

Research Article

DIELECTRIC BEHAVIOUR OF THIOPHENOL IN BENZENE, CARBON TETRACHLORIDE, CYCLOHEXANE, N-HEXANE

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ABSTRACT

Using Surber's technique of measuring reflection coefficient from the air-dielectric boundary of liquid, the dielectric constant (ϵ'), dielectric loss (ϵ'') of Thiophenol with benzene, carbon tetrachloride, cyclohexane, n-hexane and their binary mixtures for different mole fraction of thiophenol have been estimated at 15.2 GHz microwave frequency at 30°C. The values of loss tangent ($\tan\delta$), molar polarization (P_{12}) and dipole-moment (μ), of binary mixtures as well those of pure liquids are reported.

Key Words: Dielectric Parameters, Polarization, Dipole Moment, Binary Mixture, Complex Formation.

INTRODUCTION

Thiophenol (Phenyl Mercaptan (C_6H_5SH)) is used as an intermediate in the manufacture of pesticides, pharmaceuticals and amber dyes and is also used as a mosquito larvicides. It is an odorous, colourless liquid. The disagreeable odour has been described as penetrating, repulsive and garlic like. Phenyl Mercaptan depresses the central nervous system and affects the respiratory centre, similar to hydrogen sulfide, producing death by respiratory paralysis. Clinical signs of exposure are eye and mucous membrane irritation, headache, dizziness, staggering gait, nausea and vomiting. Paralysis of the locomotor muscles has also been observed.

Experimental investigation of dielectric properties of organic compounds is of great value in understanding the nature of complex formation between the molecules. The knowledge of dielectric properties of organic compounds and their mixtures at microwave frequencies helps in their characterization and applications (Kalamse *et al.*, 2002). During literature review, the author came to know that thiophenol (Phenyl Mercaptan) due to its toxicity remains untouch. Therefore this is an attempt to throw light on thiophenol and its mixture with benzene, carbon tetrachloride, cyclohexane and n-hexane.

Experimental

The measurement of dielectric constant (ϵ') and dielectric loss (ϵ'') were carried out from the Ku-band microwave bench of oscillating frequency 15.2 GHz at 30°C temperature. Then density of the pure components and their mixtures were measured by using pycnometer. The chemicals used were of AR grade supplied by spectrochem Pvt. Ltd. Mumbai and S.D. Fine chemicals Mumbai. The two liquids according to their proportions by volume were mixed well and kept for 6 hour in well stopper bottles to ensure good thermal equilibrium (Rekha Pande *et al.*, 2005).

The dielectric parameters (ϵ') and (ϵ'') were measured by using Surber's technique (Sisodia and Raghuvanshi 1990, Surber 1948) of measuring the reflection coefficient from the air-dielectric boundary of the liquid. Surber's technique for medium and high loss liquids permits rapid measurements of VSWR. The dielectric parameters (ϵ') and (ϵ'') of thiophenol + (Benzene, carbon tetrachloride, cyclohexane and n-hexane) at 30°C we calculated using following equations.

$$\epsilon' = \left(\frac{\lambda_o}{\lambda_c}\right)^2 + \left(\frac{\lambda_o}{\lambda_d}\right)^2 \quad \text{---} \quad (1)$$

$$\epsilon'' = \left(\frac{2}{\pi}\right) + \left(\frac{\lambda_o}{\lambda_d}\right)^2 \left(\frac{\lambda_g}{\lambda_d}\right) \left(\frac{d\rho}{dn}\right) \quad \text{---} \quad (2)$$

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Where λ_o , λ_c , λ_g and λ_d are the free space wavelength, cutoff wavelength, guide wavelength and wavelength in dielectric respectively ρ is the inverse voltage standing wave ratio (VSWR) and $\left(\frac{d\rho}{dn}\right)$ is the slope of ρ versus n where $n = 1, 2, 3, \dots$. Such that $n \cdot \frac{\lambda_d}{2}$ represents the length of dielectric filled in wave guide. (Narwade, 2006)

The loss tangent is calculated using relation

$$\tan\delta = \frac{\epsilon''}{\epsilon'} \quad \text{--- (3)}$$

The values of molar polarization of the mixtures were obtained by using relation.

$$P_{12} = \left(\frac{\epsilon' - 1}{\epsilon' + 2}\right) \left[\frac{M_1 X_1 + M_2 X_2}{\rho}\right] \quad \text{--- (4)}$$

Dipole moment is calculated by equation :

$$\mu = 0.0127 \times 10^{-18} \sqrt{(P_{12} - P_o)T} \quad \text{--- (5)}$$

Where $T = (273 + t^\circ\text{C})$

RESULTS AND DISCUSSION

The values of density (ρ), dielectric constant (ϵ'), loss factor (ϵ''), loss tangent ($\tan\delta$), molar polarization (P_{12}) and dipole moment (μ_D). With increasing molefraction of thiophenol in Benzene, carbon tetrachloride, cyclohexane and n-hexane are listed in table 1, 2, 3 & 4 respectively.

The variation in dielectric constant (ϵ') with mole fraction (x) of thiophenol in the mixtures with Benzene, carbon tetrachloride, cyclohexane and n-hexane are depicted in Figure (1). In all four systems, there is an increasing trend. According to Job (Job, 1928), this curve suggests occurrence of an intermolecular interaction between solute and solvents. Singh and Sharma (Singh *et al.*, 1996) observed such a behavior in the mixtures of ethylene diamine with ethyl methyl ketone and methyl isobutyl ketone.

Figure (2) depicts the variation of loss tangent ($\tan\delta$) against the mole fraction of thiophenol. It is seen that the absorption in the mixture is greater than that in pure liquids.

More than one maxima in $\tan\delta$ curve occurs in all four systems. We may explain this by considering the Debye's equation (Smyth 1955) for $\tan\delta$ for a dilute solution of a polar liquid in a non-polar solvent.

$$\tan\delta = \frac{(\epsilon' + 2)^2}{\epsilon'} \cdot \frac{4\pi \times N\mu^2}{27KT} \cdot \frac{\omega\tau}{(1 + \omega^2\tau^2)}$$

This equation suggests that the absorption will increase, if the dipole moment μ and relaxation time τ increase. Assuming the approximate validity of the Debye's equation to our case, the formation of the complex will increase the dielectric absorption (Singh *et al.*, 1996).

From Figure (3) it is observed that the molar polarization increases with concentration with thiophenol in all four systems.

In the present investigation of thiophenol + (Benzene, carbon tetrachloride, cyclohexane and n-hexane) mixtures, the amount of complex present is responsible for the shape of our polarization curves and the minimum in the curve is caused by the presence of complex or complexes (Rekha Pande, 2005).

Figure (4) shows the variation of dipole moment against molefraction of thiophenol from figure it is clear that as molefraction of thiophenol increases, dipole moment increases. This increase in μ is due to association – complexes of dipolar molecules (Debye, 1929, 1931).

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Benezene + Thiophenol

Table 1: Values of mole fraction (X) of thiophenol, density (ρ), dielectric constant (ϵ'), loss factor (ϵ''), loss tangent ($\tan\delta$), molar polarization (P_{12}) and Dipole moment (μ_D) for binary liquid system of Thiophenol + Benzene at 30°C.

X	ρ	ϵ'	ϵ''	$\tan\delta$	P_{12}	μ_D
0	0.877	2.4118	0.08632	0.03529	43.9357	0.6809
0.1103	0.902	2.7472	0.2009	0.0731	44.6558	0.7062
0.2249	0.927	2.9420	0.2084	0.0708	45.4041	0.7316
0.3428	0.952	2.9628	0.2086	0.0704	46.1740	0.7568
0.4657	0.977	3.2827	0.2747	0.0836	46.9764	0.7823
0.5921	1.002	3.3332	0.1459	0.0435	47.8018	0.8076
0.7228	1.027	3.6069	0.2333	0.0646	48.6552	0.8330
0.8593	1.052	3.7898	0.2494	0.0658	49.5465	0.8587
1	1.077	3.9206	0.2570	0.0655	50.4653	0.8844

CTC + Thiophenol

Table 2: Values of mole fraction (X) of thiophenol, density (ρ), dielectric constant (ϵ'), loss factor (ϵ''), loss tangent ($\tan\delta$), molar polarization (P_{12}) and Dipole moment (μ) for binary liquid system of Thiophenol + Carbon tetrachloride at 30°C.

X	ρ	ϵ'	ϵ''	$\tan\delta$	P_{12}	μ_D
0	1.592	2.12122	0.024830	0.010444	30.40219	0.00
0.11886	1.52762	2.65116	0.19682	0.7423	34.53947	0.072720
0.23942	1.46325	2.88293	0.20912	0.07253	37.7826	0.39910
0.36167	1.398875	2.86310	0.18235	0.06369	37.80327	0.40033
0.48571	1.3345	3.02677	0.199580	0.065938	40.06984	0.51758
0.61152	1.27012	3.2827	0.2615	0.0796	43.25117	0.64726
0.73918	1.20575	3.359	0.2523	0.07511	44.3602	0.68674
0.86864	1.14137	3.6662	0.245257	0.0668967	50.0973	0.86257
1	1.077	3.9206	0.2570	0.0655	50.4653	0.87263

Cyclohexane + Thiophenol

Table 3: Values of mole fraction (X) of thiophenol, density (ρ), dielectric constant (ϵ'), loss factor (ϵ''), loss tangent ($\tan\delta$), molar polarization (P_{12}) and Dipole moment (μ) for binary liquid system of Thiophenol + Cyclohexane at 30°C.

X	ρ	ϵ'	ϵ''	$\tan\delta$	P_{12}	μ_D
0	0.777	2.05400	0.01395	0.007075	26.49794	0
0.13136	0.8145	2.49446	0.19641	0.07873	35.75284	0.25035
0.26083	0.8520	2.76131	0.19888	0.07202	39.48726	0.48934
0.38844	0.8895	2.92152	0.23205	0.079428	41.45291	0.57663
0.48575	0.9270	3.04861	0.22835	0.07490	42.69666	0.62560
0.63831	0.9645	3.30786	0.27121	0.08199	45.42698	0.72155
0.76059	1.0020	3.52098	0.26113	0.074164	47.37096	0.78272
0.88117	1.0395	3.66626	0.23531	0.06418	48.47551	0.81544
1	1.077	3.92064	0.25741	0.06565	50.46571	0.87263

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n-hexane + Thiophenol

Table 4: Values of mole fraction (X) of thiophenol, density (ρ), dielectric constant (ϵ'), loss factor (ϵ''), loss tangent ($\tan\delta$), molar polarization (P_{12}) and Dipole moment (μ_D) for binary liquid system of Thiophenol + n-hexane at 30°C.

X	ρ	ϵ'	ϵ''	$\tan\delta$	P_{12}	μ_D
0	0.658	1.85496	0.04664	0.021913	29.0471	0
0.15460	0.71037	2.32581	0.15038	0.06465	38.78205	0.45395
0.29909	0.76275	2.54808	0.17585	0.6901	41.66103	0.58511
0.43439	0.81512	2.78443	0.21139	0.07591	44.20199	0.67960
0.56141	0.8675	2.92152	0.20921	0.071609	44.85054	0.70238
0.68088	0.91987	3.20937	0.24430	0.07612	47.26779	0.77960
0.79341	0.97225	3.57791	0.31691	0.08857	50.1730	0.85903
0.89963	1.02462	3.89390	0.30431	0.07815	50.40178	0.86956
1	1.077	4.28255	0.29804	0.06959	53.45145	0.95040

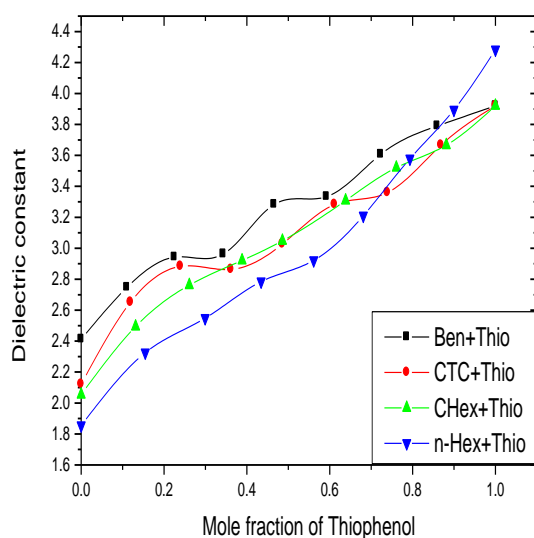


Figure 1 : The Dielectric constant for binary mixtures of Thiophenol with benzene, carbon tetrachloride, cyclohexane and n-hexane

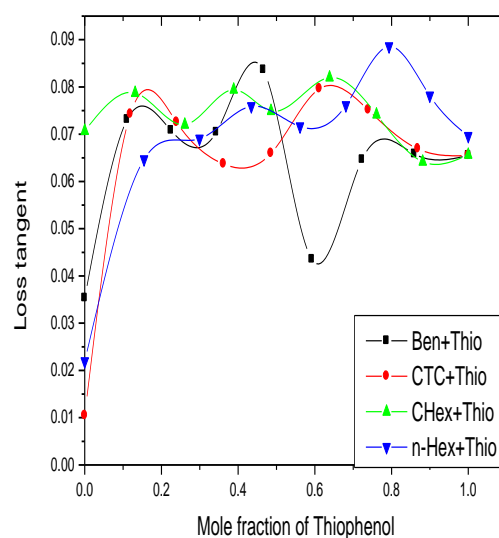


Figure 2 : The Loss tangent for binary mixtures of Thiophenol with benzene, carbon tetrachloride, cyclohexane and n-hexane

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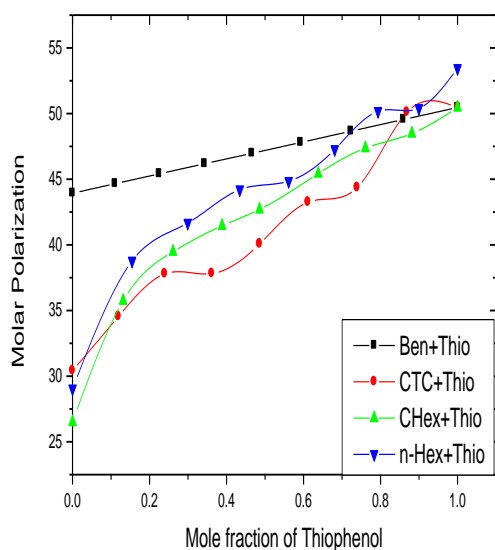


Figure 3 : The Molar Polarization for binary mixtures of Thiophenol with benzene, carbon tetrachloride, cyclohexane and n-hexane

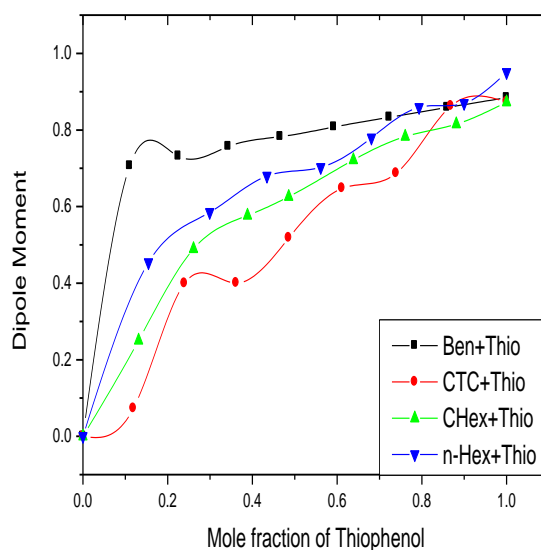


Figure 4 : The Dipole Moment for binary mixtures of Thiophenol with benzene, carbon tetrachloride, cyclohexane and n-hexane

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