



# ULTRASONIC STUDY OF INTERMOLECULAR ASSOCIATION THROUGH HYDROGEN BONDING IN TERNARY LIQUID MIXTURES

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## ABSTRACT

The ultrasonic velocity, density and viscosity have been measured for the liquid mixtures of cresols namely, m-cresols, o-cresols and p-cresols with N,N-Dimethyl formamide (DMF) in CCl<sub>4</sub> at 303, 308 and 313°K. The experimental data have been used to calculate the acoustical parameters such as adiabatic compressibility ( $\beta$ ), free length ( $L_f$ ), free volume ( $V_f$ ), internal pressure ( $\pi_i$ ), acoustic impedance ( $Z$ ) and molar volume ( $V_m$ ). The excess values of some of the above parameters have also been evaluated and fitted to Redlich-Kister Polynomials and the results are interpreted in terms of molecular interactions present in the mixtures.

**Keywords:** adiabatic compressibility, free length, free volume, acoustic impedance, internal pressure, molar volume, excess values.

## 1. INTRODUCTION

The study of molecular interaction in the liquid mixtures is of considerable in the elucidation of the structural properties of the molecules. The intermolecular interactions influence the structural arrangement along with the shape of the molecules. Dielectric relaxation studies of polar molecules in non-polar solvent using microwave absorption method have been widely used to study the molecular structures including the molecular interactions in liquid mixtures [1,2]. Since, acoustic parameters provide a better insight into molecular environments in liquid mixtures, it seemed important to study molecular interactions which motivated the authors to carry-out the present investigation in the ternary liquid mixtures of cresols (m- cresols, o-cresols and p-cresols) with N-N dimethyl formamide (DMF) in a non-polar solvent ccl<sub>4</sub> using ultrasonic technique. Apart from measuring the ultrasonic velocity, density and viscosity, other acoustical parameters and some of their excess values have also been evaluated for these ternary liquid mixtures at temperatures 303.308 and 313K, respectively. The following are the three ternary liquid systems which have been taken up for the present study,

- System-I      o-cresols      + CCl<sub>4</sub> + DMF
- System-II     p-cresols      + CCl<sub>4</sub> + DMF
- System-III    m-cresols      + CCl<sub>4</sub> + DMF

## 2. MATERIALS AND METHODS

The chemicals CCl<sub>4</sub>, DMF, m- cresol, o- cresol, p- cresol used in the study were the products from S.D fine. Chem. Ltd and E-Merck. All compounds were of AR grade with minimum assay of 99.9%. Therefore all chemicals were used without further purification. The densities of pure liquids and their ternary mixtures were measured by using single capillary pycnometer (made of Borosil glass). The capillary, with graduated marks, had a uniform bore and could be closed by a well-fitting glass cap. The marks on the capillary were calibrated by using triple-distilled water. The densities of pure water at required temperatures were taken from the literature [3].

The accuracy in density measurements was found to be  $\pm 0.0001 \text{ kg m}^{-3}$ . The ultrasonic speeds in pure liquids and in their mixtures were measured by using a single-crystal variable-path ultrasonic interferometer [Mittal enterprises, New Delhi] operating at 3MHz with an accuracy of  $\pm 3 \text{ms}^{-1}$ . The viscosities of pure liquids and their binary mixtures were measured by using Ubbelohde-type suspended level viscometer. The viscometer was allowed to stand in a thermostatic water bath for 30 min so that the thermal fluctuations in viscometer were minimized.

## 3. THEORY AND CALCULATIONS

The adiabatic compressibility is found by

$$\beta = \frac{1}{\rho U^2} \quad (1)$$

The free length ( $L_f$ ) is given by the relation,

$$L_f = K_T \beta^{1/2} \quad (2)$$

Where  $K_T$  is the temperature dependent constant.

The free volume ( $V_f$ ) is measured by using the relation,

$$V_f = \left[ \frac{M_{\text{eff}} U}{K \eta} \right]^{3/2} \quad (3)$$

Where  $M_{\text{eff}}$  is the effective molecular weight ( $M_{\text{eff}} = \sum m_i x_i$  in which  $m_i$  and  $x_i$  are the molecular weight and the mole fraction of the individual constituents respectively).

The internal pressure is calculated by

$$\pi_i = bRT \left[ \frac{K \eta}{U} \right]^{1/2} \left[ \frac{\rho^{2/3}}{M^{7/6}} \right] \quad (4)$$

Where  $b$  stands for cubic packing which is assumed to be 2 for liquids and  $K$  is a dimensionless constant independent of temperature and nature of liquids and its value is  $4.281 \times 10^9$ ,  $T$  is the absolute temperature and  $M_{\text{eff}}$  is the effective molecular weight. Where  $K$  is Boltzmann's constant and  $h$  is the Planck's constant.

The specific acoustic impedance is given by



$$Z = U\rho \quad (5)$$

Excess parameters ( $A^E$ ) by definition; represent the difference between the parameters of real mixtures  $A_{exp}$  and those corresponding to an ideal mixture  $A_{id}$ .

$$A^E = A_{exp} - A_{id} \quad (6)$$

Where  $A_{id} = \sum_{i=1}^n A_i X_i$ ,  $A_i$  is any acoustical parameters

and  $X_i$  the mole fraction of the liquid components.

The some of the excess properties of were fitted to Redlich-Kister [4] Polynomial,

$$Y^E = x_1 x_3 \sum_{i=1}^k A_i (x_1 - x_2)^i \quad (7)$$

Where  $Y^E$  refer to excess properties,  $x_1$  and  $x_3$  are the mole fraction of the components of the ternary mixtures. The coefficients ( $A_i$ ) were obtained by fitting equation (8) to experimental values using a least square regression method. In each case, the optimal number of coefficients was ascertained from an approximation of the variation in the standard deviation ( $\sigma$ ). The calculated values of  $A_i$

along with the tabulated standard deviations ( $\sigma$ ) are listed in the Table-6. The standard deviation ( $\sigma$ ) was calculated using the equation

$$\sigma^2 = \frac{1}{n-m} [Y_{expt}^E - Y_{cal}^E]^2 \quad (8)$$

Where  $n$  is the number of data points and  $m$  is the number of coefficients.

#### 4. RESULTS AND DISCUSSIONS

The values of density ( $\rho$ ), Viscosity ( $\eta$ ), ultrasonic velocity ( $u$ ) were taken for the three systems at three temperatures are displayed in the Table-1. From these observed values various acoustical parameters like adiabatic compressibility ( $\beta$ ), frelength ( $L_f$ ), free volume ( $V_f$ ), internal pressure ( $\pi_i$ ), acoustic impedance ( $Z$ ), molar volume ( $V_m$ ) have been evaluated and is presented in the Tables 2 and 3. The excess values of some of these acoustical parameters are also calculated and are displayed in the Tables 4 and 5.

**Table-1.** Density ( $\rho$ ), viscosity ( $\eta$ ) and ultrasonic velocity ( $U$ ) of.

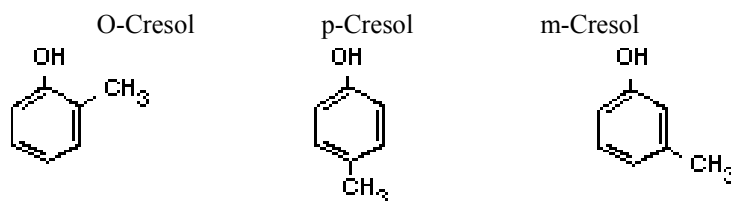
Mole fraction		Density $\rho/(kg/m^3)$			Viscosity $\eta/(\times 10^{-3} NSm^{-2})$			Velocity $U/(m/s)$		
		Temperature ( $^{\circ}K$ )								
$X_1$	$X_3$	303	308	313	303	308	313	303	308	313
<b>System I</b>										
0.0000	0.6000	1229.40	1226.38	1221.23	0.8725	0.8473	0.7389	1149.47	1148.48	1021.20
0.1000	0.5000	1235.32	1233.24	1228.73	1.1054	1.0094	0.9393	1170.96	1156.8	1144.08
0.2000	0.4000	1237.31	1235.17	1230.41	1.3536	1.2778	1.1616	1176.20	1171.97	1151.16
0.3056	0.2871	1240.60	1237.12	1234.79	1.7348	1.6285	1.4868	1178.04	1172.67	1158.00
0.4000	0.2000	1243.30	1240.24	1236.21	1.9987	1.8902	1.5912	1179.33	1173.53	1159.63
0.4998	0.1001	1245.87	1241.08	1238.73	2.2548	2.0723	1.8097	1192.44	1178.78	1164.42
0.6000	0.0000	1248.01	1244.96	1240.54	2.5316	2.3148	2.001	1204.2	1197.06	1184.23
<b>System II</b>										
0.0000	0.6000	1229.40	1226.38	1222.23	0.8725	0.8203	0.7655	1159.3	1148.48	1121.20
0.1012	0.4942	1231.91	1229.20	1225.17	1.1413	1.0332	0.9831	1170.23	1161.48	1151.03



0.2000	0.4000	1239.75	1236.12	1230.21	1.3860	1.3585	1.2539	1183.13	1167.90	1153.98
0.3055	0.2871	1242.40	1239.34	1234.85	1.9790	1.8188	1.6306	1184.24	1168.93	1154.20
0.4000	0.19996	1244.16	1240.84	1237.26	2.3663	2.1431	1.9055	1187.20	1173.48	1161.30
0.4999	0.1001	1246.84	1243.12	1240.02	2.7801	2.4661	2.2108	1190.35	1177.82	1164.83
0.6000	0.0000	1248.63	1245.36	1242.24	3.0238	2.7263	2.3857	1195.4	1182.3	1166.54
<b>System III</b>										
0.0000	0.6000	1229.40	1226.38	1221.23	0.8725	0.8203	0.7655	1159.30	1148.48	1131.20
0.1001	0.4998	1232.32	1227.84	1224.50	1.0653	1.0068	0.8802	1169.67	1155.13	1147.98
0.1999	0.3999	1236.9	1232.16	1229.03	1.4222	1.3143	1.2243	1174.06	1165.03	1149.07
0.3000	0.2999	1241.02	1236.02	1231.62	1.7632	1.6587	1.5384	1179.18	1168.93	1150.5
0.3999	0.1999	1243.03	1238.03	1233.4	1.9521	1.8012	1.6946	1182.47	1174.32	1162.23
0.4998	0.1001	1246.8	1240.91	1237.06	2.339	2.2025	1.9653	1193.76	1182.08	1168.53
0.6000	0.0000	1247.67	1242.03	1239.5	2.7786	2.6496	2.3853	1209.26	1197.18	1185.75

In all the three liquid systems, the values of density ( $\rho$ ), viscosity ( $\eta$ ) and the ultrasonic velocity ( $U$ ) increase with increasing molar concentration of cresols. Cresols are organic compounds which are methylphenols. They are a widely occurring natural and manufactured group of aromatic organic compounds which are categorized as phenols (sometimes called phenolics). Depending on the temperature, cresols can be solid or liquid because they have melting points not far from room

temperature. Like other types of phenols, they are slowly oxidized by long exposure to air and the impurities often give cresols a yellowish to brownish red tint. Cresols have an odor characteristic to that of other simple phenols. In its chemical structure, a cresol molecule has a methyl group substituted onto the benzene ring of a phenol molecule. There are three forms of cresols that are only slightly different in their chemical structure: ortho-cresol (o-cresol), meta-cresol (m-cresol), and para-cresol (p-cresol).



Cresols are isomeric substituted phenols with a methyl substituent at one of the *o*-, *m*-, or *p*- positions relative to the OH-group. Physically, they are white crystalline solids or yellowish liquids with a strong phenol-like odour. The compounds are highly flammable, moderately soluble in water and soluble in ethanol, ether, acetone, or alkali hydroxides. Chemically, these alkylphenols undergo electro-philic substitution reactions at the vacant *o*- or *p*-

positions or undergo condensation reactions with aldehydes, ketones, or dienes.

This chemical interaction may involve the association due to hydrogen bonding or due to dipole-dipole interaction or may be due to the formation charge-transfer complexes. All these processes may lead to strong interaction forces. [5]. since ortho, Meta, and para cresols structurally similar, the increase in velocity in these liquid mixtures suggest that strong molecular interaction between



the cresols and DMF. The forces responsible for these interactions may probably be dipole-induced dipole or may be due to hydrogen bonding. [6]. The increase in velocity further may also be interpreted as the concentration of cresols is increased, since DMF is polar (hydrophilic) aprotic solvent with high boiling point, it can miscible with water and majority of organic liquids, belonging to amide group, the attached methyl group of (-CH<sub>3</sub>) in o-cresol has its own effect as well as hyperconjugate effect. Hence, due to the presence of methyl group, the removal of proton in o-cresol is not facilitated as quickly as in ccl<sub>4</sub>. Thus cresol molecules may form hydrogen bonds with DMF molecules more readily, giving rise to increase in velocity. Further, due to the addition of -CH<sub>3</sub> group at ortho position in the ring, molecular association taking place between DMF and cresol molecules through hydrogen bonding [6]. The dilute solutions minimize the effect of viscosity, internal field *etc.*, therefore, for dilution apolar solvents like carbontetrachloride (CCl<sub>4</sub>), benzene (C<sub>6</sub>H<sub>6</sub>) and cyclohexane *etc.*, are used. Normally apolar solvents provide the medium and dilution for the mixture, which in turn, also minimizes the requirement of pure liquids in large quantity. Hence, in the present investigation, ccl<sub>4</sub> is used. Also, as CCl<sub>4</sub> is a non-polar solvent which is not

taking part in the reaction, so the mole fraction of ccl<sub>4</sub> does not influence the mixture. [7]

Adiabatic compressibility  $\beta$  is found to be decreased with increasing concentration of cresols. It is primarily the compressibility that changes with structure which leads to change in ultrasonic velocity. The change in adiabatic compressibility ( $\beta$ ) in liquid mixtures indicates there is a definite contraction on mixing and the variation is may be due to complex formation. This clearly shows that there is significant interaction between the DMF-cresol molecules. [8] Intermolecular free length ( $L_f$ ) shows a similar behavior as reflected by adiabatic compressibility. The decrease in compressibility brings the molecules to a closer packing resulting into a decrease of intermolecular free length. Intermolecular free length ( $L_f$ ) is a predominant factor in determining the variations of ultrasonic velocity (U) in the mixtures. As  $L_f$  increases, U decreases and vice-versa, showing an inverse behavior. The interdependence of  $L_f$  and U has been evolved from model by Eyring and Kincaid [9]. The decrease in the values of adiabatic compressibility and the free length with increase in ultrasonic velocity (U) further strengthens the strong molecular association between the unlike molecules through hydrogen bonding.

**Table-2.** Adiabatic compressibility ( $\beta$ ), free length ( $L_f$ ) free volume ( $V_f$ ) and internal pressure ( $\pi_i$ ) of.

Mole fraction		$\beta/(\times 10^{-10} \text{ m}^2 \text{ N}^{-1})$			$L_f/(\times 10^{-10} \text{ m})$			$V_f/(\times 10^{-7} \text{ m}^3 \text{ mol}^{-1})$			$\pi_i/(\times 10^6 \text{ Nm}^{-2})$		
		Temperature ( $^{\circ}\text{K}$ )											
$X_1$	$X_3$	303	308	313	303	308	313	303	308	313	303	308	313
<b>System I</b>													
0.0000	0.6000	6.0522	6.1820	6.5085	0.4909	0.5006	0.5179	1.8713	2.0241	2.1658	464.3028	459.0221	455.0376
0.1012	0.4942	5.9276	6.0305	6.1607	0.4858	0.4939	0.5039	1.3401	1.5384	1.6351	507.1634	491.6287	488.4774
0.2000	0.4000	5.7624	5.9310	6.1041	0.4789	0.4898	0.5016	1.0593	1.0706	1.1858	541.1838	547.0931	535.6310
0.3055	0.2871	5.7393	5.9052	6.0789	0.4780	0.4887	0.5005	0.6589	0.7333	0.8476	618.7299	605.8803	585.2741
0.4000	0.19996	5.7026	5.8524	5.9931	0.4765	0.4865	0.4970	0.5236	0.5970	0.7010	658.3889	639.4749	614.7878
0.4999	0.1001	5.6603	5.7987	5.9436	0.4747	0.4843	0.4949	0.4311	0.5079	0.5885	690.0555	662.8201	640.2364
0.6000	0.0000	5.6045	5.7445	5.9156	0.4724	0.4821	0.4938	0.3990	0.4584	0.5488	695.6014	673.9203	643.8837



System II													
0.0000	0.6000	6.0522	6.1820	6.5138	0.4909	0.5006	0.5182	1.8713	2.0241	2.1658	464.3028	459.0221	454.7881
0.1000	0.5000	5.9039	6.0595	6.2177	0.4848	0.4951	0.5062	1.3991	1.5744	1.7251	502.1282	490.1693	481.9979
0.2000	0.4000	5.8420	5.8944	6.1331	0.4823	0.4883	0.5028	1.0900	1.1821	1.3276	534.8676	528.5904	515.4382
0.3056	0.2871	5.8083	5.8781	6.0393	0.4809	0.4876	0.4989	0.7965	0.8698	0.9784	580.2178	571.6669	557.8971
0.4000	0.2000	5.7830	5.8547	6.0155	0.4798	0.4866	0.4979	0.6678	0.7208	0.9167	606.8182	600.3441	561.8789
0.4998	0.1001	5.6449	5.7988	5.9539	0.4741	0.4843	0.4954	0.5916	0.6600	0.7940	620.7110	606.8074	579.0706
0.6000	0.0000	5.5257	5.6055	5.7480	0.4690	0.4762	0.4867	0.5265	0.5968	0.7307	634.0063	617.0782	584.7978
System III													
0.0000	0.6000	6.0522	6.1820	6.3992	0.4909	0.5001	0.5136	1.8713	2.0241	2.1948	464.3028	459.0221	452.7734
0.1001	0.4998	5.9313	6.1037	6.1969	0.4859	0.4968	0.5054	1.4766	1.5773	1.9116	492.3581	488.4063	464.6753
0.1999	0.3999	5.8652	5.9794	6.1623	0.4832	0.4917	0.5040	1.0092	1.1229	1.2234	548.7212	536.8910	529.3363
0.3000	0.2999	5.7951	5.9210	6.1341	0.4803	0.4893	0.5028	0.7706	0.8336	0.9112	589.4618	582.1273	572.8958
0.3999	0.1999	5.7536	5.8573	6.0022	0.4786	0.4867	0.4974	0.6947	0.7757	0.8369	598.8021	585.1273	578.3005
0.4998	0.1001	5.6282	5.7672	5.9201	0.4734	0.4830	0.4940	0.5610	0.6049	0.7054	632.0867	624.5753	601.7751
0.6000	0.0000	5.4810	5.6176	5.7381	0.4671	0.4767	0.4863	0.4608	0.4875	0.5625	662.6470	659.0665	637.6672

It is observed that for all the three liquid systems, the values free volume of ( $V_f$ ) decrease and the internal pressure ( $\pi_i$ ) increase. Further, the decrease in free volume and increase in internal pressure with rise in concentration of cresols in all the systems clearly show the increasing magnitude of interactions [10]. Such an increase in internal pressure generally indicates association through hydrogen bonding [11] and hence supports the present investigation. Further, in all three liquid systems, the values of acoustic impedance ( $Z$ ) are found to be increased. When an acoustic wave travels in a medium, there is a variation of pressure from particle to particle. The ratio of the instantaneous pressure excess at any particle of the medium to the instantaneous velocity of that

particle is known as 'specific acoustic impedance' of the medium. This factor is governed by the inertial and elastic properties of the medium. It is important to examine specific acoustic impedance in relation to concentration and temperature. When a plane ultrasonic wave is set up in a liquid, the pressure and hence density and refractive index show specific variations with distance from the source along the direction of propagation. In the present investigation, it is observed that these acoustic impedance ( $Z$ ) values increase with increasing concentration of cresols. Such an increasing values of acoustic impedance ( $Z$ ) further supports the possibility of molecular interactions due to H-bonding between the DMF-cresol molecules. It is seen from the Table-3, the values of molar



volume ( $V_m$ ) increases with increase in concentration of cresols in all the three liquid systems. This is because of the fact molecular weight is directly proportional to the molar volume. The molecular weights of cresols, DMF respectively are 108.14, 73.09. Since cresols are having higher molecular weights in the solution comparing DMF (as  $CCl_4$  is a non-polar solvent, which do not taking part in the reaction) whose concentration are increasing in the

mixture which supports the calculation. Moreover, molar volume ( $V_m$ ) is also increases with rise in temperature in the present study, which may probably would be caused from the fact that thermal energy facilitates an increase in the molecular separation in the liquid mixtures which leads to an increase in molar volume ( $V_m$ ) with elevation of temperature.

**Table-3.** Acoustic impedance ( $z$ ) and molar volume ( $V_m$ ) of.

Mole fraction		Acoustic impedance $Z \times 10^6 \text{ kg m}^2/\text{s}$			Molar volume ( $V_m$ ) $\times 10^{-5} \text{ m}^3$		
		Temperature ( $^{\circ}\text{K}$ )					
$X_1$	$X_3$	303	308	303	303	308	313
<b>System I</b>							
0.0000	0.6000	1.4252	1.4085	8.5721	0.1925	0.1958	0.1990
0.1012	0.4942	1.4416	1.4277	8.8731	0.1915	0.1949	0.1981
0.2000	0.4000	1.4668	1.4437	9.0541	0.1908	0.1938	0.1971
0.3055	0.2871	1.4713	1.4487	9.3911	0.1893	0.1926	0.1960
0.4000	0.19996	1.4771	1.4561	9.5968	0.1886	0.1919	0.1954
0.4999	0.1001	1.4842	1.4642	9.8569	0.1879	0.1914	0.1948
0.6000	0.0000	1.4926	1.4724	10.1238	0.1876	0.1910	0.1944
<b>System II</b>							
0.0000	0.6000	1.4252	1.4085	8.5721	0.1925	0.1958	0.1990
0.1000	0.5000	1.4465	1.4266	8.8148	0.1916	0.1950	0.1983
0.2000	0.4000	1.4553	1.4476	9.0839	0.1908	0.1941	0.1974
0.3056	0.2871	1.4615	1.4507	9.4053	0.1898	0.1931	0.1964
0.4000	0.2000	1.4663	1.4555	9.6035	0.1892	0.1925	0.1961
0.4998	0.1001	1.4856	1.4630	9.8629	0.1888	0.1921	0.1956
0.6000	0.0000	1.5029	1.4903	10.1279	0.1884	0.1918	0.1954
<b>System III</b>							
0.0000	0.6000	1.4252	1.4085	8.5721	0.1925	0.1958	0.1990
0.1001	0.4998	1.4414	1.4183	8.8370	0.1918	0.1950	0.1986
0.1999	0.3999	1.4522	1.4355	9.0856	0.1906	0.1939	0.1972
0.3000	0.2999	1.4634	1.4448	9.3383	0.1897	0.1930	0.1962



0.3999	0.1999	1.4698	1.4538	9.6059	0.1893	0.1927	0.1959
0.4998	0.1001	1.4884	1.4669	9.8565	0.1886	0.1919	0.1953
0.6000	0.0000	1.5088	1.4869	10.1314	0.1881	0.1912	0.1946

In order to understand the nature of molecular interactions between the components of the liquid mixtures, it is of interest to discuss the same in term of excess parameter rather than actual values. Non-ideal liquid mixtures show considerable deviation from linearity in their physical behavior with respect to concentration and these have been interpreted as arising from the presence of strong or weak interactions. The extent of

deviation depends upon the nature of the constituents and composition of the mixtures. It is learnt that the dispersion forces are responsible for possessing positive excess values, while dipole-dipole, dipole-induced dipole, charge transfer interaction and hydrogen bonding between unlike molecules are responsible for possessing negative excess values [5]

**Table-4.** Excess values of adiabatic compressibility ( $\beta$ ), free length ( $L_f$ ), free volume ( $V_f$ ) and internal pressure ( $\pi_i$ ) of.

Mole fraction		Excess adiabatic compressibility ( $\beta^E \times 10^{-10} \text{ m}^2 \text{ N}^{-1}$ )			Excess free length ( $L_f^E \times 10^{-12} \text{ m}$ )			Excess free volume ( $V_f^E \times 10^{-7} \text{ m}^3 \text{ mol}^{-1}$ )			Excess internal pressure ( $\pi_i^E \times 10^6 \text{ Nm}^{-2}$ )		
		Temperature ( $^{\circ}\text{K}$ )											
$X_1$	$X_3$	303	308	313	303	308	313	303	308	313	303	308	313
<b>System I</b>													
0.0000	0.6000	-0.212	-0.237	-0.227	-0.581	-0.650	-0.622	-0.180	-0.170	-0.187	-10.885	-9.706	-10.315
0.1001	0.4998	-0.425	-0.480	-0.645	-1.460	-1.649	-2.315	-0.660	-0.610	-0.669	-52.892	-42.573	-43.866
0.1999	0.3999	-0.611	-0.614	-0.724	-2.213	-2.189	-2.624	-0.827	-0.933	-0.973	-78.749	-86.677	-81.171
0.3000	0.2999	-0.714	-0.731	-0.823	-2.667	-2.696	-3.051	-1.024	-1.074	-1.113	-128.070	-121.868	-110.736
0.3999	0.1999	-0.770	-0.802	-0.899	-2.908	-3.005	-3.376	-0.987	-1.032	-1.075	-139.331	-130.288	-118.218
0.4998	0.1001	-0.843	-0.888	-0.963	-3.219	-3.369	-3.645	-0.898	-0.935	-0.987	-138.758	-126.995	-117.980
0.6000	0.0000	-0.913	-0.964	-1.009	-3.518	-3.689	-3.837	-0.766	-0.805	-0.847	-121.372	-114.108	-103.909
<b>System II</b>													
0.0000	0.6000	-0.212	-0.237	-0.222	-0.581	-0.650	-0.601	-0.180	-0.170	-0.187	-10.885	-9.706	-10.066
0.1001	0.4998	-0.433	-0.440	-0.580	-1.493	-1.485	-2.051	-0.605	-0.576	-0.586	-47.919	-40.809	-37.586
0.1999	0.3999	-0.554	-0.651	-0.709	-2.003	-2.365	-2.586	-0.804	-0.846	-0.862	-73.320	-71.502	-64.648
0.3000	0.2999	-0.667	-0.750	-0.851	-2.471	-2.777	-3.168	-0.929	-0.979	-1.022	-101.284	-98.069	-91.685



0.3999	0.1999	-0.721	-0.801	-0.886	-2.708	-3.000	-3.322	-0.901	-0.958	-0.945	-108.373	-106.794	-86.457
0.4998	0.1001	-0.849	-0.887	-0.957	-3.243	-3.359	-3.614	-0.818	-0.859	-0.884	-104.168	-99.071	-87.476
0.6000	0.0000	-0.944	-1.018	-1.075	-3.647	-3.919	-4.114	-0.715	-0.749	-0.774	-96.766	-91.402	-80.306
<b>System III</b>													
0.0000	0.6000	-0.212	-0.237	-0.336	-0.581	-0.650	-1.059	-0.180	-0.170	-0.158	-10.885	-9.706	-8.051
0.1001	0.4998	-0.408	-0.400	-0.599	-1.393	-1.324	-2.128	-0.535	-0.573	-0.418	-39.132	-39.228	-22.004
0.1999	0.3999	-0.535	-0.582	-0.685	-1.919	-2.077	-2.482	-0.869	-0.893	-0.945	-84.479	-78.217	-75.841
0.3000	0.2999	-0.652	-0.695	-0.761	-2.413	-2.551	-2.800	-0.949	-1.007	-1.072	-107.528	-105.148	-101.891
0.3999	0.1999	-0.739	-0.800	-0.894	-2.782	-2.995	-3.355	-0.884	-0.925	-0.993	-103.562	-97.663	-96.309
0.4998	0.1001	-0.858	-0.903	-0.975	-3.282	-3.430	-3.690	-0.833	-0.887	-0.928	-109.827	-107.927	-98.802
0.6000	0.0000	-0.962	-1.014	-1.080	-3.727	-3.902	-4.135	-0.742	-0.793	-0.842	-108.199	-108.174	-101.430

In the present investigation, the excess adiabatic compressibility ( $\beta^E$ ) the excess free length ( $L_r^E$ ) and excess free volume ( $V_f^E$ ) exhibit negative values over the entire range composition in all the three liquid systems clearly indicating the presence of strong hydrogen bonding interactions between unlike molecules. This is in conformity with earlier workers [5, 12]. The strength of the interaction between the component molecules increase, when excess values tend to become increasingly negative. This also may be quantitatively interpreted in terms of closer approach of unlike molecules leading to reductions in compressibility and volume [6].

Further, the excess internal pressure ( $\pi_i^E$ ) which is usually described in terms of molecular interaction,

whose negative excess values for all the liquid systems suggest that strong molecular association between the unlike molecules. The excess values of acoustic impedance ( $Z^E$ ) which are furnished in Table 5 are all positive in the liquid systems over the entire range of composition. The positive excess values of  $Z^E$  clearly suggest that there is a strong molecular interaction existing between the DMF-cresol molecules [13]. The excess viscosity ( $\eta^E$ ) values whose positive excess values for all the three liquid systems clearly supports this prediction [13]. Similar observations were observed by earlier workers [7, 14] supports the present investigation.

**Table-5.** Excess Values of molar volume ( $V_m^E$ ), viscosity ( $\eta^E$ ) and acoustic Impedance ( $Z^E$ ) of.

Mole fraction		Excess molar volume $V_m^E \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$			Excess viscosity $\eta^E \times 10^{-5} \text{ NSm}^{-2}$			Excess acoustic impedance $Z^E \times 10^4 \text{ kg m}^2/\text{s}$		
		Temperature (°K)								
$X_1$	$X_3$	303	308	313	303	308	313	303	308	313
<b>System I</b>										
0.0000	0.6000	2.0117	2.0040	1.9976	0.8717	0.8195	0.7648	5.7062	-12.0060	40.5761





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0.1012	0.4942	2.2166	2.2084	2.2042	1.1405	1.0324	0.9824	6.3710	2.5280	56.5902
0.2000	0.4000	2.2446	2.2431	2.2521	1.3851	1.3576	1.2531	7.6016	16.8358	70.0438
0.3055	0.2871	2.3634	2.3600	2.3632	1.9778	1.8177	1.6296	6.4783	30.8643	85.8758
0.4000	0.19996	2.3123	2.3111	2.3115	2.3649	2.1418	1.9043	5.6728	43.9770	98.8535
0.4999	0.1001	2.2613	2.2624	2.2633	2.7783	2.4645	2.2093	4.7065	57.7175	113.4112
0.6000	0.0000	2.1607	2.1607	2.1643	3.0216	2.7243	2.3840	3.6673	71.4960	127.8685
<b>System II</b>										
0.0000	0.6000	2.0117	2.0040	2.0047	0.8717	0.8196	0.7648	5.7062	-12.0060	40.5313
0.1000	0.5000	2.1516	2.1391	2.1376	1.1046	1.0086	0.9386	6.8523	2.3829	55.6078
0.2000	0.4000	2.2638	2.2536	2.2559	1.3527	1.2769	1.1608	6.5505	16.9132	69.8296
0.3056	0.2871	2.3726	2.3715	2.3632	1.7337	1.6275	1.4858	5.7860	30.9810	86.2016
0.4000	0.2000	2.3161	2.3137	2.3162	1.9974	1.8890	1.5901	5.0205	43.9343	98.5849
0.4998	0.1001	2.2656	2.2710	2.2689	2.2533	2.0709	1.8084	4.7708	57.6414	113.2159
0.6000	0.0000	2.1627	2.1620	2.1699	2.5297	2.3131	1.9995	4.0731	72.5823	129.8649
<b>System III</b>										
0.0000	0.6000	2.0117	2.0040	2.0047	0.8717	0.8195	0.7648	5.7305	-11.9796	41.0462
0.1001	0.4998	2.1715	2.1747	2.1658	1.0645	1.0060	0.8795	6.3780	1.8882	55.6151
0.1999	0.3999	2.2664	2.2716	2.2643	1.4213	1.3134	1.2235	6.2635	16.1471	69.5354
0.3000	0.2999	2.3130	2.3197	2.3221	1.7621	1.6577	1.5374	6.0358	30.0378	83.5772
0.3999	0.1999	2.3175	2.3241	2.3296	1.9508	1.8000	1.6935	5.2342	43.8340	98.5818
0.4998	0.1001	2.2620	2.2718	2.2758	2.3374	2.2010	1.9639	5.4159	62.3099	113.0053



0.6000	0.0000	2.1638	2.1716	2.1733	2.7766	2.6477	2.3836	4.2556	72.3663	129.9246
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Table-6. Redlich Kister coefficients and standard deviation ( $\sigma$ ) values.

		Temperature	$a_0$	$a_1$	$a_2$	$\sigma$
$\beta^E$	System I	303	-17.8694	-47.7994	-1430.08	0.4933
		308	-18.7402	-30.7605	-1376.95	0.5209
		313	-23.4139	-108.87	-1884.71	0.5692
	System II	303	-18.6817	-70.5868	-1522.62	0.4846
		308	-20.8359	-57.1756	-1418.02	0.5230
		313	-24.2421	-87.3599	-1633.56	0.5512
	System III	303	-19.7389	-48.7874	-1315.14	0.4688
		308	-20.6026	-64.0679	-1488.65	0.4973
		313	-25.14	-123.467	-1872.78	0.5219
$L_f^E$	System I	303	-63.4397	-103.05	-5134.6	1.8876
		308	-65.7152	-22.052	-4814.44	1.9781
		313	-84.4055	-343.709	-6855.96	2.1458
	System II	303	-66.8333	-198.465	-5519.3	1.8494
		308	-74.3828	-131.395	-4979.48	1.9870
		313	-87.8587	-257.168	-5828.95	2.0857
	System III	303	-70.8033	-99.4602	-4626.78	1.7838
		308	-72.9785	-151.215	-5240.59	1.8759
		313	-91.0755	-395.999	-6777.49	1.9599
$V_f^E$	System I	303	-27.0095	-75.3797	-1136.07	0.3820
		308	-28.2843	-79.1603	-1217.94	0.4062
		313	-27.3844	11.8088	-712.78	0.4363
	System II	303	-26.633	-70.9515	-1110.23	0.3706
		308	-27.1903	-41.2753	-970.838	0.3844
		313	-27.9636	-55.1169	-1067.15	0.3994
	System III	303	-28.2539	-52.4497	-1088.34	0.3978
		308	-29.6638	-46.5683	-1057.59	0.4115
		313	-31.3325	-68.5187	-1250.78	0.4343
$V_m^E$	System I	303	79.7109	596.743	5599.46	1.50345
		308	79.8639	595.396	5599.85	1.50365
		313	79.8408	595.224	5599.87	1.50425
	System II	303	80.3495	557.761	5273.41	1.50067
		308	80.0065	552.278	5262.83	1.49741
		313	79.957	552.284	5262.83	1.50036
	System III	303	80.71	572.443	5351.44	1.50522
		308	80.6262	572.384	5351.44	1.50209
		313	80.7014	572.354	5351.45	1.50041



$\eta^E$	System I	303	47.5024	134.458	3953.38	1.4570
		308	44.449	139.528	3811.32	1.3883
		313	40.469	72.7464	3023.54	1.2529
	System II	303	46.2351	83.7455	3525.97	1.3416
		308	43.0797	50.723	3044.09	1.2298
		313	39.7901	98.7579	2897.24	1.0738
	System III	303	47.9384	-16.8147	3927.51	1.5766
		308	45.4072	6.45402	3498.43	1.4243
		313	42.1973	53.1523	3390.84	1.2541

## 5. CONCLUSIONS

From the data's of ultrasonic velocity, density and viscosity, related acoustical parameters and some of their excess values for the ternary liquid mixtures of o-cresols, p-cresols, m-cresols with DMF in carbon tetrachloride ( $\text{CCl}_4$ ) at 303, 308 and 313 K, it is very obvious that there exist a strong molecular interaction existing between the unlike molecules. The cresols such as o-cresols, p-cresols and m-cresols form strong hydrogen bonding with DMF. However, no complex formation or charge-transfer reactions were observed in the present study. The molecular interaction is stronger in DMF-cresols than in cresols-  $\text{CCl}_4$  and in DMF- $\text{CCl}_4$

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