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Determination Thermodynamic Properties for Hydrogen Bonded Complexes of Phenols with N-Methylaniline in N-Hexane Medium at Different Temperatures using Ultrasonic Technique

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Abstract: Acoustical and excess thermo acoustical properties of Phenol, 4-chlorophenol(4-ChP) with N-methylaniline (NMA) in n-hexane mixtures are investigated by measuring ultrasonic velocity (u), density (ρ) and viscosity (η) in the concentration range 0.01-0.1M at atmospheric pressure at different temperatures 298K, 303K, 308K. The trend in the acoustical and excess thermo acoustic parameters reveals the existence of hydrogen bonded and charge transfer complexes between amines and phenol. The variation of the excess parameters both in sign and magnitude within the range of concentration investigated is also discussed in terms of structural aspect and functional groups of the components involved. The formation constants of the charge transfer complexes determined using Kannappan equation in ultrasonic method.
Keywords: excess parameters, phenols, N-methylaniline, n-hexane, ultrasonic technique, thermo acoustic parameters.

1. Introduction

The study of thermodynamic properties of ternary mixtures contributes to an understanding of the behavior of different liquids and their functional groups. This information is very useful in the design of industrial process and in the development of theories for the liquid state and predictive methods. Excess thermodynamic parameters of different mixtures are useful in the study of molecular interactions and arrangements **[1]**. For engineering applications, liquid mixtures, rather than single component liquid systems are used in processing and product formulations. The thermodynamic parameters derived from the measurement of density, ultrasonic velocity and viscosity are useful in understanding the nature and type of intermolecular interactions between the compound molecules.

Study of hydrogen bonded systems is essential and helpful as hydrogen bond plays a vital role in chemical, physical and biological process. Organic compounds containing electronegative group can interact with compounds containing active hydrogen through hydrogen bond. This type of hydrogen bond takes part in role in the stability of biologically important molecules. The amines are self-associated through intermolecular hydrogen bonds. They are both π - as well as n-electron donors they allow to have specific interactions with other electron deficient molecules **[2, 3]**. The present investigation is aimed on the detection of specific interaction between chlorophenols with NMA in n-hexane medium through the acoustic method. The complexes formed between amine and phenols have been attributed to the hydrogen bonding between nucleophilic alcoholic or phenolic oxygen and active amine hydrogen.

2. Experimental Techniques

The chemicals used for the present investigation were of AR grade and they used after purification, hexane (distillation ≥0.998%), N-methylaniline (fractional distillation ≥ 0.996%), Phenol (distlliation≥0.995) and 4-Chlorophenol (distlliation≥0.995). The purity of these chemicals was ascertained by comparing the measured velocity and density of the pure components with available literature values**.**

All the liquid mixtures were prepared by weighing appropriate amounts of pure liquids and mixed in airtight stopper bottles to minimize evaporation losses. The density, ρ of the pure liquids and their ternary systems were found by using a 10 ml specific gravity bottle. All the weighing measurements were made with a digital balance(Shimadzu, Japan) of accuracy ±0.1mg. The accuracy of the mole fraction was ±1 x 10^{-4}. The ultrasonic velocities in pure liquids and their ternary liquid mixtures were measured using a single crystal variable path ultrasonic interferometer operating at 2 MHz frequency supplied by Mittal Enterprises, Model F81, with an accuracy of ±0.2 ms^{-1}. Viscosity measurements were made with an Ostwald's viscometer in which the flow time for solutions was measured through a digital stop clock of accuracy ±0.01s. The temperature of the samples was maintained constant to an accuracy of ±0.1K by digitally controlled thermostatic water bath. The results of u, ρ and η summarized in Table 1 represent the average of at least five independent measurements for each composition of the ternary liquid mixtures. From the measured values of ultrasonic velocity (u), density (ρ) and viscosity (η) various acoustical and excess thermo acoustical parameters were calculated using the standard formulae as reported in the literature **[4-6]**.

Table 1 Measured values of ultrasonic velocity, density for the two ternary systems of NMA with Phenol, 4-ChP in n-hexane at different temperatures

C Mol dm^{-3}	NMA + Phenol + n-hexane			NMA + 4-ChP+ n-hexane		
	298K	303K	308K	298K	303K	308K
u m s^{-1}						
0.01	1106.3	1086.1	1068.5	1104.1	1078.2	1055.1
0.02	1114.2	1095.7	1079.1	1113.4	1085.0	1063.3
0.03	1126.2	1104.9	1085.9	1119.7	1091.4	1070.9
0.04	1134.9	1115.8	1096.6	1125.0	1100.3	1076.8
0.05	1147.4	1123.8	1103.6	1132.6	1109.0	1084.1
0.06	1156.8	1134.0	1114.0	1139.9	1117.3	1094.0
0.07	1168.0	1143.2	1125.3	1150.5	1123.9	1101.4
0.08	1177.5	1155.8	1136.5	1159.1	1133.0	1113.2
0.09	1183.2	1164.6	1144.8	1172.8	1146.1	1124.0
0.10	1191.8	1172.2	1153.6	1183.2	1154.3	1135.0
ρ kg m^{-3}						
0.01	695.7	689.1	681.8	674.9	670.2	664.5
0.02	708.1	700.4	691.2	681.8	676.7	670.5
0.03	717.0	711.3	702.9	691.4	684.4	678.3
0.04	729.6	722.4	712.3	699.8	692.8	687.5
0.05	738.6	733.0	722.6	707.3	700.5	695.0
0.06	751.0	745.7	733.9	716.4	710.3	702.9
0.07	763.7	757.0	746.4	724.2	718.7	710.5
0.08	777.8	772.5	761.2	730.5	724.9	716.8
0.09	790.1	784.7	773.8	739.5	732.6	726.7
0.10	803.7	796.3	788.2	746.7	741.9	736.1

3. Results and Discussion

3.1 Acoustical parameters

The measured values of ultrasonic velocity, density and viscosity and the calculated acoustical parameters for the two ternary systems such as NMA with Phenol, 4-chlorophenol in hexane at 298.15 K,

303.15 K and 308.15 K are summarized in Tables 1 and 2. The graphical representation for the variations of ultrasonic velocity (u), adiabatic compressibility (κ) and internal pressure (π_i) for solutions containing equimolar concentration of solutes is depicted in Fig. 1 (a-b) and 2 (a-b)**.** An examination of the acoustical parameters in Table 2 tells that the ultrasonic velocity increases with increase in concentration and decreases with increasing in temperature in the two ternary systems. The trend in the ultrasonic velocity is depicted in Fig. 1 (a-b) which shows that the variation is similar in these two systems. The increase in velocity may be attributed to strong solute-solute interactions. It was reported that the strength of molecular interactions in liquid mixtures becomes high where the velocity maximum occurs and it may be attributed to charge transfer complex formation through hydrogen bond **[7].** Since the two chlorophenol's are structurally similar, the increase in velocity in these liquid mixtures suggests that strong molecular interaction between the phenols and NMA. The dilute solutions minimize the effect of viscosity and internal field. Hence, dilutions in apolar solvents are used in the present investigation.

Table 2 Computed values of free length (L_f), molar volume (V_m), internal pressure (π_i), free volume (V_f) and molecular cohesive energy (MCE) for the two ternary systems of NMA with Phenol, 4-ChP in n-hexane at different temperatures

C Mol dm^{-3}	NMA + Phenol + n-hexane			NMA + 4-ChP+ n-hexane		
	298K	303K	308K	298K	303K	308K
L_f / A^0						
0.01	0.6771	0.6993	0.7210	0.6889	0.7143	0.7396
0.02	0.6664	0.6875	0.7090	0.6797	0.7064	0.7306
0.03	0.6552	0.6766	0.6987	0.6711	0.6983	0.7212
0.04	0.6446	0.6648	0.6873	0.6639	0.6884	0.7125
0.05	0.6336	0.6553	0.6781	0.6560	0.6792	0.7038
0.06	0.6233	0.6438	0.6665	0.6476	0.6695	0.6935
0.07	0.6122	0.6339	0.6543	0.6382	0.6617	0.6852
0.08	0.6017	0.6206	0.6415	0.6307	0.6536	0.6749
0.09	0.5941	0.6111	0.6317	0.6195	0.6427	0.6639
0.10	0.5848	0.6027	0.6211	0.6111	0.6341	0.6532
V_m / x 10^{-4} m^3 mol^{-1}						
0.01	1.2504	1.2624	1.2760	1.2889	1.2980	1.3093
0.02	1.2394	1.2531	1.2700	1.2872	1.2970	1.3095
0.03	1.2342	1.2443	1.2594	1.2799	1.2932	1.3051
0.04	1.2225	1.2349	1.2527	1.2746	1.2877	1.2979
0.05	1.2166	1.2262	1.2442	1.2705	1.2831	1.2936
0.06	1.2050	1.2139	1.2338	1.2632	1.2744	1.2882
0.07	1.1929	1.2038	1.2214	1.2580	1.2680	1.2831
0.08	1.1788	1.1873	1.2054	1.2551	1.2652	1.2800
0.09	1.1675	1.1759	1.1930	1.2474	1.2595	1.2703
0.10	1.1544	1.1655	1.1780	1.2425	1.2510	1.2614
MCE / k J						
0.01	32.062	31.737	31.109	31.129	30.839	30.307
0.02	33.047	32.968	32.037	31.854	31.674	31.029
0.03	34.166	33.796	33.355	32.642	32.714	32.166
0.04	34.608	34.336	34.308	33.543	33.662	33.234
0.05	35.351	35.232	35.191	34.133	34.239	33.900
0.06	35.733	35.788	35.642	34.707	34.675	34.501
0.07	36.395	36.576	36.655	35.123	35.291	34.955
0.08	37.053	37.011	37.164	35.607	35.682	35.517
0.09	37.804	37.625	38.039	35.921	36.190	36.135
`0.10	38.440	38.494	38.570	36.532	36.475	36.629

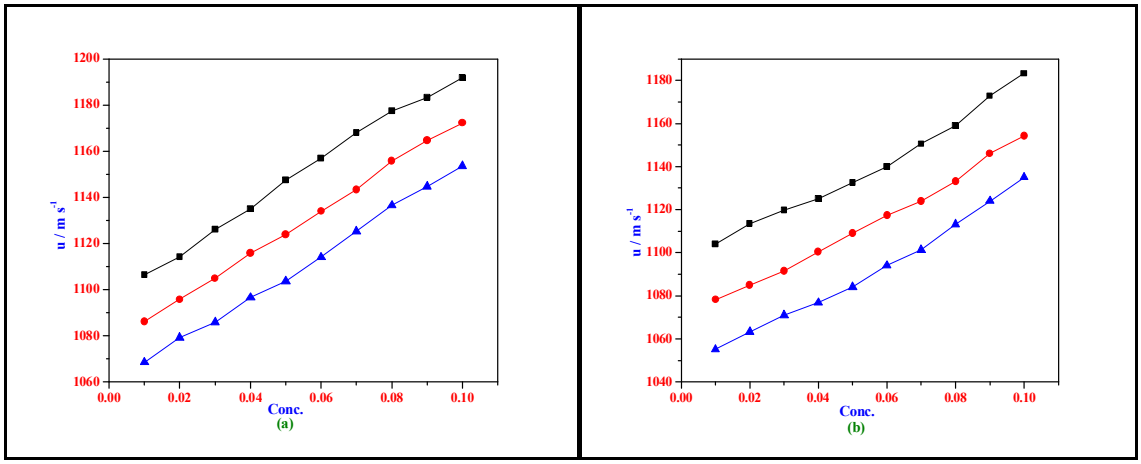

Figure 1 Plots of ultrasonic velocity versus concentration for a) Phenol and b) 4-ChP with NMA in n-hexane system at different temperatures (▮) T = 293 K, (•) 298 K and (▲) 303 K

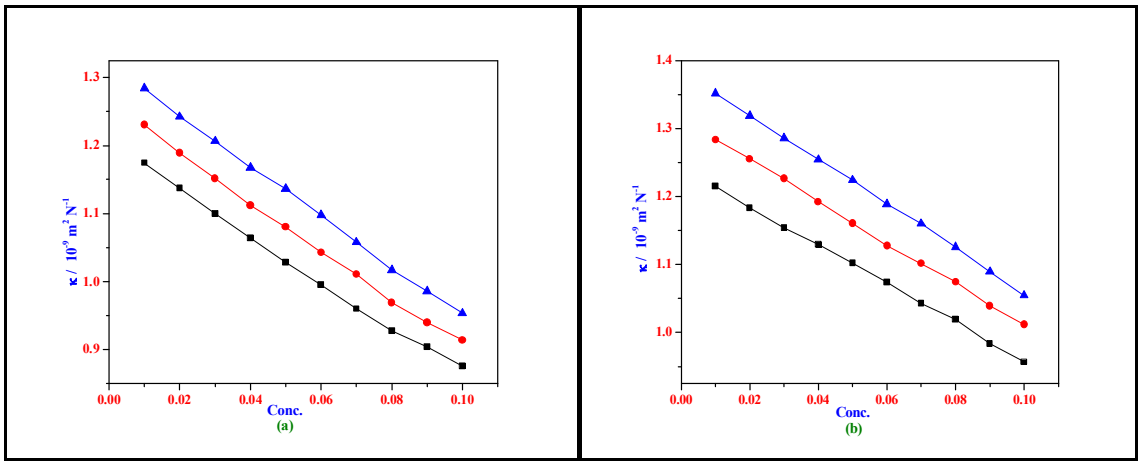

Figure 2 Plots of adiabatic compressibility versus concentration for a) Phenol and b) 4-ChP with NMA in n-hexane system at different temperatures (▮) T = 293 K, (•) 298 K and (▲) 303 K

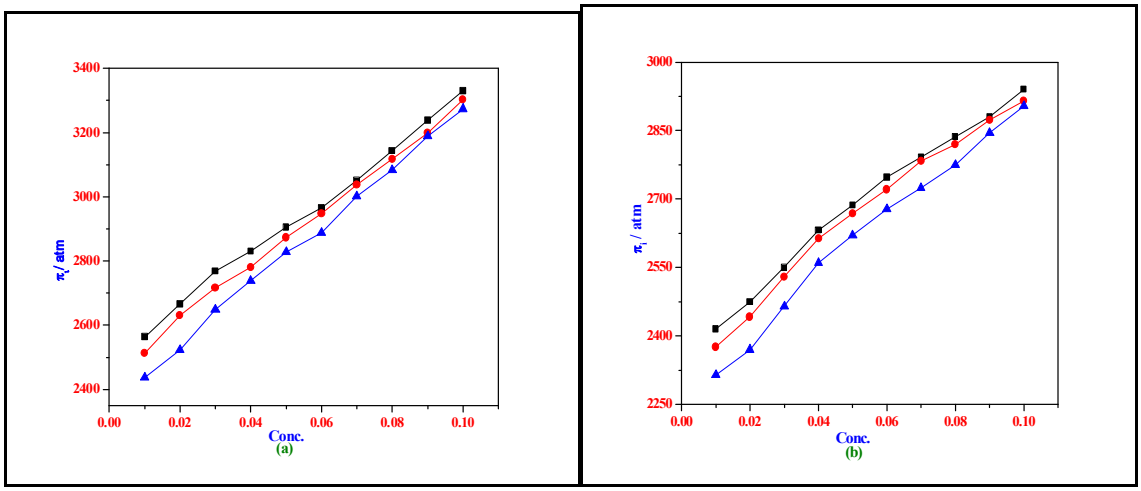

Figure 3 Plots of internal pressure versus concentration for a) Phenol and b) 4-ChP with NMA in n-hexane system at different temperatures (▮) T = 293 K, (•) 298 K and (▲) 303 K

Normally apolar solvents provide the medium and dilution for the mixture, which in turn, also minimizes the requirement of pure liquids in large quantity and hence hexane is used. Also, hexane is chemically inert and non-polar solvent and it does not interact with the other components in the ternary mixture **[8]**. It may be indicate the strength of interaction between phenols and NMA depends upon structure of phenols. Plots of 'u' versus concentration are similar in the case of the two phenols suggesting similar type of molecular interaction. Adiabatic compressibility (κ) is a measure of intermolecular association or dissociation. The structural arrangement of the molecule affects the adiabatic compressibility. The variation of adiabatic compressibility and free length with concentration shows a reverse trend as that of 'u' and 'ρ'. A continuous decrease in adiabatic compressibility (κ) and intermolecular free length (L_f) is supporting the existence of strong interactions between NMA and cholorophenol in the liquid mixtures which lead to the increasing compactness of the systems. The rapid decrease of 'κ' pointed the formation of a large number of tightly bound systems **[2]**. The disruption of molecular interactions with rise in temperature makes the molecules to move apart and the systems become more compressible. This is well reflected by the increase of free length and adiabatic compressibility with increase of temperature.

The values of internal pressure show that as the concentration increases internal pressure values increases. An exact reverse trend is observed from in the variations of free volume (V_f) as summarized in tables. The increase in the values of internal pressure with increase in concentration of component molecules at the investigating temperatures clearly explains the growing molecular association through the formation of complexes. The trend in the values of free volume 'V_f' with concentration and temperature supports the observations of 'π_i' and 'L_f'. The trend in the values of free volume with concentration suggests that there may be strong intermolecular hydrogen bonds between the amine and phenols **[7].**

3.2 Excess thermo acoustic parameters

The values of excess parameters, such as excess velocity (u^E), excess free length (L_f^E), excess molar volume (V_m^E), excess internal pressure (π_i^E) and excess free volume (V_f^E) were computed and listed in Table 3. Plots showing variation of excess free volume (V_f^E) and excess free length (L_f^E) with concentration at different temperatures are depicted in Fig. 4a-b and 5a-b. The thermodynamic excess properties of organic liquid mixtures depend on the chemical structure, size and shape of their constituent molecules.

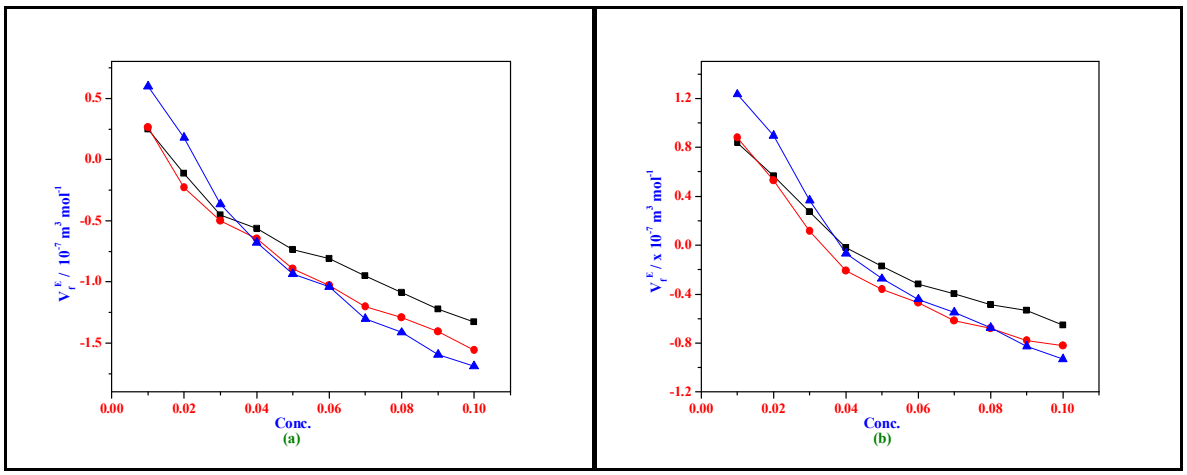

Figure 4 Plots of excess free volume versus concentration for a) Phenol and b) 4-ChP with NMA in n-hexane system at different temperatures (■) T = 293 K, (•) 298 K and (▲) 303 K

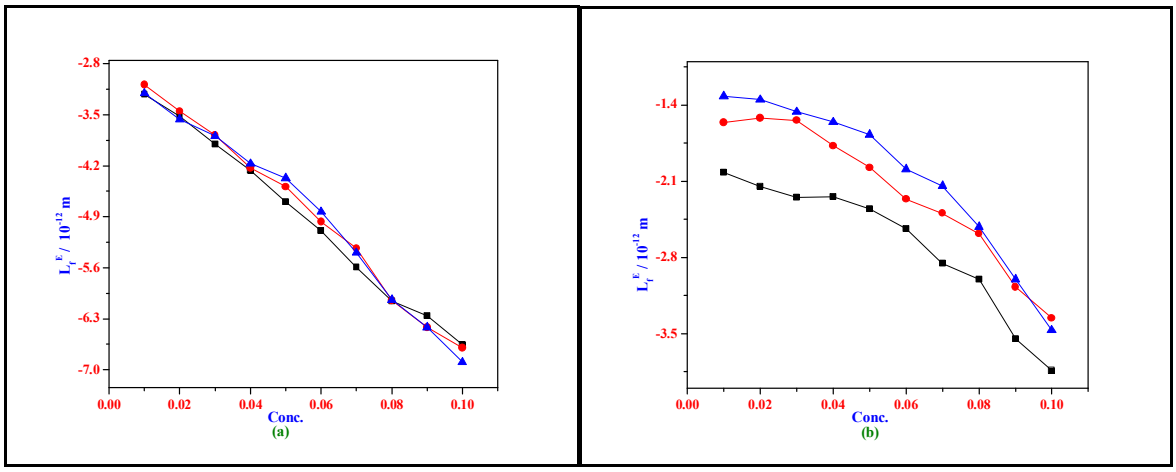

Figure 5 Plots of excess free length versus concentration for a) Phenol and b) 4-ChP with NMA in n-hexane system at different temperatures (▮) T = 293 K, (•) 298 K and (▲) 303 K

Table 3 Excess velocity (u^E), Excess adiabatic compressibility (κ^E), Excess molar volume (V_m^E), and Excess internal pressure (π_i^E) for the three ternary systems of NMA with Phenol, 4-ChP in n-hexane at different temperatures

C Mol dm^{-3}	NMA + phenol + n-hexane			NMA + 4-chlorophenol + n-hexane		
	298K	303K	308K	298K	303K	308K
u^E / ms^{-1}						
0.01	19.7	17.5	19.0	16.7	8.8	4.8
0.02	17.7	17.1	19.6	15.4	4.9	2.3
0.03	20.2	16.8	17.0	11.6	1.1	-0.4
0.04	19.9	18.6	18.6	7.3	0.2	-4.2
0.05	23.9	18.0	17.0	5.8	-0.3	-6.1
0.06	25.1	20.0	19.2	4.3	-0.8	-5.1
0.07	28.5	21.3	22.7	6.6	-2.7	-6.1
0.08	30.5	26.4	26.4	7.2	-1.7	-2.3
0.09	29.1	28.0	27.6	13.2	3.7	0.7
0.10	30.8	28.7	29.5	16.3	4.5	4.3
κ^E / x 10^{-10} m^2 N^{-1}						
0.01	-1.207	-1.177	-1.240	-0.791	-0.639	-0.563
0.02	-1.354	-1.354	-1.417	-0.889	-0.683	-0.639
0.03	-1.523	-1.509	-1.542	-0.970	-0.744	-0.736
0.04	-1.678	-1.696	-1.710	-1.012	-0.873	-0.820
0.05	-1.844	-1.811	-1.810	-1.086	-0.983	-0.905
0.06	-1.995	-1.994	-1.991	-1.179	-1.117	-1.055
0.07	-2.173	-2.131	-2.197	-1.312	-1.193	-1.142
0.08	-2.332	-2.373	-2.421	-1.385	-1.283	-1.298
0.09	-2.405	-2.500	-2.555	-1.580	-1.466	-1.484
0.10	-2.533	-2.596	-2.713	-1.689	-1.57	-1.657
V_m^E / x 10^{-6} m^3 mol^{-1}						
0.01	-5.888	-5.498	-5.164	-2.017	-1.921	-1.828
0.02	-6.358	-5.784	-5.109	-1.544	-1.363	-1.160
0.03	-6.273	-6.056	-5.538	-1.655	-1.118	-0.930
0.04	-6.877	-6.414	-5.610	-1.608	-1.076	-1.039
0.05	-6.920	-6.733	-5.894	-1.459	-0.967	-0.889
0.06	-7.562	-7.435	-6.391	-1.653	-1.296	-0.874
0.07	-8.274	-7.934	-7.117	-1.665	-1.417	-0.859
0.08	-9.214	-9.110	-8.225	-1.467	-1.200	-0.662

0.09	-9.891	-9.781	-8.988	-1.776	-1.293	-1.150
0.10	-10.77	-10.38	-10.03	-1.818	-1.696	-1.578
π_i^E / x 10^2 atm						
0.01	-0.061	-0.083	-0.570	-2.346	-2.187	-2.468
0.02	0.382	0.535	-0.235	-3.082	-2.760	-3.058
0.03	0.850	0.866	0.537	-3.594	-3.057	-3.199
0.04	0.954	1.014	0.976	-3.986	-3.328	-3.274
0.05	1.202	1.469	1.433	-4.588	-3.850	-3.659
0.06	1.322	1.766	1.617	-5.078	-4.342	-4.023
0.07	1.722	2.235	2.339	-5.683	-4.691	-4.460
0.08	2.211	2.613	2.777	-6.237	-5.249	-4.813
0.09	2.742	3.041	3.462	-6.770	-5.607	-4.936
0.10	3.260	3.694	3.967	-7.087	-6.034	-5.130

The excess values of ultrasonic velocity which are placed in Table 3 are all positive in the liquid systems in the concentration range of investigation. The positive excess values in 'u^E' clearly suggest that there is a strong molecular interaction existing between the NMA and chlorophenol's molecule **[9]**. Recent ultrasonic study on binary mixtures of cresols and anisaldehyde revealed that positive values of V^E at different concentration may be due to non-specific physical interactions such as dispersion forces or weak dipole–dipole while negative values of excess molar volume may be indicative of charge transfer forces, hydrogen bonds and other complex forming interactions **[10]**. The positive deviations in the excess internal pressure (π_i^E) support the observation of 'u^E'. Stronger magnitude of interactions gives rise to positive deviation in internal pressure **[11]**. In the present investigation, the excess adiabatic compressibility (κ^E) the excess free length (L_f^E) and excess free volume (V_f^E) and excess molar volume exhibit negative values in the concentration range investigated in all the systems clearly indicating the presence of strong hydrogen bonding interactions between unlike molecules. This is also supported by the observations of earlier workers **[12, 13]**. The negative values in these parameters also indicate the possibility of interstitial accommodation of solutes. The strength of the interaction between the component molecules increases, when excess values tend to become increasingly negative. This may also be quantitatively interpreted in terms of closer approach of unlike molecules leading to reductions in compressibility and volume **[14]**.

Conclusion

Ultrasonic investigations on the molecular interactions between phenol, 4-cholorophenol and N-methylaniline in non-polar medium like THF reveal that the interactions are through the formation of intermolecular hydrogen bond. The trend in the acoustical parameters and excess thermodynamic parameters suggest the strength and magnitude of interactions. The trend in the measured and computed parameters with concentration establishes strong solute-solute interactions and formation of hydrogen bonded complexes between NMA and phenol, 4-chlorophenol. The thermodynamic parameters identify that thermodynamically stable complexes were formed in the two ternary systems investigated and the complex formation is exothermic.

References

1. Vijayalakshmi D, Narasimha Rao C, Gowrisankar M, Sivakumar K, Venkateswarlu P, Densities, viscosities and speeds of sound of binary mixtures of ethyl benzoate with toluene, and isomeric chlorotoluenes at different temperatures. J.Molecular Liquids, 2014, 197; 272-286.
2. Santhi BS, Krishnamurthy D, Kannappan V, Kumar R, Ultrasonic and spectroscopic investigations of hydrogen bonded complexes of aromatic aldehydes with aniline in n-Hexane at 303.15K. J.Molecular Liquids, 2013, 188; 120-125.
3. Kumar R, Ashokan P, Askar Ali SJ, Spectroscopic and ultrasonic studies on the hydrogen bonded complexes of aromatic aldehydes with phenol in hexane medium. J.Molecular Liquids, 2013, 179; 124-129.
4. Vogel AI, A Textbook of Practical Organic Chemistry, 5thEdn. John Willey, New York, 1989.

5. Weissberger A, Prokaher FS, Reddick JA, Toops EE, Techniques of Organic Chemistry, Vol. VII, Organic Solvents, Interscience, New York, 1955.
6. Baldevraj, V. Rajendran, Palanichamy, Science and Technology of Ultrasonics, Narosa Publishing House, New Delhi, 2004.
7. Kumar R, Ulagendran V, Kannappan V, Jayakumar S, Thermo acoustic and spectral investigations of charge transfer interaction between aromatic amine and ketones. Fluid Phase Equilibria, 2011, 307; 113-125.
8. Aasthees Awasthi P, Shukla JP, Ultrasonic and IR study of intermolecular association through hydrogen bonding in ternary liquid mixtures. Ultrasonics, 2003, 10; 241-246.
9. Dalai B, Dash SK, Singh SK, Viscometric, Volumetric and acoustic properties of binary mixtures of a nuclear extractant with monocarboxylic acids (C1-C3) at 303.15 K. Ind J Pure Appl Phy., 2014, 52; 24-29.
10. Narendra K, Srinivasu Ch, Fakruddin Sk, Narayanamurthy P, Excess parameters of binary mixtures of anisaldehyde with *o*-cresol, *m*-cresol and *p*-cresol at T = (303.15, 308.15, 313.15,and 318.15) K. J Chem Thermodyn., 2011, 43; 1604-1611.
11. 11. Rama Rao GV, Sarma AV, Ramachandran D, Rambabu C, Evaluation of excess free volumes and excess internal pressures of binary solutions of *o*-chlorophenol at different temperatures. Ind. J. Pure Appl. Phys., 2005, 43; 602-608.
12. Mosteiro L, Casas LM, Legido JL, Surface tension, density and speed of sound for the ternary mixture {diethyl carbonate + p–xylene + decane}. J. Chem. Thermodyn., 2009, 41; 695-704.
13. Palani R, Balakrishnan S, Acoustical properties of ternary mixtures of 1–alkanols in di–isopropyl ether and 2, 2, 2–trifluoroethanol mixed solvent. Ind. J. Pure Appl. Phys., 2010, 48; 644-650.
14. Ali A, Nain AK, Sharma VK, Ahmad S, Study of molecular interaction in ternary mixtures through ultrasonic speed measurements. Physics and Chemistry of Liquids, 2004, 42; 375-383.

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