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Dielectric Investigations of Anisole in Carbon Tetrachloride Mixtures.

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ABSTRACT

Dielectric constant, refractive index and density were measured for the mixtures of anisole with carbon tetrachloride at 303K. From these measurements polarization, dipole moment and Bruggemann factor for mixtures were determined for whole range of concentration. These parameters were used to predict the nature of solute – solvent interactions. This shows the symmetric changes of dielectric properties with the concentration. Further find the theoretical dielectric constant and dipole moment were used various permittivity and dipole moment models. The importances of these models have been discussed in terms of percentage and average percentage deviations.

Keywords: Anisole, Polarization, Dipole moment, Density, Dielectric constant, Refractive index

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INTRODUCTION

The multi components systems are important due to understanding the molecular interactions. The various types of interactions are identified multi component mixtures using dielectric, refractive index, ultrasonic measurements.[1-10]

The static dielectric constant of the mixtures combined with the density, boiling point, melting point and other analytical data have wide-ranging in chemical, pharmauctical and industrial applications. The permittivity of the pure and liquid mixtures is a vital property which can play a significant role in the molecular interactions.[10-15]

The polarizations of the polar and non polar liquids classify the polar attractions. Determination of polarization provides the information on the orientation of dipoles in liquid mixtures. Excess polarizations are zero no any specific type of interactions in the mixtures. Excesses polarization is negative aligned themselves form α-multimers then polarization value is positive dipole aligned along the directions of the molecules form β-multimers.

The Bruggemann factor, polarization and dipole moment[15-20] on liquid mixers provide the information regarding the molecular interaction and orientation of the molecules in a binary polar-non polar liquid. Measurement of dielectric constant has been revealed to be a useful technique to identify the structure of molecule, molecular interaction etc., in interactions in solutions state. Many investigations [21-24] have been carried out dielectric measurements on the mixtures of polar and non polar liquids. Few investigator have been reported the dielectric characteristics of binary polar - non polar liquid systems[25-27.]

Anisole is an important due to industrial and chemical applications, electrophonic substitution reaction more quickly; enhanced nucleophilicity reflects the influence of the methoxy group, which renders the ring more electron-rich. The methoxy group strongly affects the π electron cloud of the ring, more so than the inductive effect of the electronegative oxygen. Carbon tetrachloride is also important due to the manufacture less destructive refrigerants, the detection of neutrinos and organic solvent.

The present paper reports the results of dielectric constant and related parameters like polarization, dipole moment etc., and also theoretical permittivity of the anisole – carbon tetrachloride mixture.

EXPERIMENTAL

Anisole and carbon tetrachloride are of AR grade. The chemicals were purified as for the standard methods. The dielectric constant the solutions were measured help to Toshniwal (RL09) dipole meter. The dipole meter was calibrated using standard liquid like acetone, benzene, and toluene. The refractive indices were measured using an Abbe's refractometer. Density has been measured by using a 25 ml specific gravity bottle. Using water circulating thermostat maintained temperature at 303 K during measurements. The dielectric constant, density and refractive indices, polarization and molar refraction are shown in fig.1

THEORY AND CALCULATION

Determination of dipole moment

The dipole moment of pure liquids and solutions, polarization were calculated from the permittivity measurements using the following expressions

According to the Debye model (DM) the molar polarization of the solution (P_{12}) is expressed as

$$P_{12} = \left[\frac{\varepsilon_{12}-1}{\varepsilon_{12}+2}\right]\left[\frac{m_1x_1+m_2x_2}{d_{12}}\right] \quad (1)$$

P_{12} is the sum of the polarization contributions of the two components is given by

$P_{12}=P_1X_1+ P_2X_2.$ (2)

From the equation (1) and (2) evaluated the polarization of the solute (P_2). P_2 plotted against x_2 and obtain the polarization at infinite dilution ($P_2\infty$). The values of the dipole moment were determined using the relation.

$$\mu_2 = 0.01281X10^{-18}\left[P_2\mu T\right]^{1/2} \quad (3)$$

Where $P_2\mu = P_2\infty$ -R_D and R_D is the molar refraction.

The molar polarization ($RD_)$ is evaluated using the equation

$$R_D = \left[\frac{n_2^2-1}{n_2^2+2}\right]\left[\frac{m_2}{d_2}\right] \quad (4)$$

Palit and Bannerjee (PB) determine the value of P_2^∞ using the equation

$$P_2\infty = \frac{3M_2\alpha^oV_1}{(\varepsilon_1+2)^2} + M_1(V_1+\beta^o)\left(\frac{\varepsilon_1-1}{\varepsilon_1+2}\right) \quad (5)$$

Palit method (PM) to obtain the P_2^μ using the relation (6)

$$P_2\mu = M_2\left(\frac{3(\varepsilon_1-n_1^2)}{d_1(\varepsilon_1+2)(n_1^2+2)}(1-\beta/d_1)\right) + M_2\left(\frac{3\alpha}{d_1(\varepsilon_1+2)^2} - \frac{6n_1^2\gamma}{d_1(n_1^2+2)}\right) \quad (6)$$

Where α, β, γ are the slope values of the plots of mole fractions versus ε , d and n respectively.
Above relations are modified Palit (MPM) becomes

$$P_2\mu = M_1\left(\frac{3(\varepsilon_1-n_1^2)}{d_1(\varepsilon_1+2)(n_1^2+2)}\left(\frac{M_2}{M_1}-\frac{\beta}{d_1}\right)\right) + M_1\left(\frac{3\alpha}{d_1(\varepsilon_1+2)^2} - \frac{6n_1^2\gamma}{d_1(n_1^2+2)}\right) \quad (7)$$

Guggenjeim (GM) using the equation fined the dipole moment of the solute

$$\mu^2 = \frac{27KTM}{4\pi N_a d}\frac{(\Delta\varepsilon-\Delta n^2)/X_2}{(\varepsilon_s+2)^2} \quad (8)$$

The plots drawn between mole fractions (x_2) with $\Delta\varepsilon$ - Δn^2 obtained slope hence obtain the dipole moment of the solute.

Huyskens (HM) computed the experimental quantity ω from the relative dielectric constant ε_{12}, the refractive index for sodium line n_{12}, the density d_{12} of the system and its average molecular weight M_{12}

$$\omega = \left[\frac{9KT}{4\pi N}\right]\left[\frac{(\varepsilon_{12}-n_{12}^2)(2\varepsilon_{12}+n_{12}^2)}{\varepsilon_{12}(n_{12}^2+2)^2}\right]\left[\frac{M_{12}}{d_{12}}\right] \quad (9)$$

The slope values obtained from the plots experimental quantity with mole fraction, from the slope expressions can be written as

μ_S^2 Derived from equation (9) is given by

$$\mu_2^2 = \omega_s^0 + (\omega - \omega_s^0)/X_2 \quad (10)$$

The equation 1 to 11 are used to evaluate the dipole moment of the solute and presented in table 2.

Determination of permittivity of the solution

The permittivities of the binary liquid mixtures under investigation have been finding theoretically using various mixing rules. The following relations were used for the determination of permittivity.

Looyenga (L) using the equations obtain dielectric constant of the solution is given by

$$\varepsilon = \left[\varepsilon_{12}^{1/3} + \varphi_2 \left(\varepsilon_2^{1/3} - \varepsilon_1^{1/3} \right) \right]^3 \quad (11)$$

Bottcher-Bordewijik (B-B) helps to find dielectric permittivity of the solution

$$\frac{3\varepsilon_1}{2\varepsilon + \varepsilon_1}\varphi_1 + \frac{3\varepsilon_2}{2\varepsilon + \varepsilon_2}\varphi_2 = 1 \quad (12)$$

Bruggeman asymmetric (B-A) method is also used to find the dielectric constant of the mixture is given by

$$\frac{\varepsilon_2 - \varepsilon}{\left(\varepsilon/\varepsilon_1\right)^{1/3}} = (1-\varphi_2)(\varepsilon_2 - \varepsilon_1) \quad (13)$$

Kraszewski (K) found the dielectric constant of the solution is

$$\varepsilon^{1/2} = \varphi_1 \varepsilon_1^{1/2} + \varphi_2 \varepsilon_2^{1/2} \quad (14)$$

Lichtenecker-Rother (L-R) is to obtain the relation for the determination dielectric permittivity o the mixtures,

$$\varepsilon = \varepsilon_1^{\varphi_1} \varepsilon_2^{\varphi_2} \quad (15)$$

Peon-iglensias (p-I) establish the method to obtain dielectric constant

$$\varepsilon = (\varphi_1 \varepsilon_1 + \varphi_2 \varepsilon_2) \left[1 - \frac{2}{3} \ln \left(\frac{1 + \varphi_1 \left(\frac{\varepsilon_1}{\varepsilon_2} - 1 \right)}{\left(\varepsilon_1 / \varepsilon_2 \right)^{\varphi_1}} \right) \right] \quad (16)$$

Theoretical dielectric constant are obtained using above relation a presented table 3 also find the average percentage deviation and standard deviations are given in table 4.

RESULTS AND DISCUSSION

The experimental values of dielectric constant (ε_{12}), refractive indices (n_{12}) and densities (d_{12}) for mixture of anisole in carbon tetrachloride are given in the table **1** along with molar polarization of liquid,

experimental quantity and dipole moment for different concentrations. Slope values obtained from the plots of the evaluated parameter with concentration. From the slope and intercept values find the dipole moment of the anisole, polarization at in finite dilution and molar refraction are shown in table 2.

The dipole moments of the solutes were determined by all the methods are given in table 2. The variation of polarization and dipole moment of anisole values are calculated by Debye and Guggenheim method respectively, the values are plotted with the mole fractions are given in fig. 1 and 2. The dielectric constants of anisole in carbon tetrachloride mixtures have been predicted theoretically by using various mixing rules are present table 3 along with the percentage deviations ; average percentage deviations and standard deviation are given table 4.

Table 1- Properties of the carbon tetrachloride, anisole at 303 K

Solute /Solvent	ε	n	d	p	R_d	P_2^∞	μ
Carbon tetrachloride	2.218	1.4608	1.586	27.03	27.03	0	0
Anisole	5.028	1.3957	0.995	66.62	26.52	140	1.540

Table 2- Experimental values of dielectric constant (ε_{12}), density (d_{12} kg/m^3), refractive index (n_{12}), molar polarization (P_{12}), experimental quantity (ω) and dipole moment (μ D) of the anisole in carbon tetrachloride systems

X_2	ε_{12}	n_{12}	d_{12}	P_2	ω	μ
0.1	2.39	1.466	1.518	102	3.32	1.13
0.2	2.56	1.472	1.453	70	4.59	1.12
0.3	2.75	1.477	1.389	58	5.86	1.15
0.4	2.94	1.483	1.328	52	7.00	1.16
0.5	3.15	1.488	1.268	48	8.11	1.18
0.6	3.36	1.494	1.21	44	9.07	1.19
0.7	3.58	1.499	1.153	42	9.96	1.20
0.8	3.81	1.505	1.099	39	10.79	1.22
0.9	4.05	1.51	1.046	37	11.52	1.23

Table 3- Dipole moment of the anisole with carbon tetrachloride systems using different methods

GM	PB	PM	HM	MPM	PM1
1.59	1.79	1.64	1.43	1.97	1.68

Table 4 - Dielectric constant of the anisole with carbon tetrachloride using various models

Theoretical Dielectric constant							Percentage Deviation				
X_2	ε_{12}	LM	BM	KM	L-R	PI	LM	BM	KM	L-R	PI
0.1	2.39	2.46	2.45	2.48	2.43	2.19	3.01	2.51	3.77	1.63	8.20
0.2	2.56	2.72	2.71	2.76	2.66	2.31	6.37	5.70	7.70	3.91	9.88
0.3	2.75	3.00	2.99	3.05	2.91	2.54	9.13	8.62	10.87	5.93	7.78
0.4	2.94	3.30	3.29	3.36	3.19	2.86	12.18	11.94	14.12	8.47	2.62
0.5	3.15	3.61	3.62	3.68	3.49	3.27	14.73	14.79	16.70	10.89	3.65
0.6	3.36	3.95	3.96	4.01	3.83	3.72	17.56	17.89	19.38	13.84	10.71
0.7	3.58	4.31	4.33	4.36	4.19	4.20	20.28	20.81	21.84	16.98	17.35
0.8	3.81	4.68	4.70	4.73	4.59	4.68	22.89	23.44	24.04	20.39	22.83
0.9	4.05	5.08	5.10	5.11	5.02	5.12	25.43	25.83	26.07	24.02	26.52
Standard Deviation							0.90	0.91	0.90	0.89	1.06
Average Percentage Deviation							7.62	8.08	7.59	7.64	8.31

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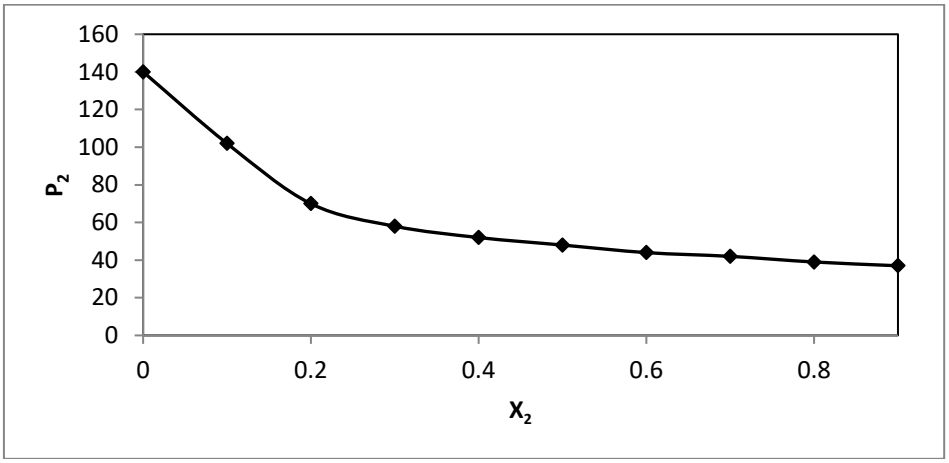

Fig. 1 plots of polarization of solute (P_2) with the concentration of anisole

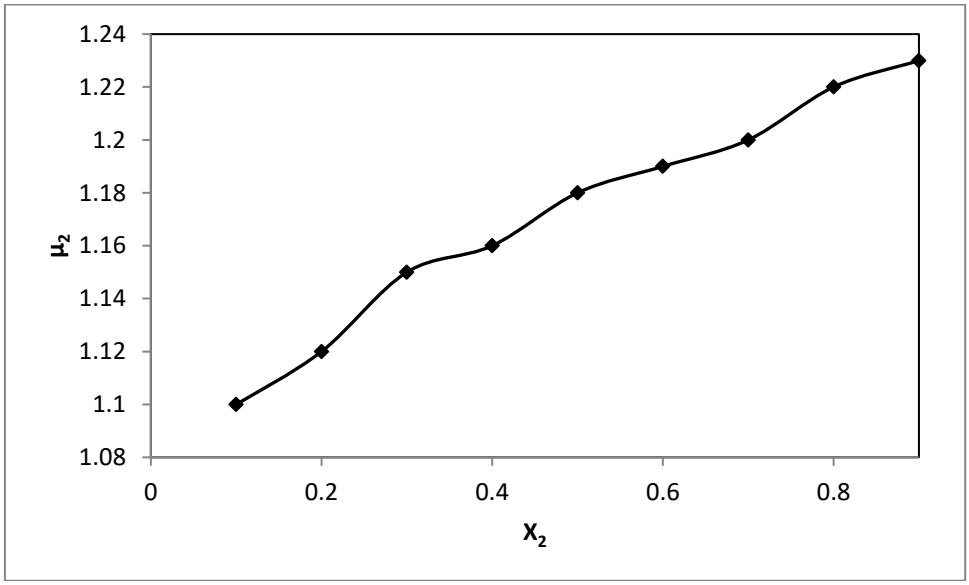

Fig. 2 plots of dipole moment of solute (μ D) with the concentration of anisole

From the polarization relation cannot predict the direct variation of polarization of solute with concentration because of the curvilinear nature of the P_2, the $P_{2\infty}$ values depending on the selecting range of concentration.

PM method given better results in the case non associated liquid in non polar solvent. But for the associated liquid in non polar solvent medium, $P_{2\infty}$ values fairly high also error is high. Huyskens on the hand included the correction factor for the value of dipole moment due to solvent only also experimental function ω only included the calculation of dipole moment.

In Huyskens method, the dipole moment value mainly depends on the slope of X_2 Vs ω only. But in the Plait and Banrgee, plait method, modified palit method, Guggenheim method values depend on the dielectric constant, density and refractive index. The dipole moment value depend on the slope of α (X_2 Vs ε_{12}) , β (X_2 Vs d_{12}) and γ (X_2 Vs n_{12}) . This is likely to introduce considerable error in the calculation. So, Huyskens method only involves the correction factor ω only. Therefore error is reduced the minimum and is better results than the other methods.

From the above fact one can conclude that the Huyskens method seems to be better for the calculation of dipole moment of the solute and this method has simplicity of the calculation error involved is

minimum compared to in other methods. The dipole moment values are closely agreed with the gas phase value. This indicate that no possibilities of solute – solvent interaction.

The theoretical permittivity of anisole in carbon tetrachloride is determined also find the Percentage deviations, average percentage deviations and standard deviations shown in table 4. The experimental and theoretical permittivity value gives the prediction ability of these models almost similar. The table 4 shows the percentage deviations and standard deviations are minimum for the Lichtenecker-Rother method give the best results compare than the other methods.

The values of polarization and dipole moment plotted against the mole fractions of anisole in fig. 1 & 2. The self association ability of the anisole is quantitatively indicated by the plots of P_2 Vs X_2 in fig. 1. The polarization values vary slightly. At infinite dilution polarization is below the polarization in pure state. These indicate no solute – solvent interaction and no self association ability of the anisole also may confirm dipole – induced dipole interactions occurs in these systems also indicated by the plots of μ_2 Vs X_2 in fig. 2. The dipole moment values vary slightly on dilution on anisole. At all range of concentration the values of dipole moment below the gas phase value. These indicate no possibility of self association made in the solute molecules.

CONCLUSIONS

Dielectric measurements have been made the anisole carbon tetrachloride system. The dipole moments computed from these measurements using various dielectric methods also find the theoretical dielectric constant of the liquids using various permittivity models. The relative merits of these methods have been discussed. Also find the polarization and dipole moment in various concentrations of these systems. From the variation polarization and dipole moment identify the molecules having dipole – induced dipole type interactions and no solute – solvent interactions occurs in these systems.

REFERENCES

[1] Anandhi R and Krishnamurthi P. Res J Pharm Biol Chem Sci 2014; 5(1): 650-658.
[2] Thenmozhili PA , Krishnamurthi P and Ramalingam HB WJPR 2017; 6(3) : 1368-1377.
[3] Meenach M, Krishnamurthi P, Shanthi C, and Ramalingam HB Der Phar Sinica 2016; 7(1) : 1-5.
[4] Krishnamurthi P, Ramalingam HB, and Sudha A Der Chem. Sinica 2016; 7(2) : 86-92.
[5] Krishnamurthi P , Ramalingam HB and Raju K Arch Appl Sci Res 2015; 7(11) : 5-9.
[6] Meenachi M and Krishnamurthi P Int J Res Phar Bio Sci 2012; 3(4) : 1719-1723.
[7] Krishnamurthi P and Balamuralikrishnan S. J Con Eng Tech Sci 2009; 1: 23-26.
[8] Krishnamurthi P and Balamuralikrishnan S. Asian J Chem 2010; 222(7): 5144-5148.
[9] Krishnamurthi P and Balamuralikrishnan S. Asian J Chem. 2010; 222(7): 5144-5148.
[10] Krishnamurthi P and Vasavi T, I J phar and Bio Research, 2013; 4(1): 126-131.
[11] Krishnamurthi P and Thenmozhili PA. I J Pharm Chem Res 2012; 4(11):4671-4677.
[12] Krishnamurthi P and Thenmozhili PA. I J Pharm Chem Res 2012; 4(11): 4677-4681.
[13] Prathima A, Karthikeyan S, Prapakaran M, and Thenappan T. 2013; 4(7): 2753-2760.
[14] Sengawa RJ, Vinita Khatri and Shobhna Choudhary. I J Chem 2010; 49A:1612-1616.
[15] Sreehari SastryS, Kumara Sastry SV, and Viswam T. I J Innovative Res in Sci 2013; 2(10): 5146-5154.
[16] Gupta KK and Singh PJ, Pramana – J Phys 2004; 62(5): 1129-1137.
[17] Smith CP, McGraw Hill Book Company Inc ,1955.
[18] Huyskens, PL, Cleuren W, Van Brabant HM, Gaverts and Vuylsteke, MA,J Phys Chem, 1980; 84: 2740.
[19] Kirkwood JG. J Chem Phys 1939; 7: 911.
[20] Hurdis EC and Smyth CP. JAm Chem Soc 1943, 65 89.
[21] Jones RAY and Katrizky AR. J Chem Soc B 1971;1795.
[22] Coomber DI and Partington JR. J Chem Soc 1938;1444.
[23] Misra CK and Saxana MC. Acta Phys Chem 1978; 24: 357.
[24] Bao JZ, Swicord ML, and Davies CC. J Chem Phys 1996;104:4441.
[25] Suryavanshi BM and Mehrotra SC. J Pure Appl Phys 1991; 29: 442.
[26] Chudhari A, Chaudhari H, and Mehrotra SC. J Chin Chem Soc 2002; 49: 489.
[27] Lone BG, Undre PB, Patil SS, Khirade PW, Mehrotra MC. J Mol Liq 2008;141: 47-53.