

# EXCESS TRANSPORT PROPERTIES OF TERNARY MIXTURES OF CRESOLS WITH BENZALDEHYDE AND TETRACHLOROMETHANE SOLUTION AT 303, 308 AND 313 K

R. Palani<sup>1</sup> and S. Kalavathy<sup>2</sup>

<sup>1</sup>Department of Physics, D.D.E., Annamalai University, Annamalainagar-608 002, India.

<sup>2</sup>Department of Physics, Sri Chandrasekarendra Saraswathi Viswa Mahavidyalaya, Enathur, Kanchipuram - 631 561

E\_mail: palani\_physics06@yahoo.co.in

**Abstract:** Density ( $\rho$ ), viscosity ( $\eta$ ) and ultrasonic velocity ( $U$ ) of ternary liquid mixtures of cresols namely *o*-cresol, *m*-cresol and *p*-cresol with benzaldehyde and tetrachloromethane solution have been determined at 303, 308 and 313 K over the entire composition range. The measured data has been utilized to estimate the excess viscosity ( $\eta^E$ ), excess Gibb's free energy ( $\Delta G^E$ ) and Grunberg's interaction parameter ( $d$ ). The variation of excess parameter indicates that there are intermolecular interactions among components of the ternary mixtures that lead to possible hydrogen bond formation between unlike molecules.

**Keywords:** Viscosity, ultrasonic velocity, gibb's free energy, hydrogen bond, interaction parameter.

## 1. Introduction

Viscosity and ultrasonic measurements are extensively used to study the molecular interaction in pure liquids and liquid mixtures. When two liquid mixtures are mixed together the resulting changes in physical and acoustical properties can be considered as a sum of several contributions due to free volume change, change in energy, change in molecular orientations and steric hindrances. The mixing of different compounds gives rise to solutions that generally do not behave as ideal solutions. The deviation from ideality is expressed by many acoustical variables particularly by excess or residual extensive properties<sup>1</sup>. The study of the solution properties of the liquid mixtures finds applications in industrial and technological process<sup>2</sup>.

The carbonyl group is a part of several biologically important molecules such as proteins, lipids and hormones<sup>3</sup>. Phenols are widely used for phonograph records, wood preservatives and selective weed killing. Cresols constitute one of the most important groups of aromatic organic compounds, which occur in three isomeric forms. They find extensive use in various fields as disinfectants, organic intermediates, textile scouring agents, herbicides, surfactants and in the production of few phenolic resins, salicylaldehyde, cummarin etc., Both ortho- and para-cresols are used as end product in azo dyes<sup>4</sup>. Many researchers<sup>5</sup> have studied the ultrasonic properties of cresols in different organic solvents. Moreover, literature survey indicates that no physico-chemical studies on these systems have been reported. Therefore, the study of intermolecular interactions in these systems will be interesting owing to their applications. Keeping these important aspects in view, the measurements on ultrasonic velocity, density and viscosity and their related excess transport parameters for mixed solvent systems of benzaldehyde and tetrachloromethane with *o*-cresol, *m*-cresol and *p*-cresol at 303, 308 and 313 K have been undertaken. The variations of excess parameters have been used to explain the nature and extent of intermolecular interaction in these mixtures.

## 2. Materials and Methods

All the chemicals used in this present research are analytical reagent (AR) and spectroscopic reagent (SR) grades of minimum assay of 99.9% obtained from E-Merck, Germany and SdFine

chemicals, India, which were used as such without further purification. The purities of the above chemicals were checked by density determination at 303, 308 and 313K  $\pm$  0.1K. which showed an accuracy of  $\pm 1 \times 10^{-4}$  gcm<sup>-3</sup> with the reported values<sup>3,6-8</sup>. The ternary liquid mixtures of different known compositions were prepared in stopper measuring flasks. The density, viscosity and ultrasonic velocity were measured as a function of composition of the ternary liquid mixture at 303, 308 and 313 K.

The substitute phenols such as o-cresol, m-cresol and p-cresol were added to a binary mixtures of benzaldehyde and tetrachloromethane. For this purpose, binaries with fixed mole ratios  $X_1/X_2 \cong 3:1$  were prepared by volume. The density was determined using a specific gravity bottle by relative measurement method. The weight of the sample was measured using electronic digital balance with an accuracy of  $\pm 0.1$  mg (Model: Shimadzu AX-200). An Ostwald's viscometer (10 ml) was used for the viscosity measurement. Efflux time was determined using a digital chronometer to within  $\pm 0.01$ s. An ultrasonic interferometer having the frequency of 3 MHz (MITTAL ENTERPRISES, New Delhi, Model: F-81) with an overall accuracy of  $\pm 0.1\%$  has been used for velocity measurement. An electronic digitally operated constant temperature bath (Raaga Industries) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. The accuracy in the temperature measurement is  $\pm 0.1$  K.

### 3. Theory and Calculation

Various acoustical and transport parameters are calculated from the measured data such as

$$\text{Adiabatic Compressibility } \beta = \frac{1}{U^2 \rho} \dots \dots (1)$$

The Gibb's free energy can be estimated from the following relation.

$$\Delta G = K_B T \ln \left( \frac{K_B T}{h} \right) \dots \dots (2)$$

where  $K_B$  is the Boltzmaan's constant ( $1.38 \times 10^{-23}$  JK<sup>-1</sup>), T the absolute temperature, 'h' the Planck's constant ( $6.626 \times 10^{-34}$  Js<sup>-1</sup>) and  $\tau$  is the relaxation time ( $\tau = \frac{4}{3} \eta \beta$ ).

Excess values of the above parameters can be determined using

$$A^E = A_{\text{exp}} - A_{\text{id}} \dots \dots (3)$$

where  $A_{\text{id}} = \sum A_i X_i$ ,  $A_i$  is any acoustical

parameters and  $X_i$  the molefraction of the liquid component. Grunberg and Nissan<sup>9</sup> formulated the following relation to determine the interaction parameter (d) regarded as a measure of the strength of molecular interactions between the mixing components.

$$\ln \eta_{\text{mix}} = X_1 \ln \eta_1 + X_2 \ln \eta_2 + X_3 \ln \eta_3 + X_1 X_2 X_3 d \dots (4)$$

### 4. Results and Discussion

The experimental values of density ( $\rho$ ), viscosity ( $\eta$ ) and ultrasonic velocity (U) of pure liquids and for the ternary liquid systems at 303, 308 and 313K are given in Table 1 & Table 2. The values of excess viscosity ( $\eta^E$ ), Gibb's free energy ( $\Delta G^E$ ) and the Grunberg's interaction parameter (d) are shown in Table 3. Further, the variation of these excess parameters of studied systems with molefraction of cresols at 303, 308 and 313 K are shown in Fig. 1 & Fig. 2 and the curves are drawn using least square fitting.

The excess properties are found to be more sensitive towards intermolecular interaction between the component molecules of liquid mixtures. The sign and extent of deviation of excess properties depend on the strength of interaction between unlike molecules<sup>10</sup>. According to Fort *et al.*<sup>11</sup>, the excess viscosity gives the strength of the molecular interaction between the interacting molecules. For systems where dispersion, induction and dipolar forces which are operated by the values of excess viscosity are found to be negative, whereas the positive values shows the existence of specific interactions leading to the formation of complexes in liquid mixtures.

Table1: Values of Density ( $\rho$ ), Viscosity ( $\eta$ ) and Ultrasonic Velocity (U) of Pure Liquids at 303, 308 and 313K

Organic liquids		$\rho/(\text{kg m}^{-3})$			$\eta/(\times 10^{-3} \text{ Nsm}^{-2})$			$U/(\text{m.s}^{-1})$		
		303K	308K	313K	303K	308K	313K	303K	308K	313K
Benzaldehyde	Exp. value	1055.3	1032.2	1027.0	1.3997	1.3855	1.3774	1451.7	1442.4	1434.6
	Literature value	1049.0 <sup>3</sup>	-	-	-	-	-	1464.0 <sup>3</sup>	-	-
Tetrachloromethane	Exp. value	1561.9	1546.9	1531.4	0.8679	0.8521	0.7919	899.6	889.6	864.6
	Literature value	1574.8 <sup>6</sup>	-	-	-	-	-	907.0 <sup>6</sup>	-	-
o-cresol	Exp. value	1044.3	1041.7	1039.6	8.1797	8.0413	7.1458	1526.4	1521.6	1507.2
	Literature value	1048.7 <sup>7</sup>	-	-	8.6430 <sup>7</sup>	-	-	1525.0 <sup>7</sup>	-	-
m-cresol	Exp. value	1027.0	1023.6	1020.9	4.5482	3.7896	2.3430	1431.2	1424.4	1421.8
	Literature value	1030.6 <sup>8</sup>	-	-	-	-	-	-	-	-
P-cresol	Exp. value	1016.4	1013.4	1011.4	3.8887	2.5679	2.3936	1400.4	1370.2	1350.5
	Literature value	1026.4 <sup>8</sup>	-	-	-	-	-	-	-	-

Table 2: Values of Density ( $\rho$ ), Viscosity ( $\eta$ ) and Ultrasonic Velocity (U) at 303, 308 and 313K for

Molefraction (X <sub>3</sub> )	$\rho/(\text{kg m}^{-3})$			$\eta/(\times 10^{-3} \text{ Nsm}^{-2})$			$U/(\text{m.s}^{-1})$		
	303K	308K	313K	303K	308K	313K	303K	308K	313K
System-I : benzaldehyde (X <sub>1</sub> ) + tetrachloromethane (X <sub>2</sub> ) + o-cresol (X <sub>3</sub> ) [(X <sub>1</sub> )/ (X <sub>2</sub> )=3:1]									
0	1410.5	1388.1	1371.1	1.2585	1.2354	1.2214	1176.4	1161.2	1159.1
0.02	1408.4	1374.1	1364.7	1.3280	1.2946	1.2715	1182.2	1174.1	1167.2
0.04	1390.5	1368.7	1352.8	1.3821	1.3481	1.3375	1191.4	1184.3	1170.3
0.06	1384.1	1361.9	1324.7	1.4800	1.4186	1.3943	1197.9	1189.1	1175.8
0.08	1374.1	1345.5	1310.5	1.5248	1.4586	1.4494	1208.6	1194.2	1189.3
0.10	1369.1	1321.9	1296.8	1.5712	1.5186	1.4927	1227.1	1218.7	1201.8
System-II : benzaldehyde (X <sub>1</sub> ) + tetrachloromethane (X <sub>2</sub> ) + m-cresol (X <sub>3</sub> )									
0	1410.5	1388.1	1371.1	1.2585	1.2354	1.2214	1176.4	1161.2	1159.1
0.02	1397.2	1366.3	1358.3	1.3110	1.2842	1.2475	1179.2	1165.8	1163.2
0.04	1382.8	1351.7	1349.2	1.3658	1.3290	1.2611	1185.6	1169.1	1164.9
0.06	1373.1	1349.1	1314.1	1.3947	1.3557	1.2851	1192.3	1174.4	1172.1
0.08	1369.9	1326.9	1301.4	1.4589	1.3989	1.3183	1203.9	1183.2	1179.1
0.10	1355.6	1319.4	1284.2	1.4918	1.4403	1.3403	1216.3	1199.4	1197.0
System-III : benzaldehyde (X <sub>1</sub> ) + tetrachloromethane (X <sub>2</sub> ) + p-cresol (X <sub>3</sub> )									
0	1410.5	1388.1	1371.1	1.2585	1.2354	1.2214	1176.4	1161.2	1159.1
0.02	1395.1	1361.8	1354.7	1.3032	1.2673	1.2456	1178.3	1164.6	1161.0
0.04	1380.3	1348.7	1344.2	1.3343	1.2941	1.2598	1181.1	1168.5	1163.2
0.06	1361.8	1346.6	1312.1	1.3922	1.3204	1.2934	1184.9	1173.2	1168.4
0.08	1354.9	1321.1	1299.2	1.4389	1.3493	1.3132	1192.9	1182.2	1172.3
0.10	1349.3	1311.2	1274.9	1.4905	1.3675	1.3365	1203.4	1196.2	1192.1

Table 3: Excess Values of Viscosity ( $\eta^E$ ), Gibbs Free Energy ( $\Delta G^E$ ) and Grunberg's Interaction Parameter (d) at 303, 308 and 313K for

Molefraction ( $X_3$ )	$-\eta^E/(\times 10^{-3} \text{ Nsm}^{-2})$			$\Delta G^E/(\times 10^{-23} \text{ KJ mol}^{-1})$			d		
	303K	308K	313K	303K	308K	313K	303K	308K	313K
System-I : benzaldehyde ( $X_1$ ) + tetrachloromethane ( $X_2$ ) + o-cresol ( $X_3$ ) [( $X_1$ )/( $X_2$ )=3:1]									
0	0.0083	0.0168	0.0197	1.13	1.45	1.15	0.07	0.04	0.10
0.02	0.0770	0.0933	0.0868	5.72	2.34	1.35	8.11	4.46	6.30
0.04	0.1611	0.1756	0.1398	7.28	0.33	10.46	4.55	2.74	5.44
0.06	0.2015	0.2409	0.2011	18.10	6.16	19.23	6.25	3.25	4.38
0.08	0.2950	0.3368	0.2641	12.95	5.74	17.79	4.28	1.78	3.67
0.10	0.3869	0.4125	0.3385	1.83	2.66	13.41	3.07	1.66	2.65
System-II : benzaldehyde ( $X_1$ ) + tetrachloromethane ( $X_2$ ) + m-cresol ( $X_3$ )									
0	0.0083	0.0168	0.0197	1.13	1.45	1.15	0.07	0.04	0.10
0.02	0.0214	0.0187	0.0156	9.08	17.39	6.01	7.79	6.40	7.20
0.04	0.0322	0.0146	0.0241	15.13	18.57	7.49	6.23	5.03	3.38
0.06	0.0689	0.0197	0.0221	12.32	15.68	15.99	3.83	3.23	2.90
0.08	0.0604	0.0062	0.0149	13.69	20.47	20.80	4.50	3.22	3.23
0.10	0.1031	0.0156	0.0109	9.24	15.62	16.53	3.52	3.13	2.90
System-III : benzaldehyde ( $X_1$ ) + tetrachloromethane ( $X_2$ ) + p-cresol ( $X_3$ )									
0	0.0083	0.0168	0.0197	1.13	1.45	1.15	0.07	0.04	0.10
0.02	0.0159	0.0112	0.0185	8.75	10.69	6.88	7.00	4.88	6.66
0.04	0.0173	0.0107	0.0274	11.47	14.29	7.59	3.76	3.43	3.11
0.06	0.0319	0.0096	0.0168	21.66	14.01	18.40	4.59	2.93	3.42
0.08	0.0376	0.0081	0.0201	22.56	18.22	20.30	4.40	2.83	2.79
0.10	0.0384	0.0162	0.0198	22.43	11.79	16.24	4.49	2.28	2.58

The excess viscosity (Fig.1) is negative through the whole range of concentration in all the three systems. From the analysis and close observation it is found that they decrease with increasing the molefraction of  $X_3$  whereas it increases with the

raising of temperature. This behaviour shows that the existence of molecular interaction between the components of mixture for all the systems studied.

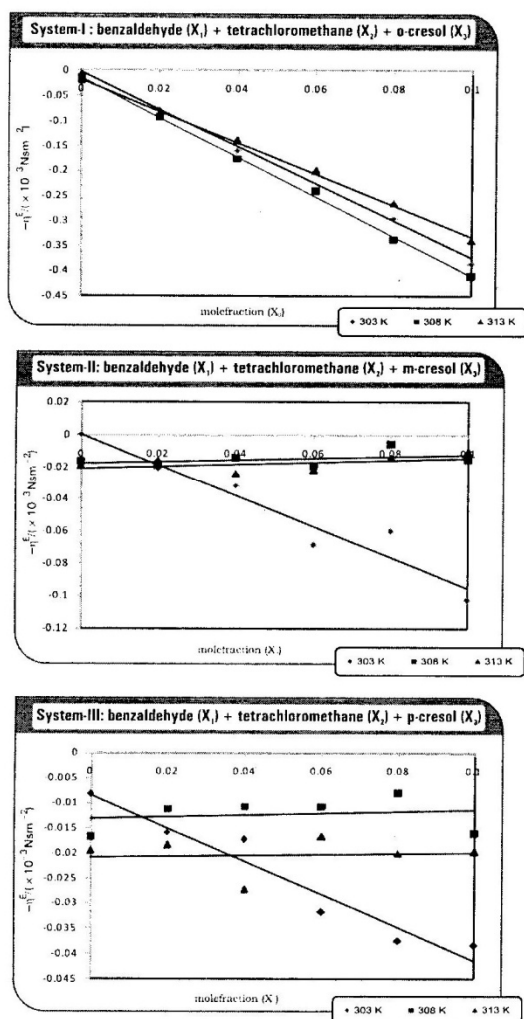


Fig.1 Variation of excess viscosity ( $\eta^E$ ) of benzaldehyde and tetrachloromethane solvent with mole fraction of cresols ( $X_3$ ) at 303, 308 and 313 K

The variation of excess Gibb's free energy shown in Fig. 2, are found to be positive in all the systems studied. The values of  $\Delta G^E$  increases with increasing the molefraction of  $X_3$  but it decreases with the raising of temperature. According to Reed *et al.*,<sup>12</sup> the positive value of  $\Delta G^E$  may be attributed to specific interactions like hydrogen bonding and charge transfer while negative values are due to the dominance of dispersion forces. In the present investigation the increasing positive  $\Delta G^E$  values shows the strong interaction between the unlike molecules and vice-versa.

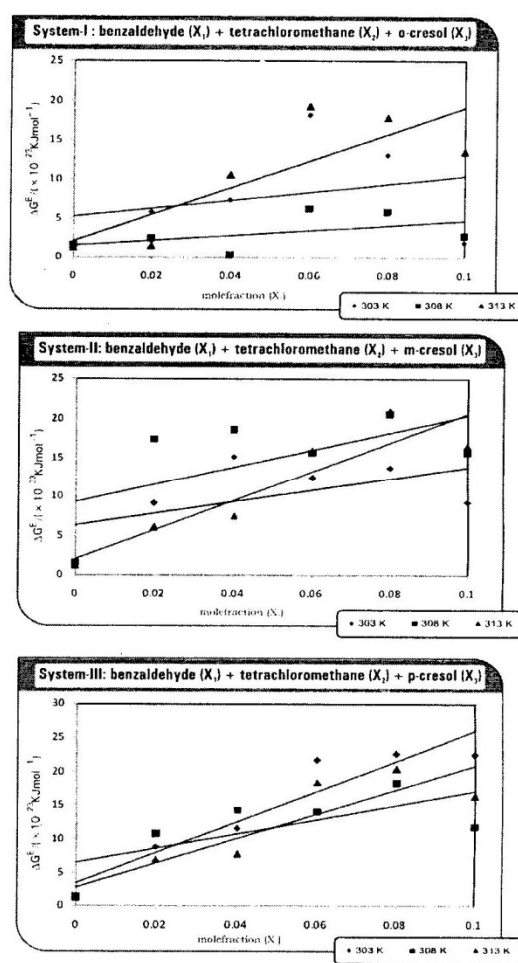


Fig.2 Variation of excess Gibbs free energy ( $\Delta G^E$ ) of benzaldehyde and tetrachloromethane solvent with mole fraction of cresols ( $X_3$ ) at 303, 308 and 313 K

The interaction parameter 'd' in equation Grunberg *et al.*,<sup>9</sup> is a measure of the strength of interaction, between the mixing components. d-values were studied to show the various types of interaction<sup>13</sup> as follows: Large and positive d-value indicated strong specific interaction; small positive value indicated weak specific interaction; large negative value indicated no specific interaction. It is evident from Table-3 that d-value is positive and it is decreases with increasing the mole fraction of  $X_3$  as well as temperature for all systems studied. The positive value of 'd' may be attributed to the dominance of specific interaction arising from the making of hydrogen bonds between hydrogen atom of cresols and carbonyl oxygen atoms of benzaldehyde.

## 5. Conclusion

Excess transport properties of ternary liquid mixtures of cresols in benzaldehyde and tetrachloromethane at 303, 308 and 313K are considered to be a reflecting agent of magnitude of polarity and size of the molecules in the interaction. The result of excess properties reveal that the strong molecular interaction exists in the mixtures which may be due to the dominance of hydrogen bonding and charge transfer between the mixing components. The strength of interaction tends to weaker with rising of temperature which may due to the presence of weak inter molecular forces and thermal dispersion forces.

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Dr. R. Palani is an Associate Professor in the Department of Physics, Annamalai University, Chidambaram 608002, India. He has 15 years of teaching experience and his field of interest is Advanced Electronics and Ultrasonics. He has over 50 international journal papers.



Dr. S. Kalavathy is an Associate Professor in the Department of Physics, Alpha College of Engineering, Chennai, India. She has 15 years of teaching experience and his field of interest is Applied Physics and Ultrasonics. She has 4 national journal papers.