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Acoustical investigations of phenol in hydrocarbons (o, p, m-xylene) at 301 K

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ABSTRACT

The ultrasonic velocity, density and viscosity of the binary mixtures of phenol with hydro carbon (o/p/m-xylene) are measured at 301K. The acoustical parameter like adiabatic compressibility (β) , free volume (V_f), relaxation time (τ) , inter molecular free length (L_f), acoustic impedance (Z) , relative association (RA) , molar volume (V_f), Lennard - Jones Potential (L-J) , Rao constant (R) and Wada's constant (W) have been found from these measurements. The results are discussed in terms of molecular interactions. The acoustical parameter indicates that there may be an interaction occurs due to the weak kind of molecular forces. The existence of molecular interactions between the molecules alters the acoustical property of liquids. The existence of bonding and the nature of molecular interaction in the mixtures have been specified. When the concentration of phenol increases the interaction between phenol-o/p/m – xylene also increases.

Keywords: Ultrasonic velocity, density, viscosity, relaxation time, Lennard – Jones potential, Wada's constant , Rao constant.

INTRODUCTION

In recent years, the ultrasonic measurement has been adequately employed in understanding the nature of molecular interaction in pure liquid and liquid mixtures [1-3]. The Acoustical measurements of ultrasonic velocity and density, viscosity and the related acoustical parameter analogous to adiabatic compressibility, inter molecular free length etc. The liquid and liquid mixtures are important owing to the molecular interactions. The binary mixtures consist of polar-polar and polar – non polar liquids are significant to pharmaceutical and chemical process. The transport and thermal properties of liquid mixtures have been frequently used to study the molecular interactions from the ideal liquid mixture behavior [4-6].

Phenol is an important in industrial product as a precursor for manufacturing many materials. o/p/m/-Xylenes are used as solvent. o/p/m/-xylene is used in the production of phthalic anhydride, isophthalic acid, terephthalic acid for polyester respectively. From the practical point of view, the mixtures investigated are especially important because of they are widely used in engineering and industries. Many researchers studied the molecular interactions of alcohols and xylenes by the dielectric, ultrasonic and refractive index measurements [8-12]. The present investigation has been the attempting of the molecular interactions of phenol with xylene (o, p, m-xylene) mixtures through ultrasonic measurements and related acoustical parameter.

MATERIALS AND METHODS

In the present investigation AR grade chemicals phenol, o-xylene, p-xylene and m-xylene were used. The samples were purified by standard procedure and drying before use. The purified sample was checked by by the measured

values of density and viscosities with a literature value and shows the high impurity. The purity of the samples has 99.99%. Ultrasonic velocities were measured using an ultrasonic interferometer (Model M-82 Mital Enterprises, New Delhi) working with a frequency of 3MHz with an accuracy of ±1 ms^{-1}. The densities were measured using Pycnometer. It was calibrated using ionized water. The viscosities have been measured using Ostwald's viscometer. This also calibrated using ionized water. The mixtures of various components were prepared by weigh measurements in chemical balance with accuracy 0.0001 gm.

THEORY AND CALCULATIONS

From the experimental values of ultrasonic velocity, density and viscosity the following acoustical parameters have been evaluated.

Adiabatic compressibility (β) may even be calculated from the speed of sound and the density of the medium using the equation of Newton and Laplace as

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

Free volume (V_f) in terms of ultrasonic velocity (u) and the viscosity of the liquid (η) as

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

Relaxation time (τ) is calculated using the relation

$$\tau = \frac{4}{3} \eta\beta \quad \text{…. (3)}$$

Determination of intermolecular free length (L_f) in liquids and in liquid mixtures has been a subject of considerable interest using semi-empirical relation to accomplish the idea of intermolecular free length in order to report the ultrasonic velocity in liquids.

$$\text{i.e } L_f = K_T \sqrt{\beta}. \quad \text{…. (4)}$$

The acoustic impedance (Z) is the product of the velocity of ultrasound in a medium and density. It can be calculated by the relation.

$$Z = U\rho \quad \text{…. (5)}$$

Relative association (RA) can be calculated from the relation

$$R_a = \left(\frac{\rho}{\rho_o} \right) \left(\frac{u_o}{u} \right)^{1/3} \quad \text{…. (6)}$$

ρ and ρ_0 is the density of the pure liquid and liquid mixture. u and u_o are the ultrasonic velocity of pure liquid and liquid mixtures.

The available volume (V_a) is a direct measure of compactness and the strength of attraction between the molecules of a liquid and liquid mixtures. It can be calculated from Schaafâ's relation

$$V_a = V\left[1-\left(\frac{u}{u_\infty}\right)\right] \quad \ldots.(7)$$

The Lennard - Jones potential is given by

$$LJP = \frac{6v_m}{V_a} \quad \ldots. (8)$$

Where, V_m and V_a represent the molar volume and available volume of the mixtures.

Rao noticed that the ratio of temperature coefficient of sound velocity u to the expansion coefficient V is virtually same for all unassociated organic liquids. According to the Rao

$$R = u^{1/3} V \quad \ldots. (9)$$

From the sound velocity in liquids, another constant has been suggested by Wada. According to Wada

$$w = \frac{m_{eff}}{\rho}\beta^{-1/7} \quad \ldots. (10)$$

The adiabatic compressibility , free volume , relaxation time , inter molecular free length , acoustic impedance , relative association , molar volume , Lenard- Johnes potential , Rao constant and Wads constant evaluated from the relation 1- 10 , and these values are reported in table 2.

RESULTS AND DISCUSSION

Ultrasonic velocity, viscosity and density of the binary mixtures of phenol with o, p, and m- xylene at 301 K are shown in table 1. The acoustical parameters were finding from the equation 1 to 10, the data were presented in the table 2 also the plots are shown in figures 1 to 10.

Table-1 The variation of ultrasonic velocity (u m/s), density (ρ gm/cm^3) and viscosity (η x10^{-3} Nsm^{-2}) of the mole fractions (X_2) of phenol with hydrocarbons at 301K

X_2	o-xylene			m-xylene			p-xylene		
	u_{12}	ρ_{12}	η_{12}	u_{12}	ρ_{12}	η_{12}	u_{12}	ρ_{12}	η_{12}
0.1	1339	902	0.134	1339	902	0.134	1350	885	0.147
0.2	1348	918	0.209	1348	918	0.209	1357	903	0.221
0.3	1357	936	0.286	1357	936	0.286	1365	922	0.296
0.4	1366	952	0.359	1366	952	0.359	1373	941	0.368
0.5	1376	969	0.435	1376	969	0.435	1382	960	0.442
0.6	1386	986	0.510	1386	986	0.510	1392	978	0.516
0.7	1399	1004	0.593	1399	1004	0.593	1403	999	0.597
0.8	1411	1021	0.668	1411	1021	0.668	1414	1018	0.671
0.9	1423	1037	0.737	1423	1037	0.737	1425	1035	0.739

Ultrasonic velocity is increases with increasing the concentration of phenol and similar trend observed in the density and viscosity for all binary mixtures. This value is diverging from the ideal liquid mixture behavior and this can be trained to the intermolecular interaction in the phenol with o/p/m- xylene mixtures. It is based on the value of pure components. This property shows the presence of large number molecules in the mixture. The increase in viscosity values indicate the existence of induced dipole – dipole interactions in the systems.

Table 2 Variation of adiabatic compressibility (β 10^{10} $kg^{-1}ms^{-2}$), free volume (V_f 10^3m^3), relaxation time (τ $10^{12}s$), inter molecular free length (L_f $10^{-10}m$), acoustic impedance (Z 10^6 kg m^{-2} sec^{-1}), relative association (R_a), molar volume (V_m m^3), Lennard - Jones Potential (LJP) , Rao constant (R m^3/mole)(m/s)$^{1/3}$, Wadas constant (m^3/mole)(nm^2)$^{1/7}$ with the mole fractions of phenol with hydrocarbon system

X_2	β	V_f	T	L_f	Z	RA	MV	VA	LJP	R	W
o-xylene											
0.1	6.39	457	0.05	5.25	1.18	0.99	0.119	19.96	3.57	1155	136.8
0.2	6.18	119	0.11	5.16	1.21	1	0.115	18.76	3.68	1144	134.6
0.3	5.99	60.7	0.17	5.08	1.24	1.02	0.112	17.59	3.81	1133	132.4
0.4	5.8	37.7	0.22	5	1.27	1.04	0.108	16.44	3.95	1122	130.3
0.5	5.63	26.6	0.27	4.92	1.3	1.05	0.105	15.38	4.1	1111	128.2
0.6	5.45	19.8	0.32	4.84	1.33	1.07	0.102	14.29	4.29	1100	126.1
0.7	5.28	15.5	0.36	4.77	1.37	1.08	0.099	13.26	4.48	1090	124
0.8	5.09	12.3	0.4	4.68	1.4	1.1	0.096	12.08	4.78	1080	121.8
0.9	4.92	10.2	0.44	4.6	1.44	1.12	0.093	11.03	5.08	1069	119.7
m-xylene											
0.1	6.41	323	0.06	5.25	1.16	0.96	0.121	19.49	3.74	1158	136.9
0.2	6.2	105	0.12	5.17	1.19	0.98	0.117	18.32	3.84	1147	134.7
0.3	6.01	56.4	0.18	5.09	1.23	1	0.114	17.25	3.95	1135	132.5
0.4	5.82	36.1	0.23	5.01	1.26	1.02	0.11	16.14	4.09	1124	130.3
0.5	5.64	25.8	0.28	4.93	1.29	1.04	0.106	15.1	4.23	1113	128.2
0.6	5.45	19.4	0.32	4.84	1.33	1.06	0.103	14.04	4.4	1102	126.1
0.7	5.28	15.3	0.36	4.77	1.36	1.07	0.1	12.99	4.62	1091	124
0.8	5.09	12.2	0.41	4.68	1.4	1.09	0.097	11.9	4.87	1081	121.8
0.9	4.91	10.2	0.44	4.6	1.44	1.11	0.094	10.88	5.16	1070	119.6
p-xylene											
0.1	6.34	402	0.05	5.22	1.18	0.99	0.119	19.7	3.61	1155	136.7
0.2	6.15	114	0.11	5.15	1.21	1	0.115	18.53	3.72	1144	134.5
0.3	5.96	59.2	0.17	5.07	1.24	1.02	0.112	17.42	3.84	1133	132.3
0.4	5.78	37.1	0.22	4.99	1.27	1.04	0.108	16.29	3.98	1123	130.2
0.5	5.61	26.3	0.27	4.91	1.3	1.05	0.105	15.24	4.14	1112	128.1
0.6	5.43	19.7	0.32	4.84	1.34	1.07	0.102	14.15	4.32	1101	126
0.7	5.26	15.4	0.36	4.76	1.37	1.09	0.099	13.12	4.53	1090	123.9
0.8	5.08	12.3	0.4	4.68	1.41	1.1	0.096	12.01	4.8	1080	121.8
0.9	4.91	10.2	0.44	4.6	1.44	1.12	0.093	10.96	5.11	1069	119.6

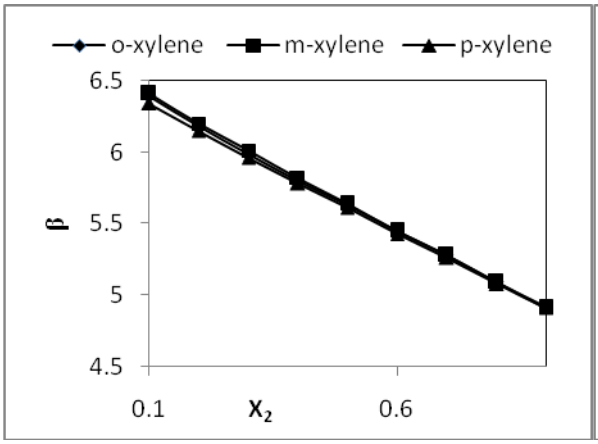

Fig. 1 Plots of β with X_2

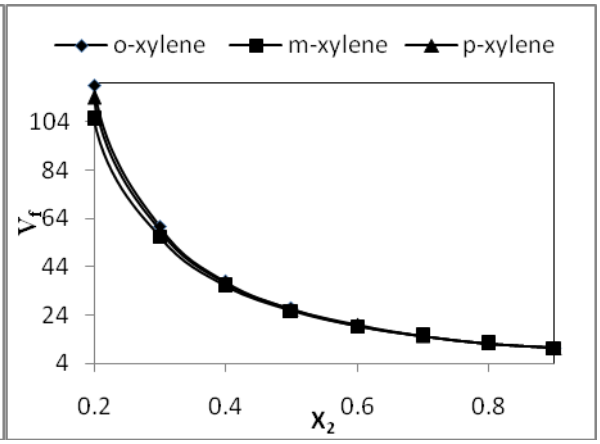

Fig. 2 Plots of V_f with X_2

Ultrasonic velocity should increase or decreases, if the inter molecular free length decreases or increases. This information was noticed in the present investigation for all the binary liquid systems. In fact, the molecular association between the molecules increases the ultrasonic velocity decrease the acoustic impedance, intermolecular free length and adiabatic compressibility. Decrease in adiabatic compressibility is suggested that the component molecules are held close to each other. The decrease in the values of adiabatic compressibility and inter molecular free length with increases in ultrasonic velocity shows the strong molecular association between the unlike molecules through dipole – dipole interactions. Xylene as non polar liquids the parameters are almost same. This fact is reflected clearly from the values of ultrasonic velocity, intermolecular free length, adiabatic compressibility and acoustic impedance for these systems.

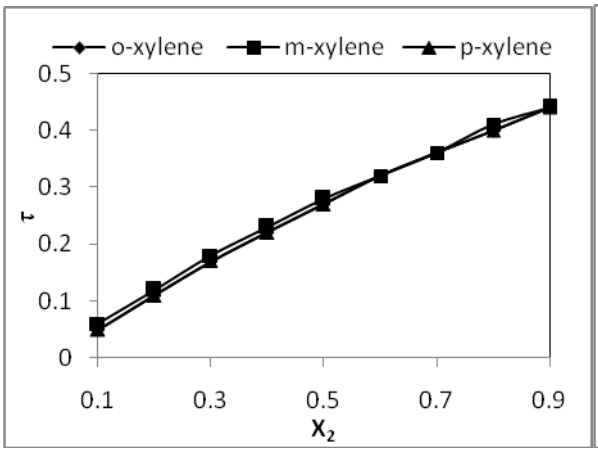

Fig. 3 Plots of τ with X_2

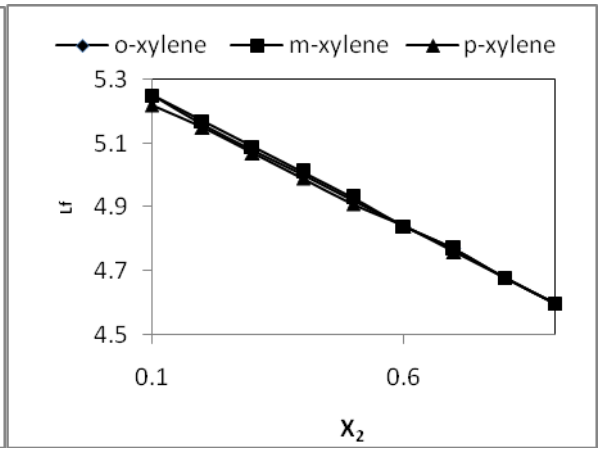

Fig. 4 Plots of L_f with X_2

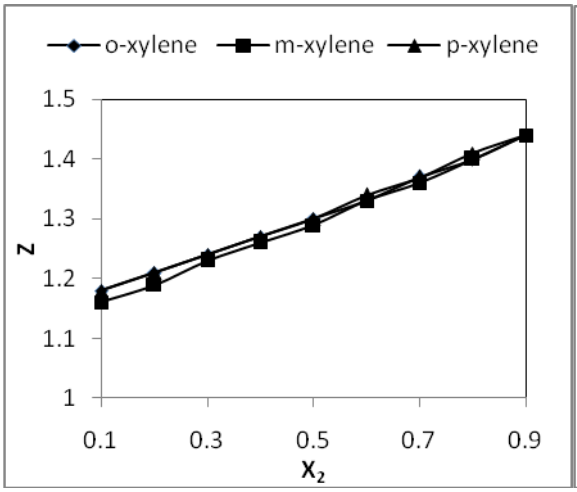

Fig. 5 Plots of Z with X_2

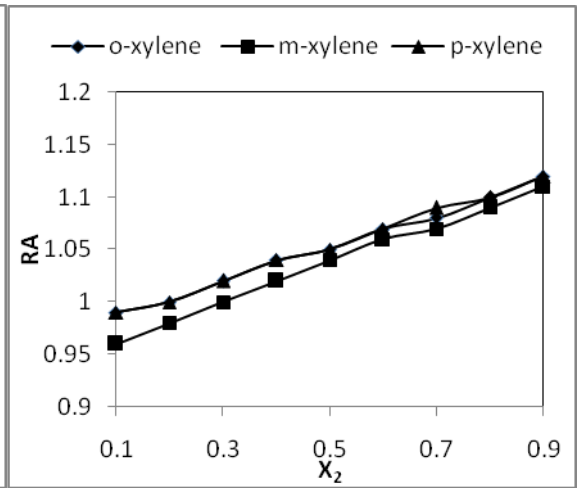

Fig. 6 Plots of RA with X_2

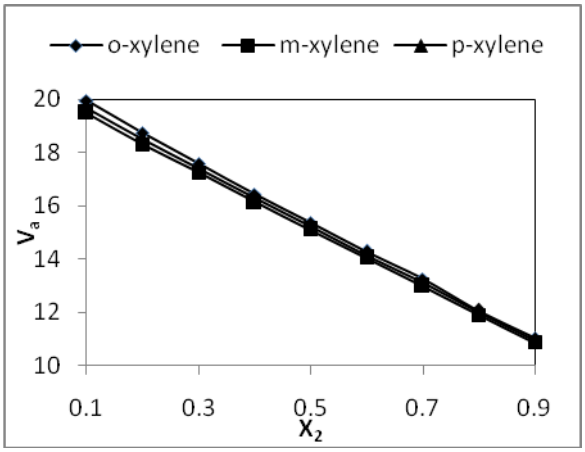

Fig.7 Plots of V_a with X_2

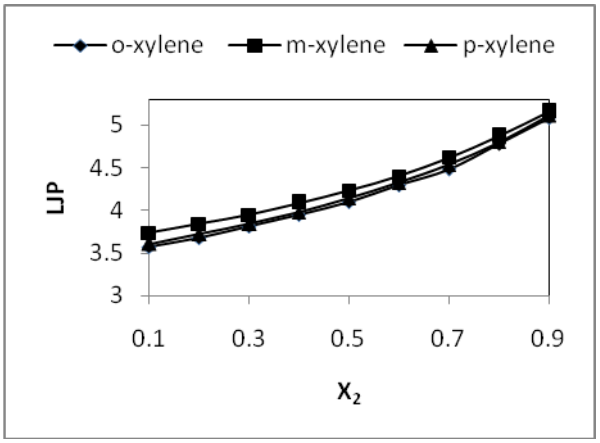

Fig. 8 Plots of LJP with X_2

Phenol generally can be present in polymeric form. In the presence of non polar molecules, they increase molecular interaction due to bond broken. With the increase concentration of phenol, the tendency for intermolecular hydrogen bonding decreases. The association is weaker and it may expect a small variation in these parameters. Eventually ultrasonic velocities of both the components are nearly equal. In this fact is reflected in increase of ultrasonic velocity and hence decrease in inter molecular free length also it can be observed that adiabatic compressibility values decreases with increasing concentrations of phenol. Acoustic impedance of a material is the opposition exerted by the medium to displacement of the medium's particles by the sound energy. It is important to measure the acoustic impedance because these studies have shown that in solvent mixtures when the molecular interaction is

occurs; acoustic impedance exhibits a non-linear variation with increasing mole fraction of phenol. This was used as an essential tool to predict molecular level interactions in binary and ternary liquid mixtures. In systems of binary liquid mixtures is always much greater than either of the polar solutes in the inert solvent. Further, the increase in free volume with rise in concentration of phenol in all the systems under study, clearly indicate the decreasing magnitude of interactions.

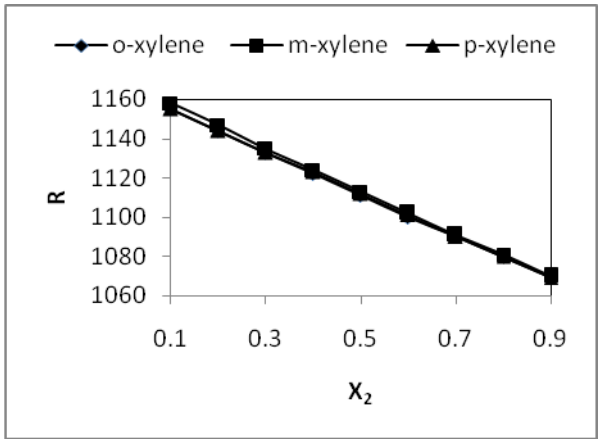

Fig. 9 Plots of R with X_2

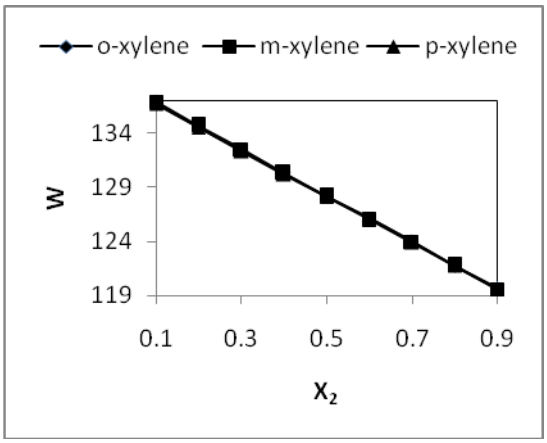

Fig. 10 Plots of W with X_2

The ultrasonic velocity (u) increase with increase in mole fraction of phenol this suggests that there's different types of molecular interactions between the parts in these mixtures. The variations in the ultrasonic velocity values in these systems behave ideality. This indicate weak induced dipole-induced dipole exist in these systems. The adiabatic compressibility (β) values for various mole fractions of binary mixtures have been computed from the measured values of ultrasonic velocity and densities. The plots of adiabatic compressibility with mole fraction of the phenol are given in figure 1. In all the systems the value of adiabatic compressibility decreases with increasing concentration of phenols over a range of concentration. This indicates weak induced dipole – induced dipole interactions exist. A competition of the value of β in these mixtures suggests that there are compressibility are in the order o-xylene > p-xylene > m-xylene. The variations in the adiabatic compressibility (β) values in these systems behave almost ideality. This indicate weak induced dipole-induced dipole exist in these systems. Free volume decreases with increase in concentration and the calculated available volume decreases with increase in concentration of phenol – o/p/m-xylene mixtures as shown in figure 2. The values of relaxation time (τ) are given in table 2 and plots shown in figure 3. There are only slight variations in relaxation time values systems. This indicates relatively a weaker interaction exists between the molecules of the two components and stronger intermolecular interactions exist between the molecules of each component. The free lengths of systems is a measure of inter molecular attraction between the liquids. The decrease in free length indicates the weakening of intermolecular interaction. It is given in tables 2 and plots given in figure 4, it is seen that the free length values increase with increase in concentration of phenol. This shows that the intermolecular attraction weakens at higher concentration.

The mathematical relations for acoustic impedance ($Z=u\rho$) and adiabatic compressibility ($\beta = \frac{1}{u^2\rho}$) show that they exhibit opposite behavior and the behavior is observed in all the liquid mixtures studied (Figure 1and Figure 5). Out of all the binary systems none exhibited a maximum in velocity curve and dip in compressibility curve. This indicates the absence of complex formation. The absence of complex formation is also confirmed by the linear variation of specific acoustic impedance. It is clear from figure 5 that specific acoustic impedance is linear and hence no indication of complex formation. The relative association (RA) values in a system can be used to determine the variation in intermolecular attraction and also to establish the existence of similar types of interaction in different binary systems. In the binary systems studied, the relative association values increase with increase in the mole fraction of the phenol- o/p/m-xylene systems given in table 2 also shown in figure 6. The values increase from unity. This trend suggests that induced dipole –induced dipole types of molecular interaction exist in all these binary systems. The LJP values indicate that dipole-dipole attractions are stronger than induced dipole-induced dipole attractions.

The plots of Rao's constant and Wada's constant for the present binary systems are shown in given in figure 9 and figure 10. It is clear that the Rao's constant and Wadas constant, the variations of these constants with mole

fractions is linear. It was reported that in a binary liquid mixtures, a linear variations of Rao's constant and Wada's constant with mole fraction shows weak induced dipole-induced dipole interaction in all binary systems.

CONCLUSION

Ultrasonic measurements like ultrasonic velocity, density and viscosity of binary mixtures of phenol in o/p/m – xylene have been made. The acoustical parameters have been evaluated from the experimental values. The natures of intermolecular interaction in the liquid mixtures have been explained on the basis of the variation of acoustical parameter. It is found that the interaction between unlike molecules increases with the increasing concentration of phenol.

REFERENCES

[1] Bojan D., Djordjevic, Ivona R., Radovic, Mirjana L. J., Kijevcanin, Aleksandar Z., Tasic, Slobodan P Serbanovic, *J. Serbian Chem. Soc.*, **2009** (74) , 5 , 477–491.
[2] Anwar ali, Anil kumar Nain, Vinod kumar Sharma , Shakil Ahamad, *Ind. J. Pure and app. Phys.*, **2004**, 42, 666-673.
[3] Aravind R Mahajan & Sunil R Mirgane, *J. Sol. Chem.*, **2013**, 42, 1146-1168.
[4] Bedare G.R., Bhandakkar V.D., Suryavanshi B.M., Euro. *J. App. Eng. Sci. Res.*, **2012**, 1, 1-4.
[5] Ezhil Pavai R., Renuka S., Balu L., Vasantharani P., *J. Exp. Sci.* **2010**, 1(6), 21-24
[6] Kannappan, A.N., Thirumaran S., Palani R., *J. Phys. Sci.*, **2009,** 20(2) , 97–108.
[7] Weber, Manfred, Weber Markus, Kleine-Boymann , Michaek , Ulmann's Encyclopedia of Industrial Chemistry . **2004 ,** Willey Online library
[8] Meenachi.M, Krishnamurthi. P, 2012, *Int. J. Res. Pharma. Bio. Sci.*, **2012** 3(4), 1719-1723.
[9] Meenachi, M, Krishnamurthi P, *Mechanica Confab*, **2013,** 2(2) , p85-92.
[10] Meenachi, M, Krishnamurthi, P, *Rasayan J. Chem.*, **2015,** 8(1), 98-104.
[11] Kannappan V, Jaya Santhi R,Ind. *J.Pure and App.Phy* , **2005**,43, 750-754.
[12] Ali Anwar ,Nabi Firdosa ,*Acta. Phys.-Chim.Sin*, **2008**, 24, 1, 47-54.