

Volumetric Studies in the Binary Mixtures of O – Chlorophenol with Amides at different Temperatures

D.V.M.Krishna Reddy¹ P.B.Sandhya Sri², S.V.G.V.A.Prasad³ K.A.K.Raj Kumar⁴ L.Vykuntha Rao^{5*}

²Department of Physics, Government Degree College, Avanigadda – 521121, Andhra Pradesh, India.

³Department of Physics and Electronics, Pithapuram Rajah's Government College (A), Kakinada – 533001, Andhra Pradesh, India.

⁴Dr. L.B.College, Vishakhapatnam-530013, Andhra Pradesh, India

^{5*} Department of Chemistry, Gitam University

Abstract

Excess thermodynamic parameters like excess molar volume (V^E), excess intermolecular free length (L_f^E), deviation in adiabatic compressibility ($\Delta\beta_{ad}$) and deviation in viscosity were computed to understand molecular interactions in the binary mixtures of O – chlorophenol with Formamide, N,N – Di Methyl Formamide- (DMF), N, N – Di Methyl Acetamide at different temperatures by using the experimental values of ultrasonic velocity(U), density(ρ) and viscosity(η) at entire mole fraction range. The excess Values are fitted The values of V^E , $\Delta\beta_{ad}$ and L_f^E have been fitted to Redlich – Kister polynomial equation to estimate binary coefficients and standard deviation(σ) between the experimental and computed values.

Key Words: Ultrasonic velocity, density and viscosity, molar volume, adiabatic compressibility, inter molecular free length.

1.Introduction

In the research of chemistry, Binary liquid intermixture often seen. Non ideal and peculiar behaviour can be observed in these mixtures. In past few decades a significant number of contributions were made in interpreting the non ideality behaviour¹⁻⁵. The use of extra properties derived from experimental data on thermodynamic parameters is a great way to learn more about how homo- and hetero-molecules interact with each other.

The volumetric studies on binary mixture solutions studies provide important information about the molecular interactions. The experimentally measured values of ultrasonic velocity, density and viscosity of binary liquid mixture solutions have been utilized to evaluate their excess properties to understand the nature of molecular interactions.

To learn more about the physical, structural, and packing phenomena⁶ that control mixing, one can use the analytical examination of excess properties of thermodynamic

parameters of mixes of binary liquids. Numerous research teams have investigated the ultrasonic velocities in binary liquid systems, which can accommodate substantial hydrogen

bonding networks^{7,8}. Numerous experiments have focused on the ultrasonic velocity, density, viscosity, excess volumes, and excess adiabatic compressibilities in binary systems in recent years⁹. Therefore, it is crucial to conduct coordinated research into these extra qualities. Because the chemical and pharmaceutical industries these findings in design process, knowledge of the excess mixing qualities of binary mixtures has relevance in both theoretical and applied areas of research^{10,11}.

Although it has several uses, O-chlorophenol is a step in the polychlorination of phenol. At room temperature, it is a liquid, whereas all the other chlorophenols are solids. Chlorophenols are employed as various pesticides, disinfectants, and disinfectant agents to control bacteria, fungi, insects, and weeds. The majority of their applications are based on their toxicity. Formamide is a hygroscopic liquid that is colorless. Alcohols and water both make it soluble. It is only somewhat poisonous. It serves as a reaction solvent and an intermediary in the synthesis of organic compounds.

N,N - Dimethyl Formamide is a dipolar aprotic solvent that has a consistency similar to water. It serves as a transporter for gases. It is used as a solvent for vinyl resins and acetylene, butadiene acid gases, polyacrylic fibers, and a catalyst for carboxylation processes in organic synthesis. Most polymers are absorbed by DMF, which causes them to expand. As a result, it is frequently found in paint strippers. The NIST advises using DMF for near-infrared spectroscopy of carbon nanotubes because it is very good at isolating and suspending carbon nanotubes.

A good medium for powerful bases like sodium hydroxide is N,N-dimethyl acetamide. It is frequently employed in the adhesive business or as a solvent for fibers. As a reaction medium, it is also used in the manufacturing of medicines and plasticizers.

Due to their extensive use in flavoring, fragrance, synthetic essences, and cosmetics, amides are attracting more and more attention in the field of thermophysics. Esters have a significant role as solvents in the plastic, paint, and pharmaceutical industries¹². The study of liquid mixes with esters as one of the components¹³⁻¹⁶ has recently attracted more attention. These studies are very important since they provide information on the structural alterations brought on by mixing in pure ester.

The body of literature thus demonstrates how extensively the solvent amides and their binary systems have been researched and used in industry. However, there is still room to further the research on compounds by combining it with other significant solvents for industry. In order to better understand these binary mixes, the author has conducted a systematic investigation using O-chlorophenol + Formamide, O-chlorophenol + N,N-dimethyl Formamide, and O-chlorophenol + N,N-dimethyl Acetamide.

The current article examines the three binary liquid mixtures in terms of their ultrasonic velocity (U), density (ρ), inter molecular free length (L_f), molar volume (V), adiabatic compressibility (β), excess values of inter molecular free length (L_f^E), molar volume (V), and deviation in adiabatic compressibility (β_{ad}). The results were examined in terms of how the inclusion of the second component affected the inter molecular free spaces between the molecules in pairs. Ultrasonic energy has recently found applications in engineering, agriculture, manufacturing, and medicine. Ultrasonic energy is used in the chemical industry to synthesize chemical compounds and investigate chemical reactions.

2. Experimental Techniques

The purity of the chemicals used is a crucial factor in any experimental study on thermodynamic properties. The impurities, like water, which the chemicals absorb, the dissociation of the chemicals after exposure or standing, association, etc. are all to blame for the inaccuracies that occur in experimental measurements. In addition to initial purification, a constant verification of the chemicals' purity is a crucial component of any thermodynamics experiment.

In the literature, a number of purification techniques have been discussed^{17,18}. These techniques have been developed depending on the nature and functional groups of the compounds that need to be purified. The various organic liquids utilized in the current study are top-notch samples. Before usage, the liquids are distilled, mixed using a burette in the required ratios, and left for 5–6 hours to reach temperature equilibrium before making experimental observations.

According to Nikam et al.¹⁹, a pulse-echo interferometer (MODEL M-81) provided by Mittal Enterprises, New Delhi and a 105 m³ double-arm pycnometer were used to measure the densities and ultrasonic sound velocities of the three studied binary liquid mixtures and pure liquids, respectively, at 303.15, 308.15, 313.15 and 318.15 K. Since 'd' can be measured with a micrometer down to a minimum value of 0.01 mm, the precision of the velocity is

mostly dependent on the accuracy of the distance that can be measured. Measurements of velocity were precise to +0.02%.

The density of the conductivity water used to calibrate the double-arm pycnometer is 995.61 kg/m³ at 303.15 K. To achieve thermal equilibrium, the specific gravity bottle was placed in the thermostat for 15 minutes. Once they reach room temperature, they are taken out of the thermostat and weighed. An accurate thermostat (0.01K) is used to keep the temperature constant. The weighings are done on a digital balance with a 0.01 mg precision made by METTLER TOLEDO (Switzerland make).

A commercial Ubbelohde capillary viscometer with a 0.55 mm diameter that was calibrated with double-distilled water was used to measure the viscosity at 303.15, 308.15, 313.15, and 318.15K. The O-Chlorophenol experimental samples, as well as the aids Formamide, N, N- Di methyl formamide, and N, N -Dimethylacetamide utilized in this work, are of a high caliber and were acquired from S.D. Fine Chemicals in India with purity > 99%. Table 1 compares experimental results with those found in the literature^{20,21}. Table 1 clearly shows that the experimental and reported values coincide fairly well.

Table-1: Comparison of Experimental Values with Literature Data [10-13] at 308.15K

Liquid	Ultrasonic Velocity(U)m/s		Density(ρ) Kg/m ³	
	Exptl	Lit	Exptl	Lit
O - Chloro phenol	1365.2	1381.4 ²⁰	1.2551	1.2550 ²⁰
Formamide	1587.0	1585.30 ²¹	1.1244	1.1245 ²¹
N,N - Dimethyl formamide	1436.0	1438.53 ²²	0.9393	0.9392 ²²
N,N- Di methyl acetamide	1431.5	1438.0 ²³	0.9317	0.9319 ²³

The acoustical parameters were assessed based on the standard formulae utilizing the experimental data.

Mean molar volume (V) evaluated by the equation $V = M / \rho$

Excess volume (V^E): $V^E = V - (V_1X_1 + V_2X_2)$

Adiabatic compressibility can be calculated by using the equation $\beta_{ad} = 1 / \rho U^2$

Deviation in adiabatic compressibility ($\Delta \beta_{ad}$): $= \beta_{ad} - (\beta_{ad1} X_1 + \beta_{ad2} X_2)$

Inter molecular free length can be computed by using the equation $L_f = K (\beta_{ad})^{\frac{1}{2}}$

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 intermolecular free length values of pure liquids in the binary mixtures. And X_1 & X_2 are the mole fractions of O - Chlorophenol and Formamide or N,N - Di methyl formamide or N,N- Di methyl acetamide

Redlich-Kister equation: $Y^E = Y_{M \text{ real}} - Y_{M \text{ ideal}}$

The standard deviations σ and (Y^E) were calculated with the help of relation

$$\sigma (Y^E) = \sum [(Y_{\text{exp}}^E - Y_{\text{cal}}^E)^2 / (m-n)]^{1/2}$$

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 .

Results

The systems are selected to study the interaction of O - Chlorophenol concentration with formamide, N,N-dimethyl formamide, and N,N-dimethyl acetamide. The computed values of molar volume (V), excess molar volume (V^E), inter molecular free length (L_f), excess inter molecular free length (L_f^E), adiabatic compressibility (β_{ad}), and deviations in adiabatic compressibility (β_{ad}) for all the systems under study are presented in Table 2 along with the experimentally determined values of ultrasonic velocity (U), density(ρ), and viscosity(η). The non-rectilinear behavior of ultrasonic velocity, adiabatic compressibility, and other thermodynamic properties of liquid mixtures with changing mole fractions can be attributed to variations in molecule size and contact strength. The acoustical characteristics were assessed based on established formulae utilizing the experimental data.

Tables 2 show that the excess intermolecular free length values vary negatively and that, for the O-Chlorophenol + Formamide system, the curves appear to peak negatively at about 0.36 mole fraction of O-Chlorophenol. However, for O-chlorophenol + N,N-dimethyl formamide systems, the highest deviation in intermolecular free length is observed at about 0.53 mole fraction, whereas for O-chlorophenol + N,N-dimethyl acetamide systems, the highest deviation is identified at 0.57 mole fraction at four different temperatures, 303.15, 308.15, 313.15, and 318.15K. For all of the systems under study, similar tendencies were

seen for excess molar volume and variation in adiabatic compressibility. Excess intermolecular free length and excess molar volume fluctuations.

Table-2: Ultrasonic velocity (U), density (ρ), deviation in adiabatic compressibility ($\Delta \beta_{ad}$), excess molar volume (V^E) and excess intermolecular free length (L_f^E) of OCP+FA/DMF/DMA systems

X_1	U m/s	ρ gm/cm ³	$\Delta \beta_{ad} \times 10^{-12} \text{ m}^2 \text{ N}^{-1}$	V^E cm ³ mol ⁻¹	$L_f^E \text{ \AA}^0$
OCP + FA					
303.15K					
0.0000	1587.00	1.1244	0.0000	0.0000	0.0000
0.0416	1579.65	1.1465	-0.6248	-0.3366	-0.0103
0.0891	1567.20	1.1655	-0.9485	-0.5845	-0.0155
0.1435	1555.59	1.1819	-1.2670	-0.7586	-0.0205
0.2068	1542.33	1.1963	-1.4957	-0.8677	-0.0241
0.2811	1527.21	1.2090	-1.6487	-0.9155	-0.0263
0.3697	1509.32	1.2202	-1.7056	-0.9013	-0.0269
0.4771	1487.62	1.2303	-1.6402	-0.8196	-0.0255
0.6100	1460.78	1.2394	-1.4080	-0.6588	-0.0215
0.7787	1426.69	1.2476	-0.9215	-0.3979	-0.0138
1.0000	1382.00	1.2551	0.0000	0.0000	0.0000
308.15K					
0.0000	1576.00	1.1197	0.0000	0.0000	0.0000
0.0416	1566.50	1.1399	-0.5119	-0.2773	-0.0082
0.0891	1556.40	1.1587	-0.9784	-0.5256	-0.0157
0.1435	1545.17	1.1753	-1.3661	-0.7141	-0.0218
0.2068	1531.58	1.1896	-1.6291	-0.8294	-0.0258
0.2811	1515.61	1.2025	-1.8029	-0.8932	-0.0283
0.3697	1496.58	1.2135	-1.8579	-0.8734	-0.0288
0.4771	1473.51	1.2234	-1.7869	-0.7910	-0.0272
0.6100	1444.97	1.2324	-1.5376	-0.6322	-0.0230
0.7787	1408.73	1.2405	-1.0096	-0.3760	-0.0147
1.0000	1361.20	1.2481	0.0000	0.0000	0.0000
313.15K					
0.0000	1564.00	1.1155	0.0000	0.0000	0.0000

0.0416	1554.89	1.1363	-0.5757	-0.3098	-0.0082
0.0891	1544.51	1.1550	-1.0566	-0.5700	-0.0157
0.1435	1532.59	1.1708	-1.4165	-0.7402	-0.0218
0.2068	1518.75	1.1847	-1.6812	-0.8469	-0.0258
0.2811	1502.49	1.1972	-1.8605	-0.9083	-0.0283
0.3697	1483.11	1.2079	-1.9207	-0.8879	-0.0288
0.4771	1459.61	1.2176	-1.8536	-0.8079	-0.0272
0.6100	1430.53	1.2263	-1.6015	-0.6499	-0.0230
0.7787	1393.61	1.2343	-1.0626	-0.4025	-0.0147
1.0000	1345.20	1.2413	0.0000	0.0000	0.0000

318.15K

0.0000	1554.00	1.1109	0.0000	0.0000	0.0000
0.0416	1545.22	1.1318	-0.6457	-0.3297	-0.0092
0.0891	1534.44	1.1508	-1.1691	-0.6172	-0.0168
0.1435	1521.86	1.1656	-1.5229	-0.7650	-0.0223
0.2068	1507.25	1.1790	-1.7968	-0.8678	-0.0263
0.2811	1490.09	1.1911	-1.9888	-0.9309	-0.0287
0.3697	1469.63	1.2013	-2.0551	-0.9057	-0.0293
0.4771	1444.83	1.2106	-1.9918	-0.8253	-0.0278
0.6100	1414.15	1.2190	-1.7329	-0.6688	-0.0235
0.7787	1375.19	1.2266	-1.1625	-0.4241	-0.0152
1.0000	1324.10	1.2330	0.0000	0.0000	0.0000

OCP+DMF**303.15K**

0.0000	1436.00	0.9393	0.0000	0.0000	0.0000
0.0778	1428.40	0.9739	-0.5304	-0.2457	-0.0069
0.1596	1421.00	1.0079	-0.9108	-0.4412	-0.0118
0.2456	1415.10	1.0414	-1.2415	-0.5926	-0.0163
0.3362	1410.30	1.0740	-1.4814	-0.6702	-0.0196
0.4317	1406.00	1.1060	-1.6118	-0.7045	-0.0216
0.5326	1403.00	1.1372	-1.6738	-0.6692	-0.0227
0.6393	1400.00	1.1678	-1.6033	-0.5990	-0.0221
0.7524	1396.00	1.1980	-1.3378	-0.4866	-0.0187
0.8724	1391.10	1.2268	-0.8591	-0.2658	-0.0122
1.0000	1382.00	1.2551	0.0000	0.0000	0.0000

308.15K

0.0000	1424.00	0.9341	0.0000	0.0000	0.0000
0.0778	1414.80	0.9688	-0.4827	-0.2722	-0.0062
0.1596	1407.60	1.0026	-0.9311	-0.4696	-0.0121
0.2456	1401.70	1.0359	-1.3153	-0.6185	-0.0173
0.3362	1396.50	1.0682	-1.5803	-0.6886	-0.0210
0.4317	1392.00	1.1000	-1.7528	-0.7177	-0.0235
0.5326	1388.10	1.1310	-1.8171	-0.6829	-0.0247
0.6393	1384.20	1.1615	-1.7525	-0.6153	-0.0241
0.7524	1379.00	1.1915	-1.4728	-0.5039	-0.0205
0.8724	1372.32	1.2203	-0.9477	-0.2945	-0.0134
1.0000	1361.20	1.2481	0.0000	0.0000	0.0000

313.15K

0.0000	1396.00	0.9303	0.0000	0.0000	0.0000
0.0778	1388.00	0.9649	-0.5350	-0.2887	-0.0062
0.1596	1381.50	0.9985	-0.9850	-0.4902	-0.0121
0.2456	1376.30	1.0315	-1.3648	-0.6419	-0.0173
0.3362	1372.00	1.0634	-1.6253	-0.7044	-0.0210
0.4317	1368.50	1.0949	-1.7969	-0.7336	-0.0235
0.5326	1366.04	1.1256	-1.8828	-0.7011	-0.0247
0.6393	1363.22	1.1559	-1.8028	-0.6369	-0.0241
0.7524	1360.18	1.1855	-1.5577	-0.5158	-0.0205
0.8724	1354.68	1.2140	-0.9895	-0.3068	-0.0134
1.0000	1345.20	1.2413	0.0000	0.0000	0.0000

318.15K

0.0000	1392.00	0.9254	0.0000	0.0000	0.0000
0.0778	1386.40	0.9599	-0.5966	-0.3087	-0.0067
0.1596	1382.30	0.9932	-1.0810	-0.5132	-0.0124
0.2456	1379.40	1.0258	-1.4638	-0.6549	-0.0174
0.3362	1377.70	1.0573	-1.7387	-0.7165	-0.0209
0.4317	1377.07	1.0885	-1.9265	-0.7458	-0.0234
0.5326	1376.95	1.1188	-1.9732	-0.7155	-0.0248
0.6393	1376.80	1.1488	-1.8583	-0.6515	-0.0241
0.7524	1377.50	1.1780	-1.6305	-0.5308	-0.0212
0.8724	1374.93	1.2063	-1.0175	-0.3335	-0.0136

1.0000	1369.00	1.2330	0.0000	0.0000	0.0000
--------	---------	--------	--------	--------	--------

OCP+DMA**303.15K**

0.0000	1431.50	0.9317	0.0000	0.0000	0.0000
0.0921	1425.80	0.9654	-0.4630	-0.1852	-0.0058
0.1858	1420.80	0.9992	-0.8621	-0.3743	-0.0109
0.2813	1416.70	1.0327	-1.1989	-0.5331	-0.0154
0.3784	1413.36	1.0655	-1.4486	-0.6196	-0.0189
0.4773	1410.00	1.0976	-1.5739	-0.6467	-0.0208
0.5780	1406.89	1.1289	-1.5975	-0.6068	-0.0214
0.6806	1403.82	1.1599	-1.5328	-0.5460	-0.0209
0.7851	1398.64	1.1902	-1.2408	-0.4306	-0.0172
0.8915	1391.37	1.2193	-0.7168	-0.2237	-0.0100
1.0000	1382.00	1.2481	0.0000	0.0000	0.0000

308.15K

0.0000	1422.50	0.9276	0.0000	0.0000	0.0000
0.0921	1415.10	0.9619	-0.4389	-0.2216	-0.0054
0.1858	1409.50	0.9962	-0.8822	-0.4205	-0.0112
0.2813	1405.10	1.0299	-1.2739	-0.5673	-0.0164
0.3784	1400.70	1.0630	-1.5300	-0.6478	-0.0200
0.4773	1396.50	1.0955	-1.6788	-0.6721	-0.0223
0.5780	1392.60	1.1272	-1.7310	-0.6319	-0.0233
0.6806	1387.70	1.1586	-1.6271	-0.5664	-0.0222
0.7851	1381.50	1.1894	-1.3465	-0.4527	-0.0187
0.8915	1372.80	1.2190	-0.7996	-0.2393	-0.0112
1.0000	1361.20	1.2481	0.0000	0.0000	0.0000

313.15K

0.0000	1406.00	0.9227	0.0000	0.0000	0.0000
0.0921	1399.70	0.9570	-0.5389	-0.2384	-0.0054
0.1858	1389.20	0.9915	-0.6477	-0.4847	-0.0112
0.2813	1378.50	1.0250	-0.5833	-0.6232	-0.0164
0.3784	1375.40	1.0578	-0.9504	-0.6959	-0.0200
0.4773	1373.00	1.0900	-1.2384	-0.7128	-0.0223
0.5780	1370.50	1.1216	-1.3975	-0.6730	-0.0233
0.6806	1366.85	1.1528	-1.3784	-0.6047	-0.0222

	0.7851	1362.43	1.1833	-1.2064	-0.4834	-0.0187
	0.8915	1355.47	1.2127	-0.7556	-0.2720	-0.0112
After the	1.0000	1345.20	1.2413	0.0000	0.0000	0.0000
components	318.15K					
have been	0.0000	1383.80	0.9186	0.0000	0.0000	0.0000
mixed, the inter	0.0921	1377.20	0.9529	-0.5443	-0.2764	-0.0067
molecular free	0.1858	1372.00	0.9869	-1.0520	-0.5116	-0.0078
length will either	0.2813	1367.50	1.0201	-1.4476	-0.6573	-0.0066
increase or	0.3784	1363.40	1.0524	-1.7243	-0.7248	-0.0115
decrease, which	0.4773	1359.50	1.0842	-1.8912	-0.7421	-0.0156
will affect the	0.5780	1355.20	1.1154	-1.9122	-0.7078	-0.0181
ultrasonic	0.6806	1350.40	1.1462	-1.7993	-0.6421	-0.0183
velocity in the	0.7851	1344.70	1.1763	-1.5209	-0.5205	-0.0163
solution. A	0.8915	1336.40	1.2051	-0.9452	-0.2940	-0.0104
sound	1.0000	1324.10	1.2330	0.0000	0.0000	0.0000

propagation model put forth by Eyring & Kincaid²⁴ led to the development of the relationship between inter molecular free length and velocity of ultrasonic sound. If the intermolecular free length increases or reduces due to the mixing of components, it is expected that the ultrasonic velocity will decrease. The current inquiry for the O - chlorophenol + Formamide, O-chlorophenol + N, N - dimethyl formamide, and O - chlorophenol + N, N - dimethyl acetamide systems has revealed this fact. Additionally, it has been found that velocity at any concentration decreases as temperature rises. Due to the breakup of hetero and homo molecule clusters at high temperatures, the ultrasonic velocity values drop with an increase in temperature.

4. Discussion

It is crucial to examine the surplus parameters in order to support the existence of molecular interaction. A liquid mixture's excess parameters serve as a quantitative indicator of how far from ideal its behavior deviates. When examining both the positive and negative contributions, molecular interactions can be used to explain the nature and sign of excess functions.

Excess Molar Volume

The kind and strength of interactions between the parts of binary mixtures, which depend on temperature, composition, size, and structure of the component molecules, are reflected in the excess thermodynamic values.

The proportional size of the expansion and contraction of the two liquids as a result of mixing determines the sign of V^E for a system²⁵. The primary factors contributing to volume expansion, also known as positive values V^E , can be identified as follows:

- (a) A solution system's one or both components being disrupted. An appropriate illustration of this is when two compounds' H-bonds break, or when associations kept together by Vander Waals forces or other weaker physical forces like dipole interactions or dipole-induced dipole interactions separate.
- (b) The molecular structure's shape, which discourages molecules from fitting together.
- (c) Steric obstruction, which resists the constituent molecules' closeness.

The following elements predominate, which leads to the negative V^E :

- (a) Strong specific interaction is the word used to describe chemical interactions between constituent molecules, such as hetero-molecular association caused by the formation of an H-bond.
- (b) Association via physically weaker forces, such as the dipolar force or any other forces of this kind.
- (c) Inclusion of molecules from one component into the structural network made up of molecules from the other component.
- (d) A molecular structure's geometry that encourages the component molecules to fit together.
- (e) For all binary systems under study, the V^E values are negative over the full mole fraction range and at all temperatures analyzed. In the binary systems under study, a feasible qualitative interpretation of the interaction between the liquid components has been examined.

The molecules of Formamide, N,N-dimethyl Formamide, and N,N-dimethyl Acetamide are associated through hydrogen bonding or dipole-dipole association because they contain molecules with strong proton-acceptor groups (C=O) and proton-donor groups (-

NH₂/N(CH₃)₂), whereas the molecules of O-chlorophenol have weak hydrogen bonds. When O-Chlorophenol and Formamide/N,N-Di Methyl Formamide/N,N-Di Methyl Acetamide are combined, the hydrogen bonds in O-Chlorophenol and Formamide/N,N-Di Methyl Formamide/N,N-Di Methyl Acetamide are mutually dissociated, and the dipole-dipole association in those two compounds is broken. New hydrogen bonds are then formed between the two compounds. The three mixtures' reported negative values of V^E point to the existence of particular interactions between amide and O-chlorophenol molecules. Compared to the other two systems, O - Chlorophenol + Formamide has larger negative V^E values.

Pure O-Chlorophenol has a high density rating, indicating that it is a densely packed chemical. It has a remarkable capacity for forming intramolecular hydrogen bonds with nearby hydroxyl and carbonyl groups; this interaction competes with nearby O-Chlorophenol molecules for intramolecular hydrogen bonds. O-Chlorophenol has a dipole moment of 3.46 D and is a polar and protic solvent.


N,N - Di Methyl Formamide and N,N - Di Methyl Acetamide are aprotic and extremely polar solvents with dipole moments of (≈ 3.24 D, ≈ 3.72 D) and 3.73 D, respectively. Formamide is a highly polar and protic solvent with a dipole moment of ≈ 3.73 D. As polar solvents, Formamide/N,N-Di Methyl Formamide/N,N-Di Methyl Acetamide are undoubtedly to some extent associated by dipole-dipole interactions; these interactions are of particular interest in N,N-Di Methyl Formamide/N,N-Di Methyl Acetamide due to the absence of any significant structural effects brought on by the absence of hydrogen bonds²⁴.

As polar solvents, Formamide/N,N-Di Methyl Formamide/N,N-Di Methyl Acetamide are undoubtedly to some extent associated by dipole-dipole interactions; these interactions are of particular interest in DMF/DMA due to the lack of any significant structural effects brought on by the absence of hydrogen bonds²⁶. O-Chlorophenol and Formamide/N,N-Di Methyl Formamide/N,N-Di Methyl Acetamide are both polar compounds, hence there is a chance that there may be dipole-dipole interactions (Keesom type) between the constituent molecules.

Rajagopal and Chentilnath²⁷ claim that the dipole moment of the interacting molecules also affects the strength of the interaction between the involved molecules. The likelihood of Keesom type Van der Waal forces, which develop in the current investigation because of the dipole moment of the constituents, results in significant interaction and negative values for $[28]$. The liquid mixture of (O-chlorophenol + Formamide / N,N-dimethyl

Formamide / N,N-dimethyl Acetamide) is therefore believed to have dipole-dipole interactions.

It is also conceivable that the addition of O-chlorophenol to formamide could cause the mutual dissociation of hydrogen-bonded structures between the O-chlorophenol and O-chlorophenol molecules, leading to the subsequent formation of a new hydrogen bond ($>C=O:HN$) between the lone pairs of electrons of the proton acceptor oxygen atom in the $>C=O$

group of O-chlorophenol and the proton in the $>NH$ ().

Volume increases due to the initial effect, while volume decreases due to the subsequent effect. However, the relative potency of these two actions determines the actual volume change. However, the phenomenon of hydrogen bonding is much apparent, which is supported by the significant volume decrement that produces negative values in the binary mixture under study²⁹. Regarding the structural contribution, the molar volumes of O-chlorophenol (102.43), Formamide (40.057), N,N-dimethylformamide (778.13), and N,N-dimethylacetamide (93.506) at 303.15 K are each represented in $10^{-6} \text{ m}^3 \text{ mol}^{-1}$. In the binary systems of (O - Chlorophenol+ Formamide), (O - Chlorophenol+ N,N - Di Methyl Formamide), and (O - Chlorophenol+N,N - Di Methyl Acetamide, geometrical fitting of smaller molecules into the voids created by the bigger molecules is advantageous. Furthermore, the magnitude of values increases as temperature rises from 303.15 K to 308.15 K. This tendency implies that as temperature rises, the degree of contact between the liquid components likewise rises. According to Rastogi et al³⁰, thermal energy activates molecules as temperature rises, which would accelerate the interaction of dissimilar molecules.

Values decrease (turn more negative) as the mixture's temperature rises, indicating that the volume expansion brought on by the higher temperature is likely being predominated by smaller molecules fitting more favorably into the spaces left by larger aggregating molecules. This causes the volume to contract, which causes the values to turn more negative as the temperature rises.

The order of strong interaction's strength with the increase in temperature is in the following order:

$$(318.15 > 315.15 > 308.15 > 303.15) \text{ K}$$

Deviation in adiabatic compressibility ($\Delta\beta_{ad}$)

When analyzing the chemical rearrangement caused by molecular interaction between the constituent molecules in liquid mixes, the sign and magnitude of α are crucial factors to consider. The variation in adiabatic compressibility can be explained by the following five factors:

1. Reduction in dipolar connection
2. Differences in size;
3. Component molecules' shapes
4. negligible Van der Waal connections
5. development of hydrogen-bonded complexes or dipole-dipole interaction between
Contrary to molecules

The first three cause sound velocity to drop and compressibility to rise, whereas the latter two cause sound velocity to rise and compressibility to fall. The real variance is determined by the outcome. The divergence in adiabatic compressibilities over the mole fraction of ethyl lactate is shown to be negative in Figs. 1(b), 2(b), and 3(b), showing the presence of potent molecular interactions. When surplus values tend to turn increasingly negative, the interaction between the components is stronger. This might be qualitatively explained by the closer proximity of dissimilar molecules causing a decrease in compressibility and volume³¹.

A negative excess compressibility is a sign of strong heteromolecular contact in the liquid mixture, while a positive sign is a sign of weak interaction and is related to dispersion forces (London forces), according to Fort and Moore³². Indicating that a mixture is less compressible than pure liquids, compressibility deviation values bearing a negative sign indicate that the molecules in the mixture are more densely packed than they would be in their pure form³³.

Interstitial accommodation of N,N - Di Methyl Acetamide into the voids of O - Chlorophenol is most favourable in (O - Chlorophenol + N,N - Di Methyl Acetamide), rather than (O - Chlorophenol + N,N - Di Methyl Formamide) and (O - Chlorophenol + Formamide), which leads to the molecular aggregation and thus the more close-packed structure in binary mixtures. Dipole-dipole interactions, the development of acid-base complexes, and the formation of H-bonds (in O - Chlorophenol + Formamide) between the

constituents of O-Chlorophenol and Formamide / N,N-Di Methyl Formamide / N,N-Di Methyl Acetamide in the binary mixture cause an increase in sound velocity, which results in a negative deviation in compressibility.

Accordingly, the order of the interaction between O - Chlorophenol and the investigated amides is as follows: (O - Chlorophenol+N,N - Di Methyl Acetamide) > (O - Chlorophenol+N,N - Di Methyl Formamide) > (O - Chlorophenol+Formamide), based on the magnitude of negative values in β_{ad} .

At any given concentration, adiabatic compressibility's negative values rise as temperature rises. In the binary system O - Chlorophenol+N,N - Di Methyl Acetamide, the mole fraction of O - Chlorophenol where the negative deviation in adiabatic compressibility peaks is around 0.57. At all temperatures, mixture components interact more strongly when dissimilar molecules are closer to one another, as indicated by the negative ad values. As a result, ad also supports the existence of strong specific interactions in the binary mixtures of O-Chlorophenol + Formamide/N,N-Dimethylformamide/N,N-Dimethylacetamide, and the negative values of ad increase with temperature, which implies that the occurrence of specific interactions increases with increased molecular thermal energy³⁴. Hence, values of $\Delta\beta_{ad}$ are observed to follow the trend: (318.15 > 313.15 > 308.15 > 303.15) K.

Intermolecular free length (L_r^E) :

It was discovered that a number of physical or chemical components affected both the sign and size of the computed results. While the chemical contributions entail the breakdown of hydrogen bound complexes, which produces positive values, whereas dispersion forces or weak vander Waal forces are due to physical contributions. The system becomes more ordered as a result of enhanced inter molecular interactions when certain interactions, such as complex formation, dipole-dipole interactions between component molecules, and the production of additional hydrogen bonds, result in negative values.

From Figs. 1(a) to 3(c), it can be observed that values are negative for the binary mixtures of O- chloro phenol and N, N- dimethy lacetamide, O - chlorophenol and N,N-dimethylformamide, and O- chloro phenol and formamide at all temperatures and over the full range of mole fraction, indicating the predominance of strong interaction among the components of hetero molecules. The liquid mixture's structural modifications toward a less compressible phase and closer packing of the molecules, as well as the specific interactions

between unlike molecules in the liquid mixture, are the main causes of the liquid mixture's negative values.

The negative L_r^E values, in accordance with Ramamurthy and Sastry³⁵, refer that the sound wave must move a greater distance. This might be explained by the predominance of interactions between dissimilar molecules. All three systems under study exhibit tendencies that are comparable to adiabatic compressibility at all temperatures. Further supporting the occurrence of molecular connections is the fact that the ad and minima occur at the same concentrations³⁶. According to Jacobson^{37,38}, the inter molecular free length is a better way to study adiabatic compressibility.

When compared to (O - Chlorophenol + N,N - Di Methyl Formamide), the mixture of (O - Chlorophenol + N,N - Di Methyl Acetamide) exhibits high negative values, which indicate stronger interactions in the case of (OCP+DMA) binaries than the other two systems at all reported temperatures. Thus, (O-Chlorophenol + N,N-Di Methyl Acetamide) > (O-Chlorophenol + N,N-Di Methyl Formamide) > (O-Chlorophenol + Formamide) is the order of interaction.

5. Conclusion:

Density, viscosity and ultrasonic speed for the binary mixture O - Chlorophenol (1)+ N,N - Di Methyl Acetamide) / N,N - Di Methyl Formamide / Formamide) have been measured experimentally over the entire composition range at T = (303.15, 308.15, 313.15, 318.15) K. To explore the nature of interaction in the present binary systems, the experimental data have been used to compute the parameters, $\Delta\beta_{ad}$, V^E and L_r^E . The deviations/excess properties are fitted to Redlich Kister type polynomial equations. In the investigated binary mixtures, observed negative values of $\Delta\beta_{ad}$, V^E and L_r^E clearly indicates dominance of specific interaction among the binary liquids. Both adiabatic compressibility ($\Delta\beta_{ad}$) and inter molecular free length (L_r^E) have an inverse relationship with ultrasonic velocity (U). The observed positive/negative values of excess/deviations properties are attributed to the dipole-dipole interactions, specific acid-base interactions, geometrical fitting of smaller molecules into the voids of bigger molecules and Hbonding interactions among the components of hetero-molecules. The order of strong interaction among the component molecules in binary liquids is as follows: (O - Chlorophenol + N,N - Di Methyl Acetamide) > (O - Chlorophenol+N,N - Di Methyl Formamide) > (O - Chlorophenol + Formamide).

Table 3: The values of Redlich - Kister Coefficient and Standard Deviations (σ) of OCP+FA/DMF/DMA systems

OCP+FA						
Deviation in Adiabatic Compressibility ($\Delta\beta_{ad}$)						
T/K	A₀	A₁	A₂	A₃	A₄	σ
303.15K	-6.2735	-6.8261	4.9256	12.2641	-23.6655	0.1238
308.15K	-7.0679	-1.8735	-3.9725	-5.3645	4.8554	0.0324
313.15K	-7.2764	-3.2785	-1.6953	-0.6485	-3.1441	0.0106
318.15K	-7.7951	-4.1000	-0.5909	1.7557	-7.7621	0.0341
Excess Molar Volume(V^E)						
303.15K	-3.1647	-2.6092	-0.5927	0.3214	-3.7202	0.0137
308.15K	-3.0823	-1.8245	-2.2151	-2.2139	1.9447	0.0113
313.15K	-3.1325	-2.2453	-1.4635	-0.6574	-1.1832	0.0074
318.15K	-3.1904	-2.5166	-1.2141	0.2085	-2.6964	0.0185
Int.Mole Free Length(L_f^E)						
303.15K	-0.0970	-0.1172	0.0815	0.2045	-0.3947	0.0021
308.15K	-0.1075	-0.0343	-0.0672	-0.0906	0.0830	0.0005
313.15K	-0.1087	-0.0574	-0.0291	-0.0123	-0.0493	0.0002
318.15K	-0.1137	-0.0710	-0.0109	0.0267	-0.1241	0.0005
OCP+DMF						
Deviation in Adiabatic Compressibility ($\Delta\beta_{ad}$)						
303.15K	-6.6472	0.7664	-1.3698	-0.6563	-0.0356	0.0153
308.15K	-7.2279	0.8436	-1.7793	0.4005	1.6089	0.0121
313.15K	-7.4154	0.9263	-1.9233	0.0640	1.0077	0.0104
318.15K	-7.8858	0.3399	-0.7596	0.6124	-1.0634	0.0274
Excess Molar Volume(V^E)						
303.15K	-2.7666	-0.7168	-0.3960	0.0968	0.3402	0.0102

308.15K	-2.8147	-0.7184	-0.6842	0.0735	0.1428	0.0081
313.15K	-2.8797	-0.6756	-0.9691	-0.1105	0.3649	0.0072
318.15K	-2.9329	-0.6504	-0.9605	-0.0855	-0.1624	0.0054

Int.Mole Free Length(L_f^E)

303.15K	-0.08975	0.01619	-0.0204	-0.0088	0.0003	0.0002
308.15K	-0.09769	0.01737	-0.0255	0.0059	0.0227	0.0002
313.15K	-0.09722	0.01863	-0.0275	0.0015	0.0142	0.0002
318.15K	-0.10115	0.01136	-0.0110	0.0099	-0.0151	0.0004

OCP+DMA

Deviation in Adiabatic Compressibility ($\Delta\beta_{ad}$)

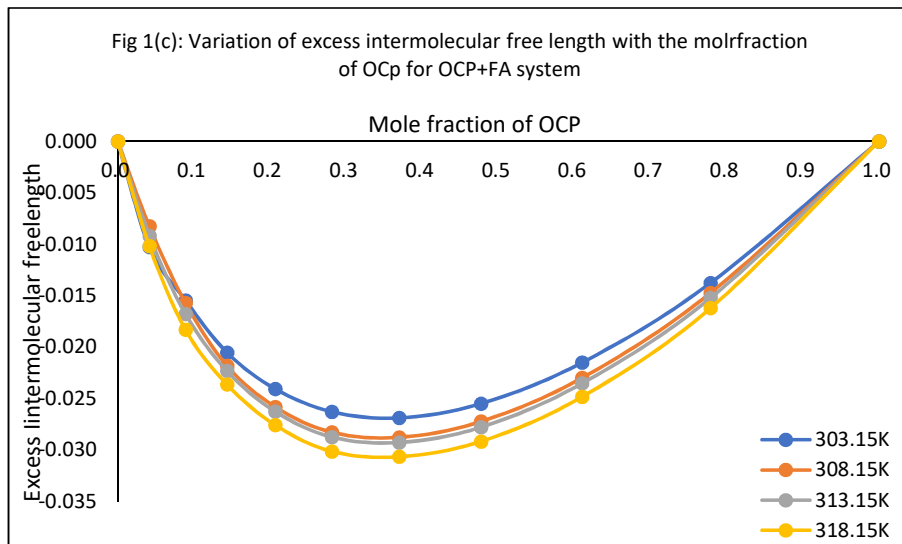
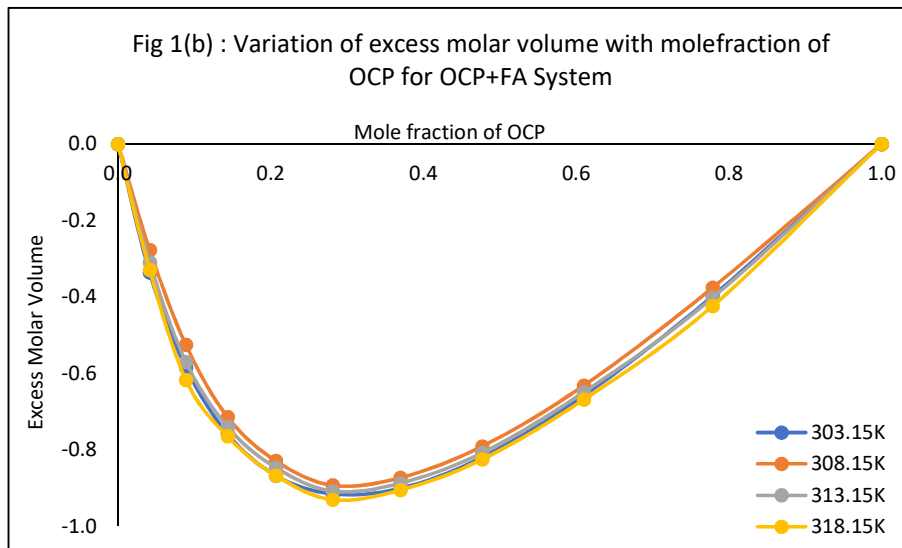
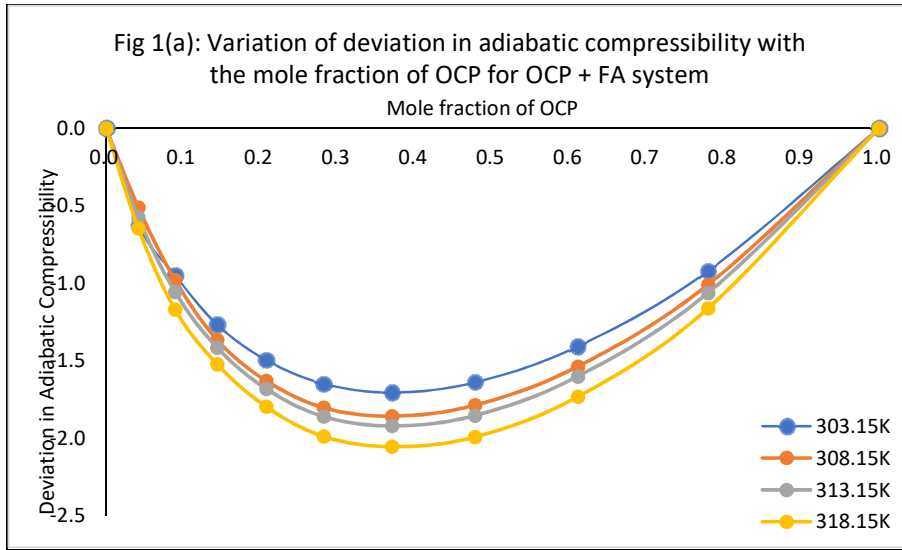
303.15K	-6.3772	1.5674	-1.2981	-0.6670	1.7789	0.0142
308.15K	-6.7912	1.4285	-1.4077	0.6477	2.1722	0.0090
313.15K	-5.2138	5.2713	5.3248	-6.3418	-12.7156	0.0738
318.15K	-7.6358	1.2625	-0.9850	1.2574	0.1576	0.0100

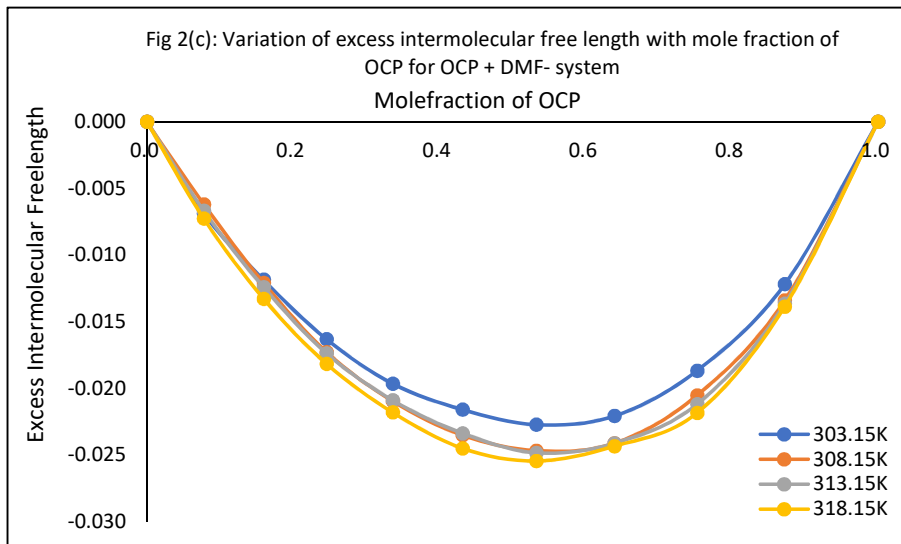
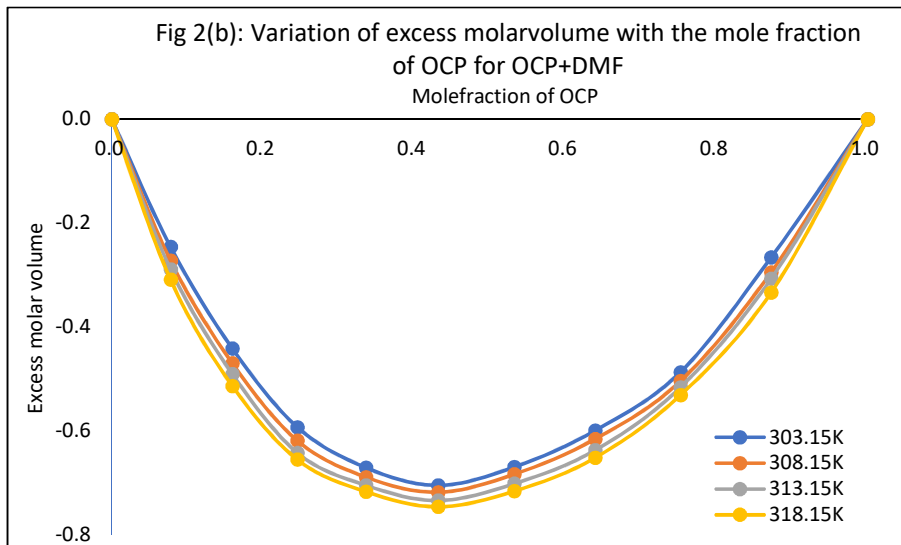
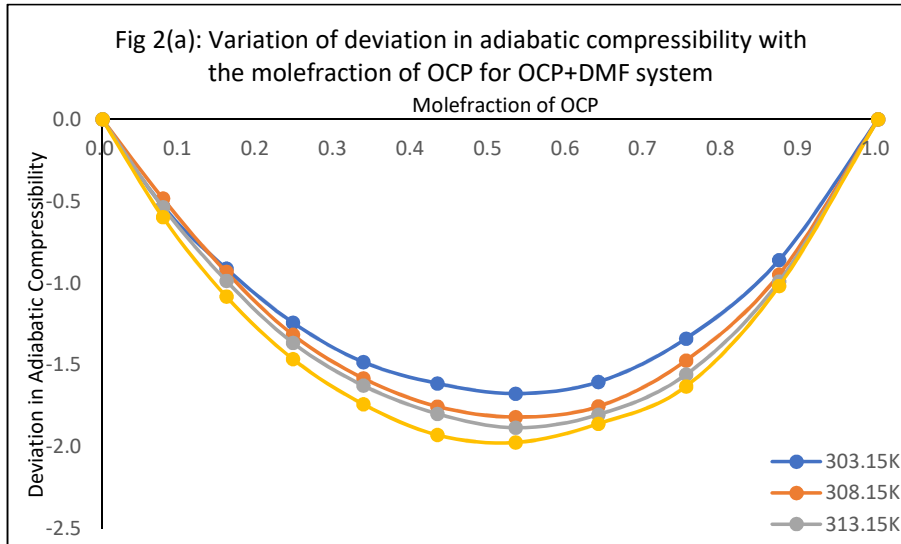
Excess Molar Volume(V^E)

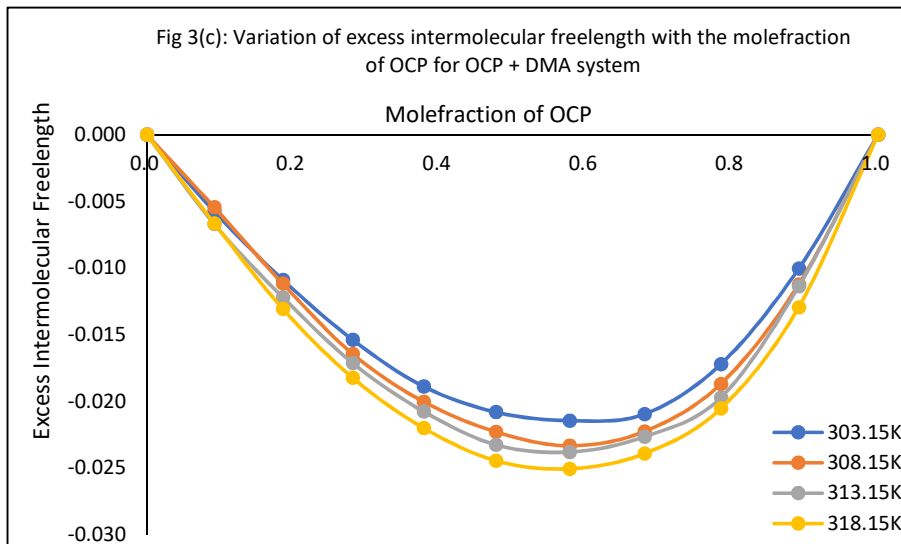
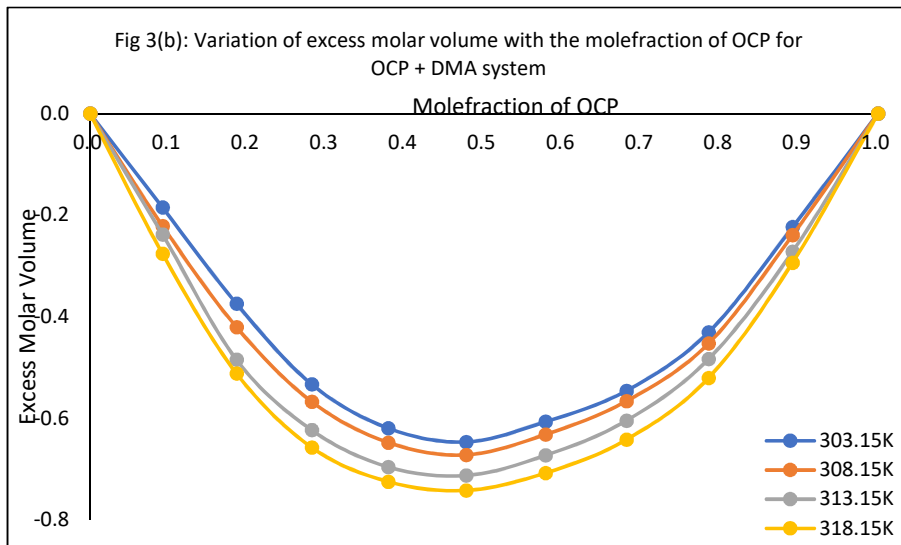
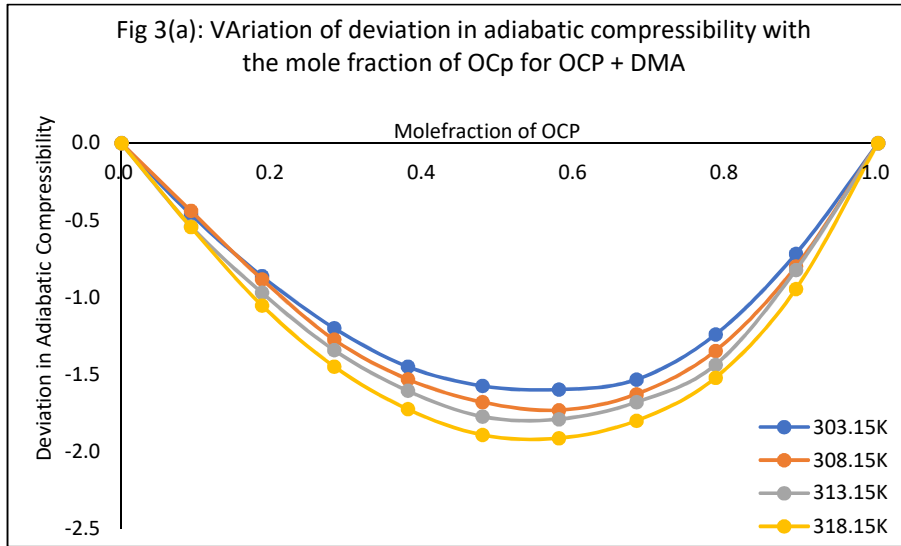
303.15K	-2.5811	-0.2403	-0.1001	0.4172	0.9089	0.0093
308.15K	-2.6803	-0.2917	-0.2237	0.2542	0.6301	0.0094
313.15K	-2.8351	-0.4509	-0.7631	0.6294	1.1700	0.0087
318.15K	-2.9556	-0.3695	-1.0408	0.3000	1.0873	0.0053

Int.Mole Free Length(L_f^E)

303.15K	-0.0846	0.0280	-0.0199	-0.0102	0.0266	0.0002
308.15K	-0.0904	0.0258	-0.0209	0.0087	0.0308	0.0001
313.15K	-0.0663	0.0776	0.0707	-0.0869	-0.1738	0.0010
318.15K	-0.0990	0.0230	-0.0142	0.0178	0.0015	0.0001







References

1. H.P. Vankar, V.A. Rana. *Materials Today: Proceedings*, 47(2), 722 (2021)
2. Nitin Srivastava, B.K. Rathour, Soniya Singh, Shashi Singh. *Chemical Physics Impact*, 6, 10014 (2023)
3. N. Srivastava, B.K. Rathour, S. Singh, *Russ. J. Phys. Chem.*, 96, 15 (2022)
4. Archana Saxena and Chandra Mohan Saxena, 13(08), 2159 (2022)
5. S.K.Bindhani, G.K.Roy &Y.K.Mohanty, *Russ J of Physical Chemistry A*. 94, 1827 (2020)
6. Dharendra Kumar Sharma, Seema Agarwal and Akil Khan, *Der Pharma Chemica*, 14(10) (2022)
7. Xin-Xue Li, Gui-Chen Fan, Yan-Wei Wang, Min Zhang, Yi-Qiang Lu, *J Mol Liq*, 151, 62 (2010).
8. StephanieLOutcalt , Arno Laesecke, Tara J Fortin, *J Mol Liq*,15, 50 (2010)
9. Yasmin M, Singh K P, Praveen S,Gupta M & Shukla J P, *Acta physica Polonica*, 115, 890 (2009)
10. Anil Kumar Nain, *Fluid Phase Equilibria*, 265, 46 (2008)
11. Juan AntonioGonzalez, Ismael Mozo, Marta Fernandez, Isaias Garcia de la Fuente & Jose Carlos Cobos, *J Mol Liq*, 133,2007, ,pp 77.
12. Y.-W. Sheu and C. H. Tu, *Journal of Chemical and Engineering Data*, 51(2), 545–553 (2006).
13. J. N. Nayak, M. I. Aralaguppi, and T. M. Aminabhavi, *Journal of Chemical and Engineering Data*, 48, 1489 (2003).
14. W. V. Steele, R. D. Chirico, A. B. Cowell, S. E. Knipmeyer, and A. Nguyen, *Journal of Chemical and Engineering Data*, 47(4), 667 (2002).
15. N. Indrswati, Mudjiati, F. Wicaksana, H. Hindarso, and S. IsmadjiS, *J of Chem and Eng Data*, 46(3), 696 (2001).

16. M. Hasan, A. P. Hiray, U. B. Kadam, D. F. Shirude, K. J. Kurhe, and A. B. Sawant, *J of Chem and Eng Data*, 55(1), 535 (2010).
17. Reddick J A, Bunger W B & Sankano T K, *Organic Solvents*, Vol II 4th Ed, Weissberger A Ed, Wiley Interscience, New York, 1986.
18. Weissberger A, Proskaner E S, Riddick J A & Toops E E Jr, *Organic Solvents*, Vol II 2 nd Ed, Weissberger A Ed, Wiley Interscience, New York, 1955.
19. P.S. Nikam, L.N. Shirsat and M. Hasan, *Journal of Indian Chemical Society*, 77, 244 (2000)
20. G. R. Satyanarayana.; D. Bala Karuna Kumar.; K. Sujatha.; G. Lakshmanarao and C. Rambabu., *Journal of Molecular Liquids.*, 2016, 216, 256
21. T.Kalimulla , Shaik.Babua, D.Das , M. Gowrisankar , K.Govinda Rao, *J. Pharm. Sci. & Res.*, 11(7), 2645, (2019)
22. B.Nagarjun, A,Sharma, G.R.Rao, C.Rambabu, *J of Thermodynamics*, <https://doi.org/10.1155/2013/285796>, (2013)
23. H. Eyring J. F. Kincaid, *J Chem Phys*, 6, 620 (1938)
24. Sathyanarayana, N. Satyanarayana, *J. Chem. Thermodyn.*, 39, 16 (2007)
25. K. Liu, E. Kiran, *Viscosity, Ind. Eng. Chem. Res.*, 46, 5453 (2007)
- 24.S.Thrumaran, T.Alli, D.Priya and A.Selvi, *e J of Chemistry*, 7(S1), 217 (2010)
26. P. Umadevi, K. Rambabu, M.N. Rao, K.S. Rao, C. Rambabu, *Phys. Chem. Liq.* 30, 29 (1995).
27. A.N. Kannappan¹, S. Thirumaran, R. Palani, *J. Phys. Sci.* 20, 97 (2009).
28. K. Rajagopal, S. Chenthilnath, *Indian J. Pure & Appl. Phys.* 48, 326 (2010) .
29. Sk. Md Nayeem, M. Kondaiah, K. Sreekanth, D. Krishna Rao, *Arabian J. Chem.* <http://dx.doi.org/10.1016/j.arabjc.2015.08.005>, 2015.
30. M. Rastogi, A. Awasthi, M. Gupta, and J.P. Shukla, *Indian J. Pure & Appl. Phys.* 40 () 256.
31. 30.J.G. Baragi, V.K. Mutalik, S.B. Mekali, *Int. J. Pharma Bio Sci.* 3 (2013) 185.

32. K.S. Reddy, *J. Chem. Thermodyn.* 16, 943 (1984)
33. R.J. Fort, W.R. Moore, *J. Trans. Faraday Soc.* 61, 2102 (1965)
34. L.Syamala, C.Venkatramana, K.Narasimha Rao, P. Sivakumar, P. Venkateswarlu, R.L. Gardas, *Fluid Phase Equilib.* 397, 68 (2015)
35. S.Comelli, R.Ottani, C.Francesconi, J. Castellari, *J. Chem. Eng. Data* 47, 93 (2002)
36. Ramamurthy M,& Sastry O S, *Indian J Pure Appl Phys*, 21, 579 (1983)
37. A.M.E. Raj, L.B. Resmi, V.B. Jyothy, M. Jayachandran & C. Sanjeeviraja, *Fluid Phase Equib.*, 281 (2009) 78.
38. B. Jacobson, *Acta Chem Scand.* 5 (1951) 1214.
39. B. Jacobson, *Acta Chem Scand.* 34 (1975) 121.