.0000	1345.2	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	σ	-0.1838	-0.1903	-0.2151	-0.1945	-0.2600		
	$\chi2$	5.6141	6.0015	7.5934	6.2567	10.8529		
				318.15K				
0.0000	1343.4	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
0.1231	1355.8	-1.0509	-1.109	-1.2728	-1.0990	-1.4743	1.026	0.0260
0.2401	1365.5	-1.8904	-1.9894	-2.2626	-1.9758	-2.5920	1.0468	0.0468
0.3514	1371.3	-2.4427	-2.5678	-2.9059	-2.5550	-3.3438	1.0608	0.0608
0.4573	1377.0	-2.9846	-3.1225	-3.4876	-3.1132	-3.9756	1.0736	0.0736

0.5583	1381.1	-3.4116	-3.5505	-3.9110	-3.5460	-4.3559	1.0831	0.0831
0.6547	1374.5	-3.0888	-3.2189	-3.5501	-3.2192	-3.9738	1.075	0.0750
0.7468	1365.0	-2.5577	-2.6691	-2.9474	-2.6734	-3.3313	1.0617	0.0617
0.8349	1354.0	-1.9121	-1.9953	-2.1995	-2.0015	-2.4755	1.0455	0.0455
0.9192	1341.0	-1.1100	-1.1560	-1.2670	-1.1611	-1.4153	1.0258	0.0258
1.0000	1324.1	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	σ	0.0485	-0.0107	-0.2491	-0.0569	0.0280		
	χ2	0.3653	0.0178	9.1423	0.49640	0.1234		

<table>
<tbody>
<tr><td colspan="9" align="center">OCP + Ethyl salicylate
303.15K</td></tr>
</tbody>
</table>

0.0000	1355.5	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
0.1280	1365.9	-0.5860	-0.4845	-0.8253	-0.6738	-1.2666	1.0167	0.0167
0.2482	1378.3	-1.3028	-1.1303	-1.6962	-1.4613	-2.3728	1.0348	0.0348
0.3614	1389.5	-1.9183	-1.7012	-2.3976	-2.1299	-3.2411	1.0497	0.0497
0.4682	1399.0	-2.4016	-2.1628	-2.9119	-2.6480	-3.8320	1.0609	0.0609
0.5691	1406.9	-2.7640	-2.5238	-3.2607	-3.0260	-4.1709	1.0685	0.0685
0.6645	1405.0	-2.4423	-2.2179	-2.8920	-2.7011	-3.7812	1.0604	0.0604
0.7550	1402.5	-2.0736	-1.8820	-2.4454	-2.3067	-3.2632	1.0508	0.0508
0.8408	1395.6	-1.3892	-1.2460	-1.6581	-1.5728	-2.3184	1.034	0.0340
0.9224	1387.7	-0.6217	-0.5426	-0.7656	-0.7286	-1.2092	1.0155	0.0155
1.0000	13820	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	σ	-0.1582	-0.1415	-0.1933	-0.1765	-0.2630		
	χ2	4.4380	3.6063	6.4493	5.4461	11.4117		

<table>
<tbody>
<tr><td colspan="9" align="center">308.15K</td></tr>
</tbody>
</table>

0.0000	1338.6	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
0.1280	1350.0	-0.6926	-0.6061	-0.9484	-0.7741	-1.3318	1.0192	0.0192
0.2482	1362.0	-1.4139	-1.2668	-1.835	-1.5609	-2.441	1.0377	0.0377
0.3614	1373.0	-2.0481	-1.8629	-2.5618	-2.2441	-3.3003	1.0533	0.0533
0.4682	1382.0	-2.5281	-2.3243	-3.0759	-2.7561	-3.8931	1.0645	0.0645
0.5691	1389.0	-2.8588	-2.6538	-3.3933	-3.1011	-4.2048	1.0715	0.0715
0.6645	1387.0	-2.5545	-2.3628	-3.0391	-2.7934	-3.8304	1.0637	0.0637
0.7550	1383.5	-2.1397	-1.9760	-2.5414	-2.3549	-3.2712	1.0528	0.0528
0.8408	1378.0	-1.5764	-1.4542	-1.8672	-1.7455	-2.4495	1.0384	0.0384
0.9224	1368.4	-0.7080	-0.6405	-0.8642	-0.8065	-1.2383	1.0175	0.0175
1.0000	1361.2	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	σ	-0.1688	-0.1545	-0.2066	-0.1857	-0.2683		
	χ2	4.88080	4.1315	7.1453	5.8480	11.6489		

<table>
<tbody>
<tr><td colspan="9" align="center">313.15K</td></tr>
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0.0000	1324.0	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
0.1280	1336.0	-0.7539	-0.6727	-1.0152	-0.8319	-1.3583	1.0206	0.0206
0.2482	1348.5	-1.5280	-1.3900	-1.9582	-1.6685	-2.4995	1.0403	0.0403
0.3614	1359.5	-2.1771	-2.0033	-2.7021	-2.3643	-3.3668	1.0563	0.0563
0.4682	1368.0	-2.6352	-2.4439	-3.1955	-2.8528	-3.9191	1.0671	0.0671
0.5691	1374.6	-2.9505	-2.7580	-3.4975	-3.1816	-4.2194	1.0738	0.0738
0.6645	1373.0	-2.6817	-2.5019	-3.1779	-2.9095	-3.8931	1.0667	0.0667
0.7550	1369.0	-2.2380	-2.0843	-2.6497	-2.4430	-3.2941	1.0552	0.0552
0.8408	1364.0	-1.7161	-1.6015	-2.0143	-1.8771	-2.5093	1.0415	0.0415
0.9224	1353.7	-0.800	-0.7365	-0.9602	-0.8937	-1.2719	1.0195	0.0195
1.0000	1345.2	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	σ	-0.1788	-0.1654	-0.2175	-0.195	-0.2723		
	χ2	5.3432	4.6067	7.7518	6.3007	11.8226		

<table>
<tbody>
<tr><td colspan="9" align="center">318.15K</td></tr>
</tbody>
</table>

0.0000	1306.8	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
0.1280	1324.0	-0.8749	-0.633	-0.9581	-0.9951	-1.3290	1.0194	0.0194

0.2482	1341.5	-1.7402	-1.3302	-1.871	-1.9574	-2.4856	1.0385	0.0385
0.3614	1357.0	-2.4303	-1.9153	-2.5819	-2.7208	-3.3752	1.0537	0.0537
0.4682	1370.0	-2.9185	-2.3530	-3.0714	-3.2578	-3.9471	1.0644	0.0644
0.5691	1380.5	-3.2127	-2.6447	-3.353	-3.5749	-4.1850	1.0706	0.0706
0.6645	1383.9	-2.9974	-2.4680	-3.1159	-3.3559	-3.8971	1.0654	0.0654
0.7550	1384.0	-2.5408	-2.0893	-2.6318	-2.8653	-3.3176	1.0548	0.0548
0.8408	1382.0	-1.9247	-1.5885	-1.9850	-2.1811	-2.4838	1.0409	0.0409
0.9224	1376.0	-1.0087	-0.8230	-1.0380	-1.1588	-1.3083	1.0211	0.0211
1.0000	1369.0	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	σ	0.0485	-0.0107	-0.2491	-0.0569	0.0280		
	χ2	0.3653	0.0178	9.1423	0.4964	0.1234		

OCP + Benzyle salicylate
303.15K

0.0000	1498.4	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
0.1692	1489.0	-0.1043	-0.8360	-3.8964	-0.1503	-2.7750	1.0827	0.0827
0.3143	1484.0	-0.5155	-1.7127	-6.1491	-0.598	-4.8204	1.1353	0.1353
0.4400	1479.0	-0.9396	-2.3972	-7.2915	-1.0487	-6.1771	1.1635	0.1635
0.5500	1474.0	-1.3768	-2.9325	-7.7401	-1.5024	-6.9622	1.1748	0.1748
0.6470	1468.0	-1.7605	-3.2837	-7.6652	-1.8926	-7.2162	1.1729	0.1729
0.7333	1451.0	-1.4164	-2.8080	-6.5669	-1.5452	-6.4391	1.1455	0.1455
0.8105	1435.0	-1.1441	-2.3074	-5.2775	-1.2586	-5.4012	1.1145	0.1145
0.8800	1415.0	-0.5969	-1.4494	-3.5178	-0.6858	-3.7671	1.0742	0.0742
0.9429	1396.0	-0.1174	-0.5800	-1.6511	-0.1683	-1.9174	1.0339	0.0339
1.0000	1382.0	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	σ	-0.0807	-0.1876	-0.5309	-0.0897	-0.4822		
	χ2	1.4373	6.4921	45.5765	1.7219	37.7513		

308.15K

0.0000	1485.9	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
0.1692	1477.0	-0.1953	-0.9788	-4.119	-0.2445	-2.829	1.0878	0.0878
0.3143	1470.0	-0.5317	-1.8152	-6.358	-0.6199	-4.8048	1.1404	0.1404
0.4400	1465.1	-1.0235	-2.5859	-7.5842	-1.1401	-6.2025	1.1709	0.1709
0.5500	1458.3	-1.4005	-3.0699	-7.9754	-1.5350	-6.9379	1.1808	0.1808
0.6470	1450.0	-1.6901	-3.3267	-7.7970	-1.8316	-7.1075	1.1763	0.1763
0.7333	1434.4	-1.495	-2.9887	-6.8148	-1.6329	-6.4691	1.1516	0.1516
0.8105	1415.6	-1.08360	-2.3345	-5.3602	-1.2064	-5.3009	1.1165	0.1165
0.8800	1398.1	-0.7650	-1.6799	-3.7814	-0.8601	-3.8871	1.0801	0.0801
0.9429	1377.0	-0.1899	-0.6870	-1.776	-0.2445	-1.9385	1.0365	0.0365
1.0000	1361.2	0.0000	0 0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	σ	-0.0848	-0.1997	-0.5513	-0.0944	-0.4821		
	χ2	1.4745	7.0969	48.1288	1.7859	37.1668		

313.15K

0.0000	1471.8	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
0.1692	1463.0	-0.2186	-1.0163	-4.1862	-0.2688	-2.8046	1.0893	0.0893
0.3143	1456.7	-0.6203	-1.9268	-6.5053	-0.7103	-4.8155	1.144	0.1440
0.4400	1452.2	-1.1582	-2.7481	-7.7800	-1.2771	-6.2458	1.1758	0.1758
0.5500	1444.1	-1.4644	-3.1646	-8.1043	-1.6015	-6.8942	1.1842	0.1842
0.6470	1435.2	-1.7296	-3.3972	-7.8980	-1.8739	-7.0451	1.1789	0.1789
0.7333	1419.5	-1.5392	-3.0612	-6.9123	-1.6798	-6.4263	1.1540	0.1540
0.8105	1402.0	-1.2288	-2.5022	-5.5439	-1.3538	-5.3475	1.1208	0.1208
0.8800	1383.6	-0.8573	-1.7892	-3.9026	-0.9541	-3.8844	1.0829	0.0829
0.9429	1361.7	-0.2314	-0.738	-1.8337	-0.2870	-1.9139	1.0377	0.0377
1.0000	1345.2	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	σ	-0.0917	-0.2089	-0.5638	-0.1015	-0.4810		
	χ2	1.6538	7.6162	49.612	1.9900	36.6387		

				318.15K				
0.0000	1457.0	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
0.1692	1447.0	-0.1828	-1.0224	-4.2667	-0.2372	-2.6986	1.0911	0.0911
0.3143	1441.1	-0.6613	-2.0358	-6.7072	-0.7586	-4.7680	1.1490	0.1490
0.4400	1432.5	-0.9671	-2.6445	-7.7821	-1.0960	-5.9998	1.1759	0.1759
0.5500	1425.5	-1.3974	-3.1896	-8.2206	-1.5459	-6.7790	1.1872	0.1872
0.6470	1415.2	-1.6132	-3.3725	-7.9548	-1.7694	-6.8489	1.1803	0.1803
0.7333	1398.0	-1.3580	-2.9653	-6.8861	-1.5103	-6.1451	1.1534	0.1534
0.8105	1381.1	-1.1286	-2.4727	-5.5655	-1.2639	-5.1493	1.1213	0.1213
0.8800	1363.0	-0.8173	-1.8006	-3.9474	-0.922	-3.7461	1.0839	0.0839
0.9429	1342.5	-0.3310	-0.8649	-1.9761	-0.3910	-1.9156	1.0407	0.0407
1.0000	1324.1	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	σ	0.0485	-0.0107	-0.2491	-0.0569	0.0280		
	$\chi 2$	0.3653	0.0178	9.1423	0.4964	0.1234		

DISCUSSION

Salicylates are known to exist in self associated molecular forming inter molecular hydrogen bonding through oxygen and OH group in ortho position. The effect of hydrogen bonding on the molar volumes of polar liquid mixtures was studied by Boule[26]. He found that the formation of complexes is hydrogen bonding is accompanied by a decrease in volume which is characteristic of extent of bonding.

When salicylate are mixed with solvents like OCP, change in volume of mixing can be due to (i) depolymersation of self associated hydrogen bonded salicylates (ii) formation of new hydrogen bonds between salicylates and OCP (iii) specific solute solvent interactions between salicylate and OCP. The first factor leads to positive excess volumes and second and third factors contribute to negative. The net volume change depends on the relative contributions of these factors.

In the present case, the actual change in volume in the reported binary systems is attributed to the dominance of second and the third factors of the above as well as the difference in size and shape of the component molecules. The negative deviation in all the systems shows that these systems have specific interactions between unlike molecules through hydrogen bonding. The order of V^E values is given below.

Benzyl salicylate<Ethyl salicylate<Methyl salicylate

Same results were reported earlier workers[27]. Several workers[28-30] reported that negative excess volumes indicate strong interactions between the components of mixtures. The VE values become more and more negative[31,32] as the temperature is increased from 303.15K to 318.15K. This indicates that as the temperature increases the inter hydrogen bond in the associated salicylates become weaker and dipole. Dipole interactions between the hetero molecules get increased leading to greater contraction in volume.

Another interesting parameter, which is a representative of structural adjustment in solution, is inter molecular free length. Valuation of L_f a function of composition and temperature for all the systems indicates that L_f decreases with increase in mole fractions of OCP. Though strong interactions between unlike molecules are involve, the very small change in L_f is attributed due to braking of inter hydrogen bonding in the salicylates followed by the specified interactions between the molecules. The excess L_f values for all the systems show negative deviations indicating strong interactions between the components.

The deviations for all this systems are positive at all the temperatures. The volume and magnitude of $\Delta\eta$ depends on the combined effects of the factors like molecular and shape of the components in addition to inter molecular forces. In systems when all types of interactions are operating, the values of $\Delta\eta$ will be determined by the predominant effect. The deviations in viscosities in the present case are all positive in the entire range of composition at all temperatures indicate that specific interaction between unlike molecules are predominant which is in agreement with the conclusions drawn from data of velocity and other related parameters.

It is responsible for the constraints and approximations integrated into these theories. All of the molecules are thought to be spherical in shape, which is not always true. In Nomoto 's theory, when mixing, it is believed that the volume does not change. Therefore, no interaction has been taken into account between the components of liquid mixtures. The assumption for the development of the optimal mixing relationship is that the ratio of ideal mixtures' unique heats and volumes are also equal. Again, it does not take into account any molecular interaction. Similarly, as per the belief of the theory of the Collision Factor, the molecules are handled, which is not really the case, as real non-elastic substances. But the interaction between the molecules of the two liquids happens when two liquids are combined due to the presence of different kinds of forces, such as dispersion forces, charge transfer, hydrogen bonding, dipole-dipole and dipole-induced dipole interactions. Therefore, the variations found in the velocity values measured using different models from the experimental values suggest that there is a molecular interaction between the different molecules in the liquid mixture. The computed estimations of ratio in velocity (U^2/U^2_{imx}) from measured estimations of ultrasonic velocity (U) are graphically shown in Fig 1.5, 2.5 and 3.5. The ratio (U^2/U^2_{imx}) is used as an important tool to measure the non-ideality in liquid mixtures, especially in these cases where the properties other than sound velocity are not known. The values of the (U^2/U^2_{imx}) are positive[33] for the studied binary mixtures at all the different temperatures and over the entire composition range of OCP, which indicates dominance of associations over dispersion forces among the molecules of liquid mixture. Fig 1.5, 2.5 and 3.5 represent the variation of (U^2/U^2_{imx}) with mole fraction of OCP with branched alkanols. It is observed at 0.5 mole fraction systems show maximum positive deviation at all the temperatures, which infers the maximum hetero molecular associations at this mole fraction of OCP. The deviation of the ratio (U^2/U^2_{imx}) from unity is a direct measure of non ideality of the system as a consequence of association or dissociation.
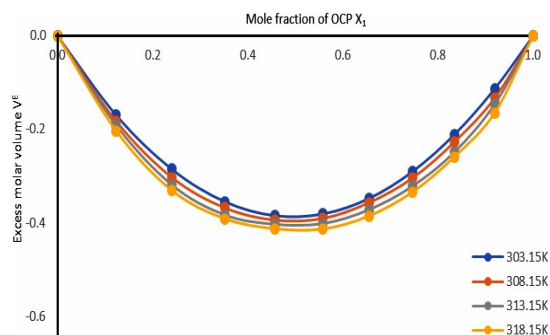
Fig. 1.1. Variation of excess molar volume with the mole fraction of OCP for OCP+MS system
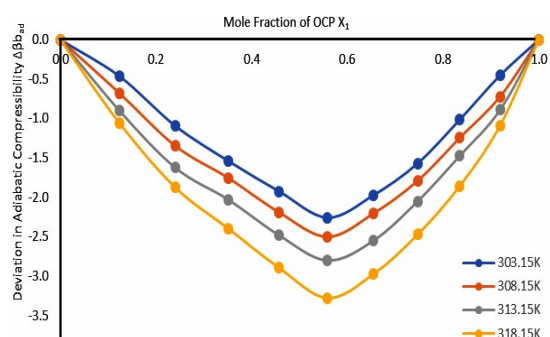
Fig. 1.2. Variation of Adiabatic Compressibility with the molefraction of OCP for OCP+MS system
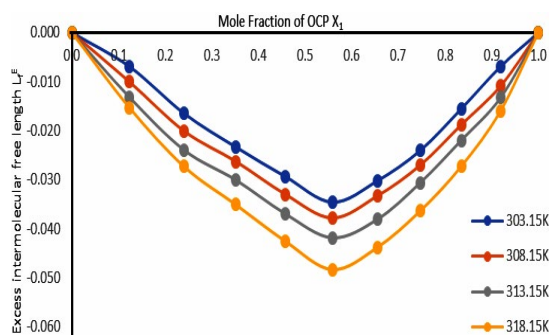
Fig. 1.3. Variation of excess intermolecular free length L_f^E with molefraction of OCP for OCP + MS system
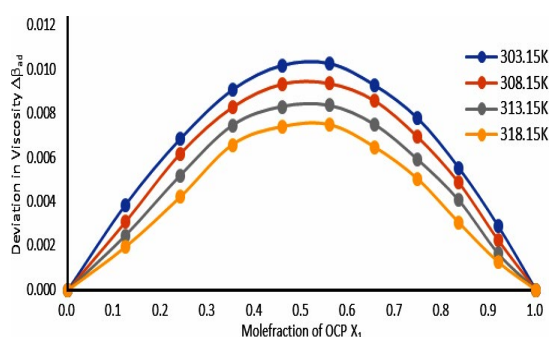
Fig. 1.4. Variation of deviation in viscosity with the molefraction of OCP for OCP+MS system
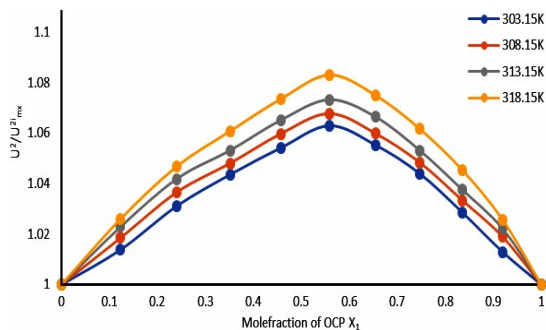
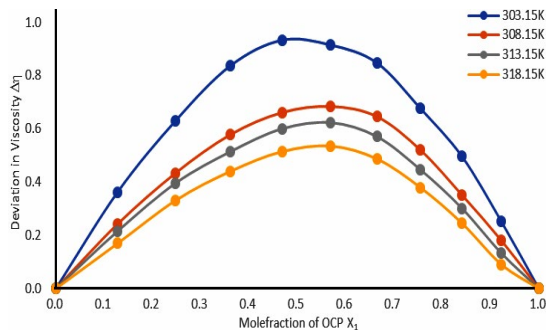**Fig. 1.5. Variation of U²/U²$_{imx}$ with the molefraction of OCP for OCP + MS system**

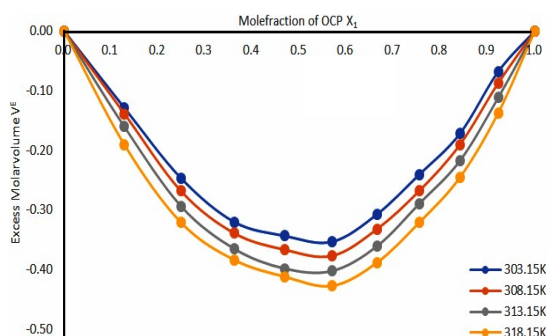**Fig. 2.4. Variation of deviation in viscosity with the mole fraction of OCP for OCP+ES system**

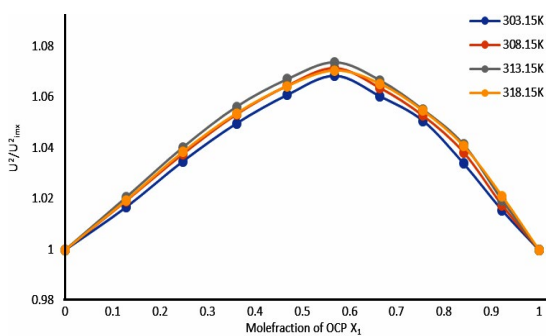**Fig. 2.1. Variation of excess molar volume with the molefraction of OCP for OCP+ES system**

Fig. 2.5. Variation of U²/U²$_{imx}$ with the mole fraction of OCP for OCP+ES system
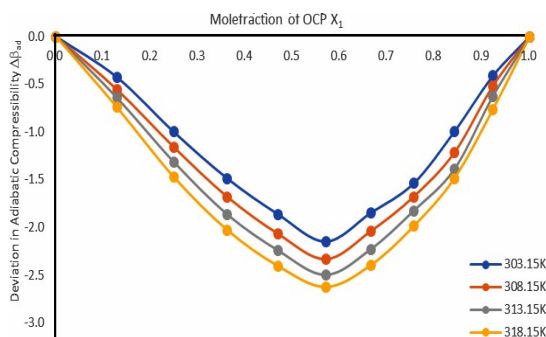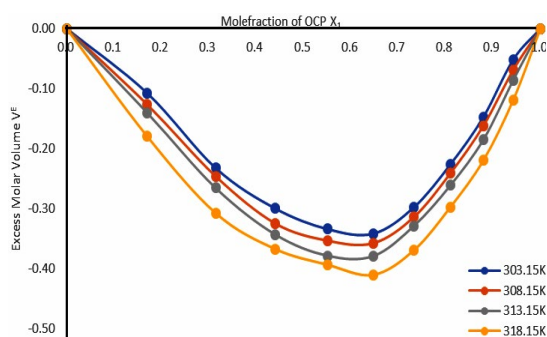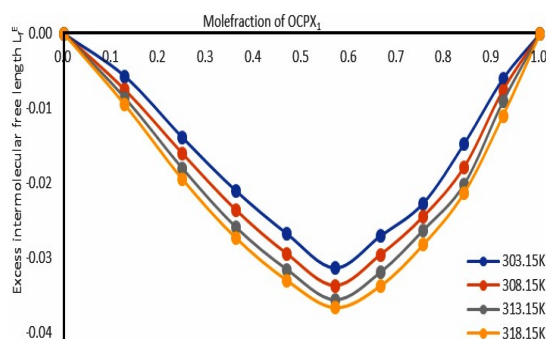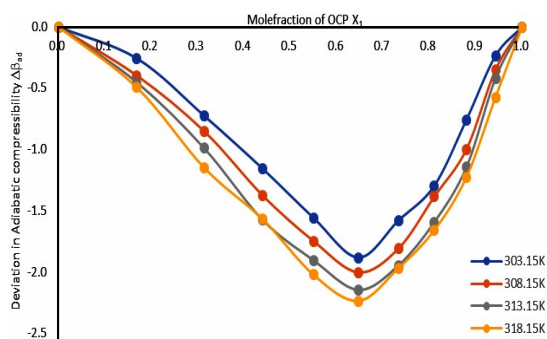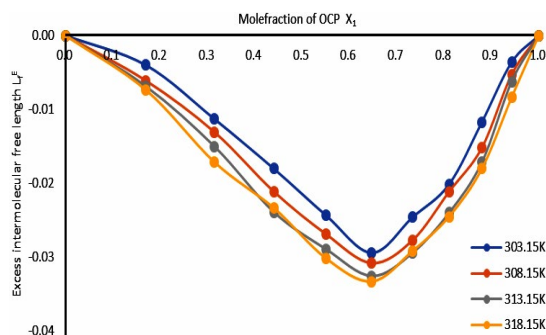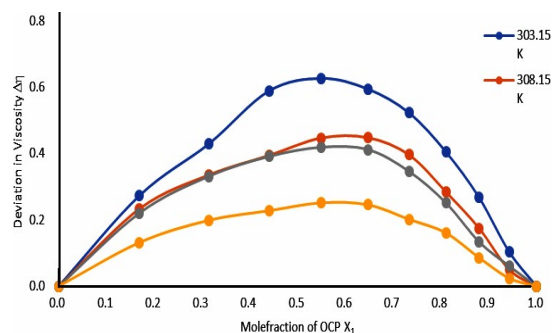

Fig. 2.2. Variation of deviation in adiabtic compressiblity with the molefraction of OCP for OCP+ES system

Fig. 3.1. Variation of excess molar volume with the molefraction of OCP for OCP+BS system

Fig. 2.3. Variation of excess intermolecular free length with the molfraction of OCP for OCP+ES system

Fig. 3.2. Variation of deviation in adiabatic compressibility with the molefraction of OCP for OCP+BS system

Fig. 3.3. Variation of deviation in excess intermolecular free length with the mole fraction of OCP for OCP+BS system

Fig. 3.4. Variation of deviation in viscosity with the molefraction of OCP for OCP+BS system
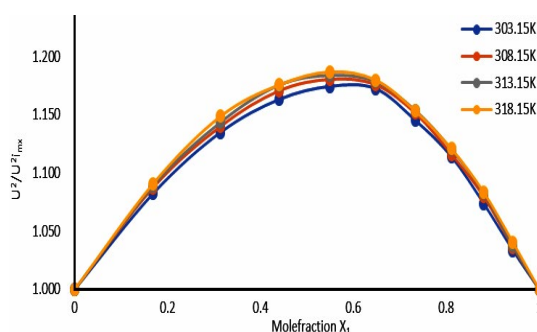

Fig. 3.5. Variation of U^2/U^2_{imx} with the mmolefraction of OCP for OCP+BS system

The predicted ultrasonic velocities using various theories are reasonably close to the experimental values for and the three studied binary mixtures thus showing the validity of studied theoretical models for binary mixtures. These theories generally fail to predict accurately the ultrasonic velocities where strong interactions are supposed to exist and the average absolute percentage relative deviation is small in systems where the interactions are less or nil[34].

The experimental values are close to the values computed using impedance relation in for OCP+Methyl salicylate, benzyl salicylate systems, where in the case of OCP+ethyl salicylate Nomoto's theory is best suited. The deviation of the ratio (U^2/U^2_{imx}) from unity is positive which indicates strong interaction between the consecutive molecules[35].

Conflict of interest

The author declare that we have no conflict of interest.

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