

Thermodynamic Properties of Phenetole with 2-Chlorophenol and 3-Chlorophenol at Different Temperatures

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Abstract

Acoustical and excess thermo acoustical properties of 2-Chlorophenol (2-ChP), 3-Chlorophenol (3-ChP) with Phenetole in Tetrahydrofuran (THF) mixtures are investigated by measuring ultrasonic velocity (u), density (ρ) and viscosity (η) in different concentration range at atmospheric pressure at different temperatures. The trend in the acoustical parameters and magnitude of excess thermo acoustical parameters has been used to identify the existence of intra and intermolecular interaction through charge transfer complex formation. The formation of 1:1 complex was also confirmed by UV-Visible spectroscopic method at 303.15 K in these systems. It may be pointed out that the formation constants of the charge transfer complexes determined by Benesi-Hildebrand spectroscopic method and Kannappan equation in ultrasonic method. Thermodynamic parameters such as ΔG , ΔH and ΔS for these equilibria are determined.

Keywords: Excess parameters, phenols, Phenetole, THF, ultrasonic technique, thermo acoustic parameters.

1. Introduction

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 Phenetole are self-associated through intermolecular hydrogen bonds. They are both π - as well as n -electron donors and they allow specific interactions with other electron deficient molecules [1,2]. The present investigation is Phenetole on the detection of specific interaction between 2-ChP, 3-ChP with Phenetole in THF medium through the acoustic method. The complexes formed between Phenetole and phenols have been attributed to the hydrogen bonding between oxygen and active hydrogen.

2. Experimental

The density, ρ of the pure liquids and their ternary systems were found by using a 10 ml specific gravity bottle. 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 $\pm 0.2 \text{ ms}^{-1}$. 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 $\pm 0.01 \text{ s}$.

Table 1. Ultrasonic velocity, MCE and excess internal pressure for the two ternary systems of Phenetole with 2 – ChP, 3 – ChP in THF at different temperatures

C Mol dm ⁻³	Phenetole + 2-chlorophenol + THF			Phenetole + 3 chlorophenol + THF		
	303 K	308 K	313 K	303 K	308 K	313 K
U / m s ⁻¹						
0.01	1244.0	1222.1	1200.4	1251.2	1230.5	1207.5
0.02	1244.9	1222.4	1201.1	1251.8	1230.9	1207.9
0.03	1245.3	1222.8	1201.6	1252.4	1231.7	1208.6
0.04	1246.2	1223.5	1202.1	1253.3	1232.0	1209.3
0.05	1246.8	1223.9	1202.8	1254.2	1232.9	1210.0
0.06	1247.0	1224.7	1203.7	1255.0	1233.3	1210.8
0.07	1247.5	1225.6	1204.3	1255.8	1234.0	1211.4
0.08	1248.5	1227.9	1205.2	1256.0	1234.7	1212.1
0.09	1249.5	1228.0	1205.9	1256.7	1235.3	1213.0
0.10	1250.9	1229.1	1206.8	1257.9	1236.5	1214.3
MCE / kJ						
0.01	32.201	32.370	32.296	31.978	32.164	31.893
0.02	32.191	32.358	32.330	32.017	32.212	31.983
0.03	32.191	32.411	32.453	32.050	32.244	32.045
0.04	32.192	32.446	32.487	32.102	32.312	32.086
0.05	32.167	32.469	32.462	32.158	32.367	32.147
0.06	32.174	32.470	32.540	32.196	32.448	32.222
0.07	32.263	32.468	32.614	32.247	32.503	32.276
0.08	32.291	32.458	32.663	32.297	32.554	32.280
0.09	32.283	32.490	32.700	32.344	32.577	32.353
0.10	32.286	32.529	32.777	32.400	32.661	32.426
$\pi_i^E \times 10^{-2}$ atm						
0.01	-3.147	-2.952	-2.786	-5.485	-4.884	-4.902
0.02	-3.394	-3.200	-2.960	-5.864	-5.193	-5.152
0.03	-3.619	-3.356	-3.033	-6.232	-5.512	-5.422
0.04	-3.828	-3.540	-3.198	-6.564	-5.782	-5.703
0.05	-4.073	-3.714	-3.427	-6.884	-6.064	-5.958
0.06	-4.272	-3.921	-3.543	-7.220	-6.305	-6.188
0.07	-4.374	-4.122	-3.645	-7.530	-6.567	-6.433
0.08	-4.539	-4.322	-3.789	-7.838	-6.823	-6.728
0.09	-4.699	-4.476	-3.917	-8.132	-7.112	-6.939
0.10	-4.871	-4.604	-3.990	-8.402	-7.319	-7.136

3. Result and discussion

3.1. Acoustical parameters

Ultrasonic velocity, MCE and excess internal pressure for the two ternary systems of Phenetole are arranged in Table 1. The ultrasonic velocity versus concentration is similar in the two ternary systems suggesting the presence of a similar type of interaction in two systems. The increase in velocity may be attributed to strong solute-solute interactions. The strong polar nature of the chlorophenols may disrupt the dipolar association in pure phenetole leading to the possibility of unlike molecular attraction. The steep increase in the ultrasonic velocity may be an indication of stronger molecular interactions such as

dipole-dipole or charge transfer complex formation [3]. MCE also increases non-linearly with concentration in two systems. The valley in the two systems indicates the rupture of hydrogen bonds due to interaction between chlorophenol and solvent molecules (dipole-induced dipole) and above this concentration the interactions between chlorophenol and molecules of Phenetole dominate. The magnitude of molar cohesive energy substantiates the possibility of hydrogen bonded interaction [4]. The strength of interaction increases with concentration as evident from the table of MCE against concentration.

3.2. Excess thermo acoustic parameters

Plots showing variation of excess velocity (u^E) with concentration at different temperatures is depicted in, Figs. 1a–b. The thermodynamic excess properties of organic liquid mixtures depend on the chemical structure, size and shape of their constituent molecules. The negative deviations in ultrasonic velocity explain the non-ideal nature of these two ternary liquid mixtures and greater deviations suggest stronger intermolecular interactions between the component molecules [5]. It was reported that strong intermolecular interactions such as hydrogen bonding and charge transfer complexes lead to negative deviation in ultrasonic velocity. The negative deviation in internal pressure is an indication of stronger adhesion between the components in the mixture [6].

Table 2. The values of stability constants K and correlation coefficient for various donors 'D' at different temperatures and thermodynamic parameters obtained by ultrasonic method at 303.15 K

D	Solvent: THF			Acceptor: Phenetole			Correlation coefficient
	K (mol ⁻¹)			ΔG	ΔH	ΔS	
	303.15K	308.15K	313.15K	(kJmol ⁻¹)	(kJmol ⁻¹)	(JK ⁻¹ mol ⁻¹)	
2-ChP	18.01	15.70	13.64	-7.282	-29.830	-74.415	0.987
3-ChP	20.55	17.15	15.07	-7.615	-32.466	-82.017	0.999

Table 3. Thermodynamic parameters of stability constant K (by Benesi-Hildebrand equation), free energy of formation ΔG , wave length of maximum absorption of charge transfer complex $\lambda_{\max}$, absorptivity and correlation coefficient obtained by UV spectrometric technique for different proton donors at 303.15K

Solvent: THF		Proton acceptor: Phenetole		
Proton donor	k (mol^{-1})	ΔG (kJ mol^{-1})	$\lambda_{\max}$ (nm)	ϵ ($\text{dm}^2 \text{mol}^{-1}$)
2-Chlorophenol	38.20	-9.18	232	2171
3-Chlorophenol	76.91	-10.94	241	1033

3.3. Thermodynamic parameters

The values of equilibrium constant for the charge transfer of Phenetole with chlorophenols in THF solutions were calculated at 303, 308 and 313 K by employing Kannappan equation [7–9] from the measured values of ultrasonic velocity. Formation constants of the two charge transfer species stabilized through hydrogen bond at three different temperatures are given in Table 2. The thermodynamic parameters obtained by UV-spectrometric technique are arranged in Table 3. The decreasing trend of K with increase in temperature reveals that the charge transfer interaction between the chlorophenols and Phenetole is exothermic. Fairly good correlation is obtained between $\ln K$ values and $1/T$ in accordance with van't Hoff equation (Fig. 2a-b). The enthalpy changes for protonation equilibrium are obtained from the slopes of the plots of $\ln K$ vs. $1/T$. The computed values of free energy of formation (ΔG), enthalpy changes (ΔH) and entropy changes (ΔS) are summarized in Table 2. The negative values of free energy of formation suggest that the charge transfer species are stabilized through hydrogen bond.

4. Conclusion

The present investigation deals with determination of thermodynamic properties of charge transfer complexes formed between an Phenetole and 2ChP,

3ChP in THF medium by ultrasonic method. The formation constant values computed by ultrasonic method. The trend in the acoustical properties and negative values of entropy of formation clearly establish the formation of donor-acceptor complex between these two component molecules in a non-polar medium. The stability is in the order 3ChP-Phenetole > 2ChP-Phenetole. The negative values of free energy of formation of these two complexes indicate that these complexes are thermodynamically stable.

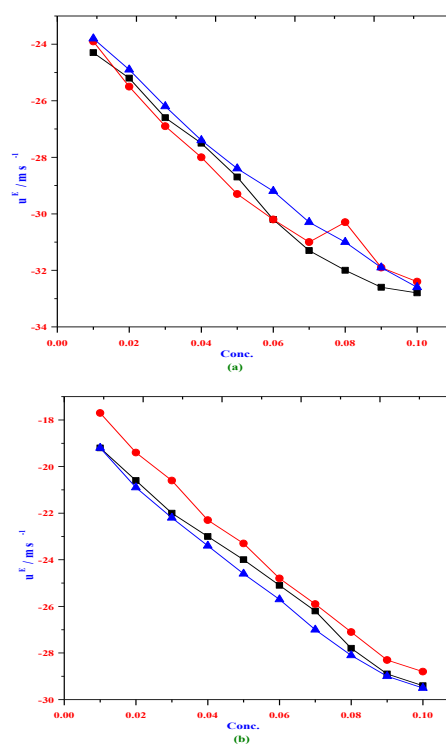
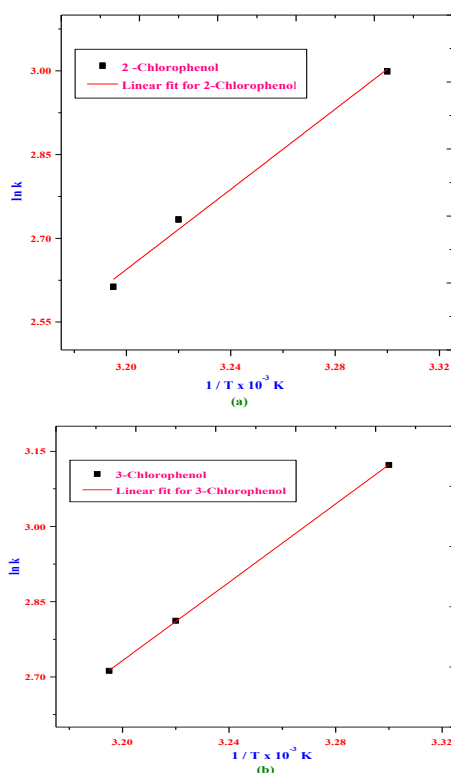


Figure 1. Plot of Excess velocity versus concentration
a) 2-ChP b) 3-ChP with Phenetole in THF system at
different temperatures $T = (\blacksquare)$ 303 K, $(\bullet)$ 308 K and
 $(\blacktriangle)$ 313 K



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Figure 2. Plot of reciprocal of temperature versus logarithm of stability constant for a) 2-ChP b) 3-ChP with Phenetole in THF solution

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