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DIELECTRIC STUDIES OF THE BINARY MIXTURES OF DIMETHYL KETONE WITH NON – POLAR SOLVENTS

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ABSTRACT

The dielectric constant, density and refractive index were measured the binary mixtures of dimethyl ketone with non-polar solvents such as 1, 4 dioxane, carbon tetrachloride, benzene and toluene at 301 K. The dipole moment of the polar liquids has been investigated the following methods like Polarization, Palit and Bannerjee, Palit, Modified Palit, Guggenheim method. Guggenheim method also finds the dipole moment of the solutions with different concentration. Dipole moment methods were checked and report the relative merits of these methods. From the variation of dipole moment of the solution, identify the nature of solute – solvent interactions. The weak type of solute – solvent interactions occurs in these systems. The order of the solute solvent interactions are 1, 4 dioxane < carbon tetrachloride < benzene > toluene.

INTRODUCTION

Dipole moment is one of the important dielectric properties have been widely used to understanding the different type of molecular interactions and their molecular structure in the liquid system.[1] The nature of solute – solvent interactions can be explained from dielectric measurements[2] although gives the information regarding the alignment of molecule and ability to interact with them. Dipole moment is made used to study of interaction taking place between same or different liquids. Many authors[3-6] have investigated the nature of self-association and solvent effect use the dielectric properties. Most authors conclude that the low permittivity liquids having least interaction than the high permittivity liquids.[7] The non-polar solvents can be used to understanding the self association of polar liquids.[8] The dipole moment investigation of a liquid, one should separate the same molecules from one another, which are normally expected to the gas phase value.[9] In the present study, evaluate the dipole moment of the dimethyl ketone by using various permittivity models also study the solvent effect of dimethyl ketone.

EXPERIMENTAL

AR grade dimethyl ketone, 1,4 dioxane, carbon tetrachloride, benzene and toluene were purchased from Sd Fine Chem Ltd.,. The chemicals were purified in standard methods prior to use with purity is 99.99%. The dielectric constants were measured using dipole meter (RL09) supplied by Toshniwal, India operated at 220 volts and working in the heterodyne principle with an oscilloscope null indication. It has a measuring frequency 300 KHz. The refractive indices of the solutions under investigations were determined using Abbe's refractometer. Density of the liquid and liquid mixtures was measured using 5 ml specific gravity bottle at 301K. The temperature of the solution controlled by using water circulated thermostat at 301 K. Specific gravity bottle, refractometer and dipole meter were calibrated using standard liquids like carbon tetrachloride, benzene, toluene.

DETERMINATION OF DIPOLE MOMENT

a) Polarization method (PM)

According to Debye model, the polarization of the solution P is expressed as

$$P = \left(\frac{\varepsilon - 1}{\varepsilon + 2}\right)V \qquad (1)$$

Where ε is the dielectric constant and V is the molar volume since $V = m/\rho$, m is the effective molecular weight, ρ is the density of the solution, P is the sum of the polarization contributions of the two components $P = P_1X_1 + P_2X_2$ (2)

Using the relation (2) find the polarization of the solute by the known values of the polarization of the solvent. P_2 plotted against x_2 and the resultant curve be extrapolated at infinite dilution to obtain the polarization at infinite dilution P_2^∞. This value of P_2^∞ include the electronic and atomic polarizations which taken into consideration gives the orientation polarization of the solute molecule and thereby the value of the dipole moment calculated from the following relation.

$$\mu = \left(\frac{9\,K\,T\,P_2^{\mu}}{4\pi N} \right)^{1/2} \qquad (3)$$

The parameter P_2^{μ} related to the molar refraction is given

$$P_2^{\mu} = P_2^{\infty} - R_D \qquad (4)$$

Here R_D is the molar refraction obtained from the pure value of refractive index (n_s) of the solvent is given by

$$R_D = \left(\frac{n_s^2 - 1}{n_s^2 + 2} \right) \left(\frac{m}{d} \right) \qquad (5)$$

Where m and d is the molecular weight and density of the solvent.

b) Palit and Bannerjee (P)

According to Palit and Bannerjee method determine the value of P_2^{∞} can be determined with the help of the following relation.

$$P_2^{\mu} = \left(\frac{3m_2 \alpha V_1}{(\varepsilon_1 + 2)^2} \right) + (m_1 v_1 + \beta) \left(\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} \right) \qquad (6)$$

$$\text{Where} \quad P_2^{\mu} = \frac{4\pi N \mu^2}{9KT} \quad ,$$

$$\varepsilon = \varepsilon_1 + \alpha X_2 \quad \text{and} \quad V = V_1 + \beta X_2 \qquad (7)$$

c) Palit method (PM)

The method based on the concept of partial quantities for representing dielectric polarization data has developed a method for the evaluation of dipole moment of solute molecule from solution data. According to the method,

$$P_2\mu = M_2 \left(\frac{3(\varepsilon_1 - n_1^2)}{d_1(\varepsilon_1 + 2)(n_1^2 + 2)} (1 - \beta / d_1 \right) + M_2 \left(\frac{3\alpha}{d_1(\varepsilon_1 + 2)^2} - \frac{6n_1^2 \gamma}{d_1(n_1^2 + 2)} \right) \qquad (8)$$

d) Modified Palit method (MPM)

Modified Palit method based on the weight fraction and mole fraction as the concentration unit and has also shown that the molar polarization of a solute molecule in the isolated state P_2^{∞} with mole fraction X_2 as the concentration unit. Palit becomes

$$P_2\mu = M_1 \left(\frac{3(\varepsilon_1 - n_1^2)}{d_1(\varepsilon_1 + 2)(n_1^2 + 2)} \left(\frac{M_2}{M_1} - \frac{\beta}{d_1} \right) \right) + M_1 \left(\frac{3\alpha}{d_1(\varepsilon_1 + 2)^2} - \frac{6n_1^2 \gamma}{d_1(n_1^2 + 2)} \right) \qquad (9)$$

The equation 3, 4, 6 and 7 are used for the determination of the dipole moment of liquids. All the above methods are based on the Debye equation, which assumes the local field equal to be the Lorentz field. The question of the local field was attempted by many investigations but the results were not uniform over a wide range of molecules.

e) Huyskens Method (HM)

Huyskens method assumed the molecules to be spherical and the neighborhood of each solute molecule to be a band without discrete structure. The experimental quantity ω computed from the relative dielectric constant, the refractive index for sodium D line and the density of the solution.

$$\omega = \left[\frac{9KT}{4\pi N}\right]\left[\frac{(\varepsilon_{12} - n_{12}^2)(2\varepsilon_{12} + n_{12}^2)}{\varepsilon_{12}(n_{12}^2 + 2)^2}\right]\left[\frac{M_{12}}{d_{12}}\right] \qquad (10)$$

Find the mean square dipole moment using the following relation

$$\mu_S^2 = \mu_B^2 = \omega + \left(\frac{\partial\omega}{\partial X_2}\right)(1 - x_2), \qquad (11)$$

f) Guggenheim method

According to this method, the following equation is used to calculate the dipole moment of the solute

$$\mu^2 = \frac{27KTM}{4\pi N_a d}\frac{(\Delta\varepsilon - \Delta n^2)/X_2}{(\varepsilon_s + 2)^2} \qquad (12)$$

Where $\Delta\varepsilon$ and Δn^2 are the differences in the permittivity and square of refractive indices of solution and solvent. The plots drawn between mole fractions (x_2) with $\Delta\varepsilon$ -Δn^2 obtained slope hence get the dipole moment of the solute.

Guggenheim method also find the dipole moment in various concentration, the relation is given by.

$$\mu^2 = \left[\frac{27KT}{4\pi N}\right]\left[\frac{(\varepsilon - \varepsilon_s)(n^2 - n_s^2)}{(\varepsilon_s + 2)^2}\right] \qquad (13)$$

Where N is the number of dipole per unit volume, i.e. N=$\frac{N_a\, d\, x}{m}$, *m* is the molecular weight, d is the density. ε and ε_S is the dielectric constant of the solution and solvent respectively.

Mean square dipole moment determined from the experimental values and using the equation (9). The values are plotted in figure 4.

The equation 3 to 8 are used to evaluate the dipole moment of the solute and presented in table 5.

RESULTS AND DISCUSSION

The dielectric constant (ε), refractive indices (n) and densities (d) for the binary mixture of dimethyl ketone with solvents such as 1,4 dioxane, benzene, toluene and carbon tetrachloride are given in the table 1 also presented the polarization (P) and experimental quantity (ω). The data are plotted the dimethyl ketone in 1, 4 dioxane system as shown in fig 1 to 4. Similar plots had drawn all other solvents, but not shown here. The parameter P_2^μ is obtained the polarization method, palit method, modified palit method and Palit and Banarjee method from the relations (4), (6), (8) and (9). The observed values of $P_2\mu$ for all the systems studied here use these values obtained the dipole moment in pure state. These methods based on Debye model. Guggenheim method and Huyskens also used to find the dipole moment in pure state. The first method obtained from the plots of ω Vs $X_{2,}$ the second method having the plots of difference of the permittivity and permittivity in high frequency Vs $X_{2.}$ The dipole moment obtained from the relation (11) and (12). The dipole moment is determined in various concentrations by the Guggenheim method from the relation (13). The plots of dipole moment with the mole fraction as given in figure 6. The dipole moment of the solutes was calculated by all the methods are given in table 2.

Table 1 Variation of dielectric constant (ε), density (ρ), refractive index (n), polarization (P) and experimental quantity (ω) with mole fraction of dimethyl ketone in solvent systems at 301 K.

X_2	1,4 Dioxane					Benzene				
	ε	ρ	n	P_2	ω	ε	ρ	n	P_2	ω
0.1	3.20	1.009	1.415	137.9	8.26	3.31	0.868	1.487	139.3	7.20
0.2	4.40	0.985	1.409	123.8	15.4	4.51	0.859	1.473	124.8	14.3
0.3	5.78	0.961	1.403	111.6	23.2	5.89	0.851	1.458	112.2	22.0
0.4	7.34	0.936	1.396	101.4	31.7	7.45	0.842	1.444	101.7	30.3
0.5	9.10	0.912	1.390	92.6	40.9	9.20	0.834	1.430	92.6	39.5
0.6	11.04	0.888	1.384	85.1	50.8	11.13	0.825	1.416	85.1	49.4
0.7	13.18	0.864	1.377	78.6	61.5	13.25	0.817	1.401	78.5	60.2
0.8	15.50	0.839	1.371	73.0	72.9	15.55	0.808	1.387	72.9	71.8
0.9	18.00	0.815	1.365	68.1	84.8	18.03	0.800	1.373	68.0	84.1

X_2	Carbon tetrachloride					Toluene				
	ε	ρ	n	P_2	ω	ε	ρ	n	P_2	ω
0.1	3.22	1.507	1.450	155.0	8.4	3.42	0.862	1.482	156.3	9.4
0.2	4.42	1.427	1.440	138.8	16.3	4.62	0.854	1.469	138.4	17.4
0.3	5.80	1.348	1.430	124.6	24.8	6.00	0.846	1.455	123.1	25.9
0.4	7.36	1.268	1.420	112.5	34.0	7.56	0.838	1.441	110.2	35.0
0.5	9.12	1.189	1.410	101.9	43.9	9.30	0.831	1.427	99.1	44.5
0.6	11.06	1.109	1.399	92.7	54.5	11.22	0.823	1.414	89.8	54.4
0.7	13.19	1.030	1.389	84.5	65.4	13.32	0.815	1.400	81.8	64.8
0.8	15.51	0.950	1.379	77.1	76.6	15.60	0.807	1.386	75.0	75.5
0.9	18.01	0.871	1.369	70.2	87.3	18.06	0.799	1.372	69.0	86.4

Table: 2 Dipole moment of the dimethyl ketone with solvents at 301 K.

Solvents/ Methods	μ_{GM}	μ_{P}	μ_{PB}	μ_{H}	μ_{PM}	μ_{PM}
1,4 dioxane	1.7	1.6	1.87	1.28	1.72	1.9
Benzene	1.7	1.69	1.87	1.31	1.81	1.9
Carbon tetrachloride	1.8	1.67	1.94	1.34	1.58	1.95
Toluene	1.7	1.67	1.97	1.32	1.78	1.97

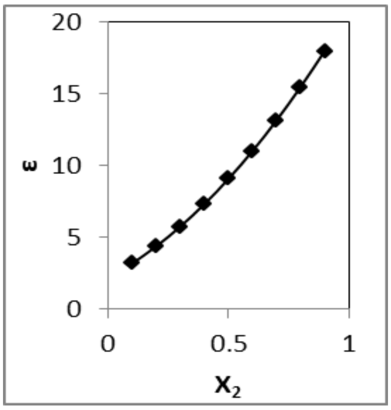

Figure 1 plots of ε VS X_2

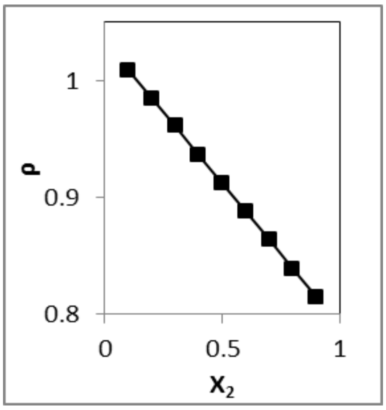

Figure 2 plots of ρ VS X_2

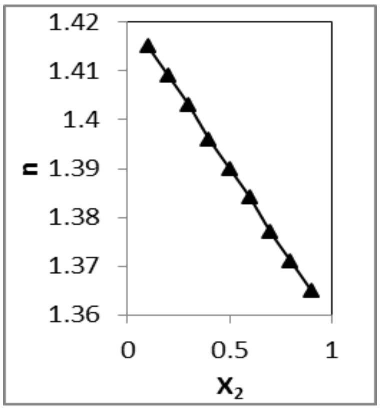

Figure 3 plots of n Vs X_2

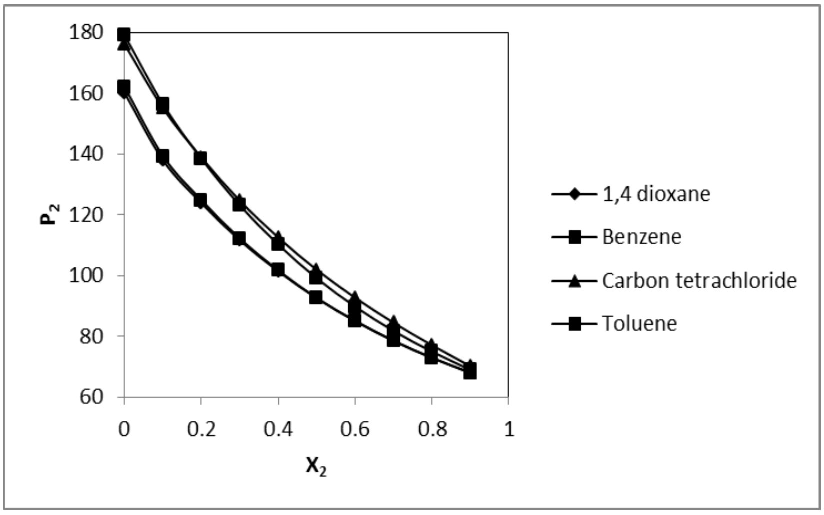

Figure 4 Plots of polarization (P_2) of dimethyl ketone with solvent systems

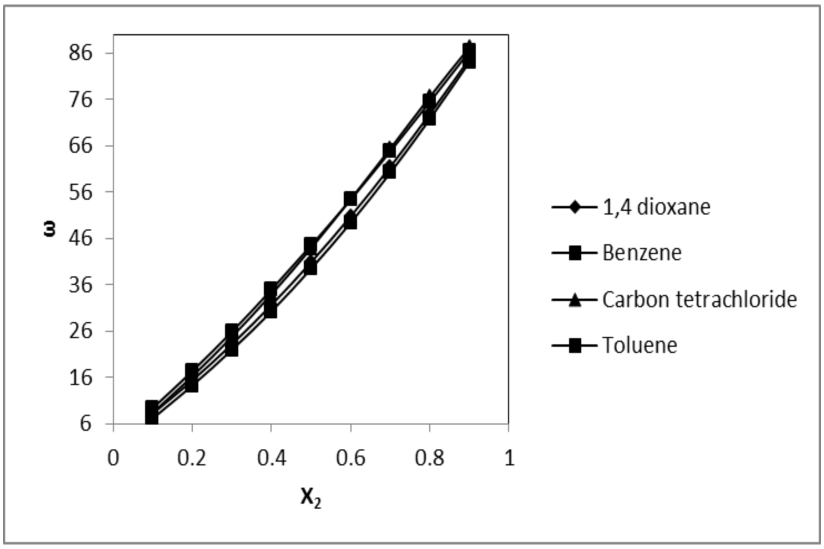

Figure 5 Plots of experimental quantity (ω) of dimethyl ketone with solvent systems

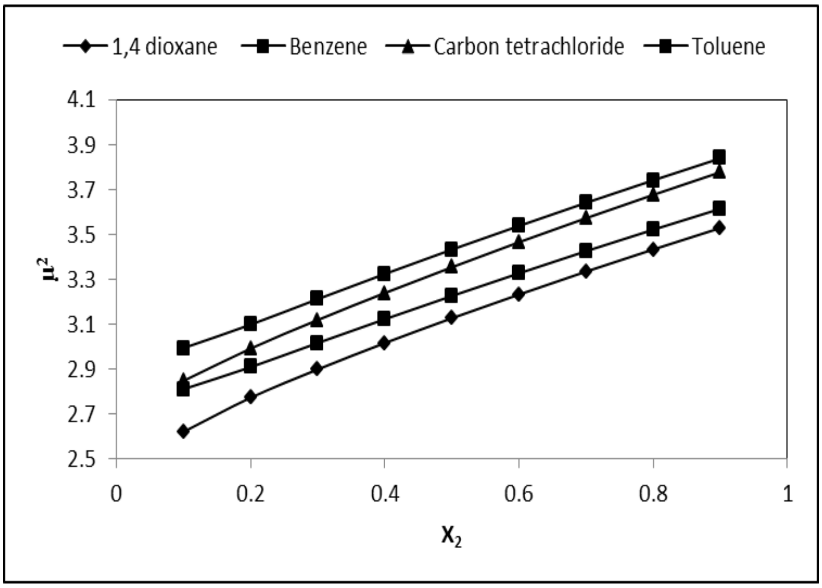

Figure 6 Plots of dipole moment (μ D) with the mole fractions (X_2) of dimethyl ketone in solvent systems

The dipole moment of the liquids is agreed with the gas phase value indicates no possibility of association. If dipole moment of the solute increases due to dipole – dipole interactions occurs. If the values decreases weak solute – solvent interactions occurs. i.e., polarization interactions occur. So it indicates no possibilities of solute –solvent interaction.

The dipole moments determined by limiting polarization method are higher in all the cases than the modified Palit method. The dipole moment determined by modified Palit and Huyskens method agrees closely in all the cases and the calculated from these methods are closely related to the gas phase value.

Huyskens on the other hand included the correction factor for the value of dipole moment due to the solvent. One can expect $\varepsilon = n^2$ for non-polar solvent, where n is the refractive index. In practice as the experimental refractive index differs from the internal refractive index, an experimental function ω is included in the calculation of dipole moment by Huyskens method, which is likely to introduce considerable error in the calculation. So, Huyskens method only involves the correction factor ω only. Therefore error is reduced to minimum and is better than the modified Palit method. 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 for the calculation and the error involved is minimum compared to other methods. So the Huyskens method has been chosen for the calculation of dipole moment of the complex.

In the present notes, the validity of the equation 1, 2, 3 and 4 is demonstrated with a method to evaluate μ of organic liquids in which polarization method the $P_2\infty$ value is fairly higher than the modified Palit method. This modified Palit method involves the slope of the ε, n, d Vs mole fraction but the simplification lies in the fact that the Huyskens method involves only the slope of the ω Vs X_2, which is sufficient to yield quickly the proper values of dipole moment of the solute. So the Huyskens method is better for the calculation of dipole moment. The dipole moment values are closely agreed with the gas phase value. Further studies about the nature of association were made by using the variation of dipole moment. To understand the nature of self association studied using Guggenheim method by the variation of dipole moment with mole fraction. The dipole moments are calculated by the equation (4) for all the mixture. The plots of μ^2 with mole fractions of the solute for all the systems studied are shown in figure 6. The function $\boldsymbol{\mu^2}$ $\boldsymbol{\mu}$ will be larger than $\boldsymbol{\mu_1}$ when non-cyclic aggregates predominate whereas this function is smaller than $\boldsymbol{\mu_1}$ when the majority molecules are involved in cyclic aggregate. Dielectric measurements should give useful information regarding the nature of the association and shape of the entities in the liquid. In the present investigation dimethyl ketone, which are taken for the molecular interaction studies, have been subjected to dielectric measurements to identify the nature of the self-association in those liquids.

The self-associating ability of the various types of molecules in liquid phase are qualitatively indicated μ^2 Vs X_2 in figure 6. the μ^2 values vary very slightly on dilution in the case of dimethyl ketone. At very low concentration the μ^2values reach above the value of μ^2_{gas} which possibility of association either cyclic or non cyclic aggregate. The order of associations are toluene > benzene > carbon tetrachloride > 1,4-dioxane. At very low concentration the μ^2 values reach almost the value of μ^2_{gas} which indicates no possibility of association.

CONCLUSION

Dielectric measurements have been made the dimethyl ketone with the non polar solvent systems. The dipole moments have been computed in various methods and relative advantages of these models are reported. The natures of intermolecular interaction in the liquid mixtures have been explained on the basis of the variation of dipole moment. The value of μ^2 is below the value of μ^2_{gas}. These behaviors indicate no specific interaction occurs in these systems. The weak type interactions occur in these systems studied here. Based on that it is found that the order of interaction are toluene > benzene > carbon tetrachloride > dioxane with dimethyl ketone as one of the components.

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