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Dielectric Studies of Binary Mixtures of Aromatic Aldehyde with Polar and Non Polar Solvents.

R Anandhi and P Krishnamurthi*

Department of Physics, Varuvan Vadivelan Institute of Technology, Dharmapuri, Tamilnadu, India-636703.

ABSTRACT

The dielectric measurements of dielectric constant, density and refractive index has been measured at 301 K for the systems of benzaldehyde, and substituted benzaldehyde with solvents like acetone, carbon tetrachloride and benzene. Make use of these measurements to calculate the dipole moment for Huysken's method. The dipole moment of acetone not match with the literature value indicates that acetone more associative than the other solvents also predict the Kirkwood - Frohlich linear correlation factor (g). The data provide information about the nature of interactions. The order of interactions of the solvents are acetone > benzene > carbon tetrachloride with benzaldehydes and chloro substituted benzaldehyde as one of the components.

Keywords: Dipole moment, benzene, linear correlation factor, solute-solvent, benzaldehyde

**Corresponding author*

INTRODUCTION

The dielectric constant, refractive index, ultrasonic studies of polar-polar and polar-non polar solutions are attractive one to give valuable information about molecular interactions to understand the structure of liquids. [1-6] Many workers [7-10] have studied the estimation of the dipole moment of a polar solute in non-polar solvents.

In the present investigation predict the dipole moments for the benzaldehyde and substituted benzaldehyde in the solvents benzene, carbon tetrachloride and acetone are compared with the gas phase value. From these conclude that the estimated dipole moment gives good agreement with gas phase values. Also evaluate the Kirkwood- Froehlich correlation factor, which is a shape dependent one is a measure of local ordering of the solute in non polar solvents. Kirkwood correlation factors are a measure of the short range intermolecular forces that lead to dipole- dipole interactions in solutions.

THEORY

The polarization of the following were determined by Debye [11] theory for benzaldehyde, *o*-chlorobenzaldehyde and *p*-chlorobenzaldehyde in solvents carbon tetrachloride, benzene, and acetone also evaluate dipole moment by Huysken's method [12] and linear correlation factor [13] details given below

Determination of polarization of solute

According to Debye determine the polarization in dilute solution $P_{12} = \left[\frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \right] \left[\frac{m_1 x_1 + m_2 x_2}{d_{12}} \right]$ and P_{12} is the sum of the polarization contributions of the two components.

$$P_{12} = P_1 X_1 + P_2 X_2$$

P_2 determined from the above relations also plotted against x_2 and the resultant curve may be extrapolated to $X_2 = 0$ to obtain the polarization at infinite dilution P_2^∞ .

Determination of dipole moment

Huyskens computed the experimental quantity ω from the dielectric measurements of the system and its average molecular weight M_{12} .

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

Where ω is a molar quantity derived from the theory of Onsager and μ^2 calculated from ω is given by $\mu_2^2 = \omega_s^0 + (\omega - \omega_s^0) / X_2$

Kirkwood correlation factor

From the dielectric parameter, the information about the liquid structure as well as orientation of dipoles in polar liquids could be obtained using the Kirkwood correlation factor. The expression for 'g'

$$g = \frac{9kTM}{4\pi N\mu^2\rho} \left(\frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} \right)$$

Where ρ is the density of liquid at T K, M is the molecular weight, k is the Boltzmann constant, N is the Avogadro's number and μ is the dipole moment of polar molecule in gas phase. ϵ_∞ is taken as square of refractive index. The choice of ϵ_∞ value i.e., $\epsilon_\infty = n^2$ or $\epsilon_\infty = 1.1 n^2$ and the μ value in gas phase of in different non polar solvent are the major reason for g value differing from various sources. Nevertheless, the compactable magnitude of the evaluated g values of various groups and homogeneous series molecules is important to understand the range of dipolar ordering and the strength of H-bond formation. In present study we have used $\epsilon_\infty = n^2$.

For the mixtures of two polar arrangements, the effective Kirkwood correlation factor g^{eff} of the different molecular is evaluated from the modified Kirkwood equation. The modified Kirkwood equation for the binary mixture is expressed as

$$g^{\text{eff}} \left(\frac{\mu_a^2 \rho_a X_a}{M_a} + \frac{\mu_b^2 \rho_b X_b}{m_b} \right) = \left(\frac{9kT}{4\pi N} \right) \left(\frac{(\epsilon_{12} - \epsilon_{\infty 12})(2\epsilon_{12} + \epsilon_{\infty 12})}{\epsilon_{12}(\epsilon_{\infty 12} + 2)^2} \right)$$

The corrective correlation factor, g^f equally affecting the Kirkwood correlation factor of pure substance A and B is given by

$$g^f \left(\frac{\mu_a^2 \rho_a g_a X_a}{M_a} + \frac{\mu_b^2 \rho_b g_b X_b}{M_b} \right) = \left(\frac{9kT}{4\pi N} \right) \left(\frac{(\epsilon_{12} - \epsilon_{\infty 12})(2\epsilon_{012} + \epsilon_{\infty 12})}{\epsilon_{12}(\epsilon_{\infty 12} + 2)^2} \right)$$

X_a and X_b are the mole fraction of liquids a and b respectively for $x_1 = 1$ and $x_2 = 0$ required equation (1) giving the g value of pure liquid 'a' and vice versa in equation 4 the value of g^{eff} will change from g_1 to g_2 as the concentration of molecule is increased from 0 to 1.

where 0, 1, 2 and 12 represents pure liquids, solvent, solute and solution, ϵ is the dielectric constant, μ is the dipole moment in the gas phase, ρ is the density at temperature T, M is the molecular weight, k is the Boltzmann constant, N is the Avogadro's number, W is the weight fraction, X is the mole fraction, g is linear correlation factor.

The deviations of Kirkwood correlation factor from unity is an indication for the molecular association. It means that if $g > 1$ indicates the parallel orientation among the dipoles, $g < 1$ indicates the anti – parallel orientation among the dipoles and $g = 1$ represents an equilibrium between the multimers or non – association among the dipoles.

EXPERIMENTAL

The refractive indices of the solutions under investigations were determined using Abbe's refractometer and density of the solution were measured using 5ml specific gravity bottle. The dielectric constants were determined from capacity measurement using dipole meter RL09 supplied by Toshniwal, India operated on 220 volts and working in the heterodyne principle with an oscilloscope null indication. It has a measuring frequency 300 KHz. The samples were placed in a cell containing a co-axial brass cylinder and the cell was immersed in water by means of precision thermostat with an accuracy of $\pm 0.1^\circ\text{C}$ supplied by Concord Instruments Pvt. Ltd., Chennai. The scale of the dipole meter is calibrated using the standard liquids of carbon tetrachloride, benzene, n-hexane and cyclohexane. The temperatures of all the measurements were maintained at 301K using water circulating thermostat with an accuracy $\pm 1^\circ\text{C}$.

RESULTS AND DISCUSSION

The dielectric constant, density, refractive index of benzaldehyde, p-chlorobenzaldehyde, m-chlorobenzaldehyde in two non polar (carbon tetrachloride, benzene) and polar solvents (acetone), measured at 301 K and utilize these measurements evaluate the dipole moment using Huysken's method and polarization predicted from the Debye presented in table 2 along with gas phase value. The polarization of solute and the linear correlation factor were predicted and the plots of polarization (P_2) and linear correlation factor (g) of solute with mole fraction as shown in fig. 1 to 6.

Table 1-The dipole moment and Polarization of pure liquids.

Solute	Dipole moment in Debye			P_2^u		
	CCl_4	Benzene	Acetone	CCl_4	Benzene	Acetone
Benzaldehyde	3.23	3.15	3.67	360	350	108
o-chlorobenzaldehyde	1.52	1.48	2.37	170	165	99
p-chlorobenzaldehyde	2.07	2.02	3.76	175	170	108

Table 2 - Values of P_2 and g with the mole fraction of benzaldehyde (B)

Solvent	CCl_4		C_6H_6		$(\text{CH}_3)_2\text{O}$	
	P_2	G	P_2	g	P_2	g
0.014	314.815	0.133	300.468	0.057	111.344	1.994
0.021	289.904	0.176	276.854	0.079	114.297	2.008
0.028	274.460	0.217	262.612	0.100	115.878	2.023
0.035	262.986	0.257	252.226	0.122	116.751	2.037
0.042	253.665	0.295	243.901	0.143	117.270	2.051

0.049	245.699	0.333	236.853	0.164	117.587	2.064
0.064	232.332	0.408	225.104	0.205	117.794	2.091
0.071	226.579	0.443	220.089	0.226	117.853	2.104
0.086	216.370	0.513	211.208	0.268	117.851	2.130
0.132	192.592	0.713	190.473	0.394	117.280	2.203
0.147	186.270	0.776	184.939	0.436	117.057	2.225
0.187	172.823	0.929	173.069	0.545	116.387	2.279
0.228	161.959	1.076	163.353	0.658	115.671	2.329

Table 3 - Values of P_2 and g with the mole fraction of o-chlorobenzaldehyde(OCB)

solvent	CCl_4		C_6H_6		$(CH_3)_2O$	
	P_2	G	P_2	g	P_2	g
Mole fraction of OCB						
0.018	314.815	0.133	300.468	0.057	111.344	1.994
0.027	289.904	0.176	276.854	0.079	114.297	2.008
0.037	274.460	0.217	262.612	0.100	115.878	2.023
0.046	262.986	0.257	252.226	0.122	116.751	2.037
0.055	253.665	0.295	243.901	0.143	117.270	2.051
0.064	245.699	0.333	236.853	0.164	117.587	2.064
0.083	232.332	0.408	225.104	0.205	117.794	2.091
0.092	226.579	0.443	220.089	0.226	117.853	2.104
0.111	216.370	0.513	211.208	0.268	117.851	2.130
0.167	192.592	0.713	190.473	0.394	117.280	2.203
0.186	186.270	0.776	184.939	0.436	117.057	2.225
0.233	172.823	0.929	173.069	0.545	116.387	2.279
0.281	161.959	1.076	163.353	0.658	115.671	2.329

Table 4 - Values of P_2 and g with the mole fraction of p-chlorobenzaldehyde (PCB)

solvent	CCl_4		C_6H_6		$(CH_3)_2O$	
	P_2	G	P_2	g	P_2	g
Mole fraction of PCB						
0.037	150.229	0.097	147.549	0.041	110.468	1.728
0.046	143.831	0.112	141.447	0.049	111.135	1.732
0.055	139.248	0.125	137.134	0.057	111.463	1.735
0.064	135.713	0.139	133.849	0.064	111.597	1.738
0.083	130.421	0.166	129.015	0.080	111.547	1.743
0.092	128.322	0.178	127.127	0.087	111.428	1.745
0.111	124.789	0.204	123.983	0.103	111.081	1.749
0.167	117.069	0.277	117.219	0.149	109.628	1.752
0.186	115.041	0.300	115.449	0.165	109.081	1.750
0.233	110.668	0.355	111.614	0.205	107.659	1.742
0.281	107.005	0.408	108.355	0.246	106.199	1.727

The g^f is used to explain the formation of multimers in the mixture[11-12]. The linear correlation factor provides qualitative information about multimer formation in the mixture as follows.

1. If $g^f = 1$ indicates that there is interaction between the unlike molecules.

2. If $g^f < 1$ indicates that the interaction between the unlike molecules is such that the total effective dipoles get reduced due to anti parallel orientation. This suggests that the unlike molecules may form the multimers due to less effective dipoles.
3. If $g^f > 1$ indicates that the interaction between the unlike molecules is such a way that the total effective dipole moment increases due to the parallel orientation. There is a tendency to form monomers and dimers and dipole aligned in parallel direction.

Fig 1: Plots of linear correlation factor g_2 vs concentration of Benzaldehyde system.

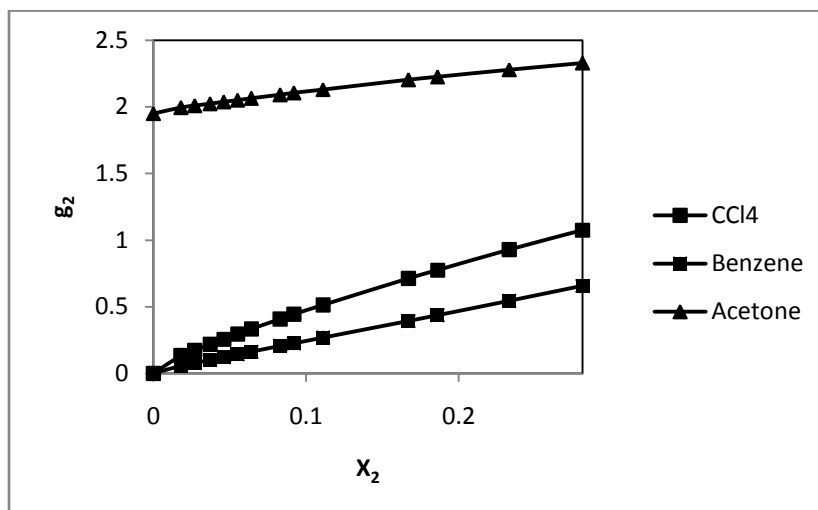


Fig 2 - Plots of linear correlation factor g_2 vs concentration of o-chlorobenzaldehyde system

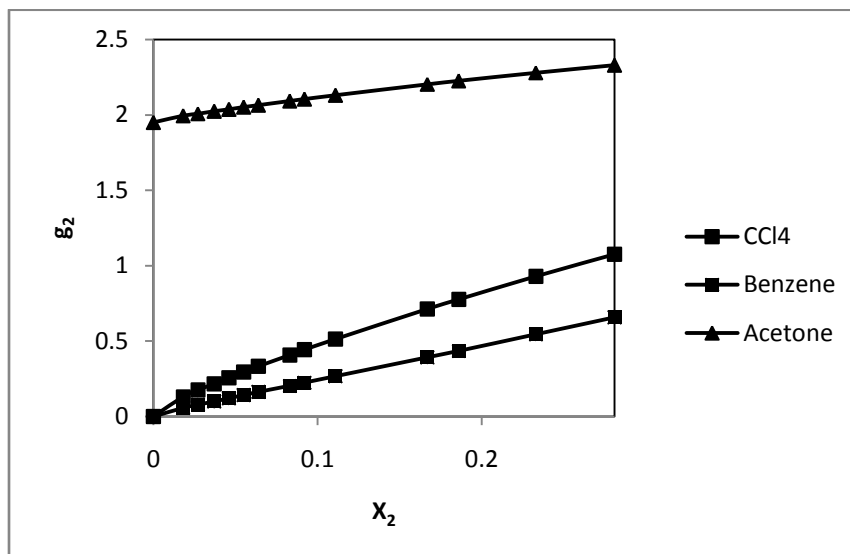
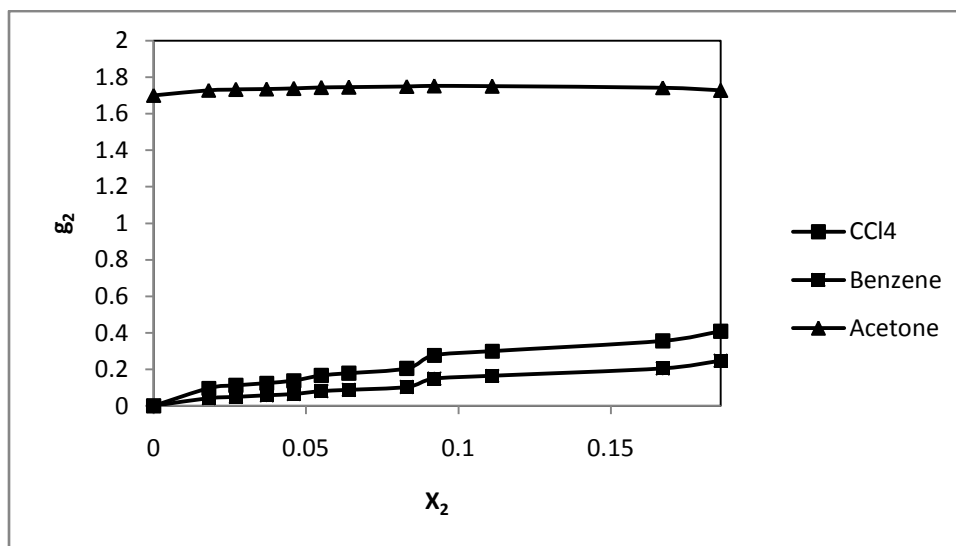


Fig 3 - Plots of linear correlation factor g_2 vs concentration of p-chlorobenzaldehydesystem


The values of g^f plotted with the molfraction of benzaldehyde and o/p-chlorobenzaldehyde is shown in fig. 1 to 3. In benzaldehyde with polar solvents (acetone) systems, the g^{eff} value increase with increase the concentration of benzaldehyde in the solution. For pure liquids, $g^{eff} < 1$, indicates the anti parallel orientation of dipoles. g^{eff} values increases above the unity in carbonyl reach region indicating the parallel alignment of dipoles in the region. This indicate intermolecular interaction between aldehyde and acetone increases in the number of carbonyl molecules in the solution. Similar behavior observed in mixtures of p-chlorobenzaldehyde, o-chloeobenzaldehyde and acetone as one of the components. The interaction between the unlike molecules provide an electric field which makes dipoles to have parallel orientation. In other mixtures studied, the value of g^f is less than unity for all concentrations. This may indicate the presence of weak interaction between the aldehyde and other non polar solvent systems.

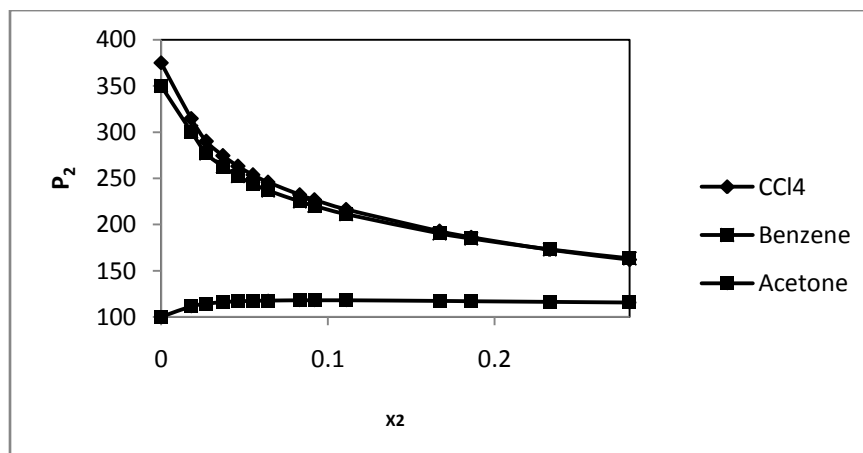
Fig 4 - Plots of polarization (P_2) vs concentration of benzaldehydesystem.


Fig 5 - Plots of polarization (P_2) vs concentration of o-chlorobenzaldehyde system

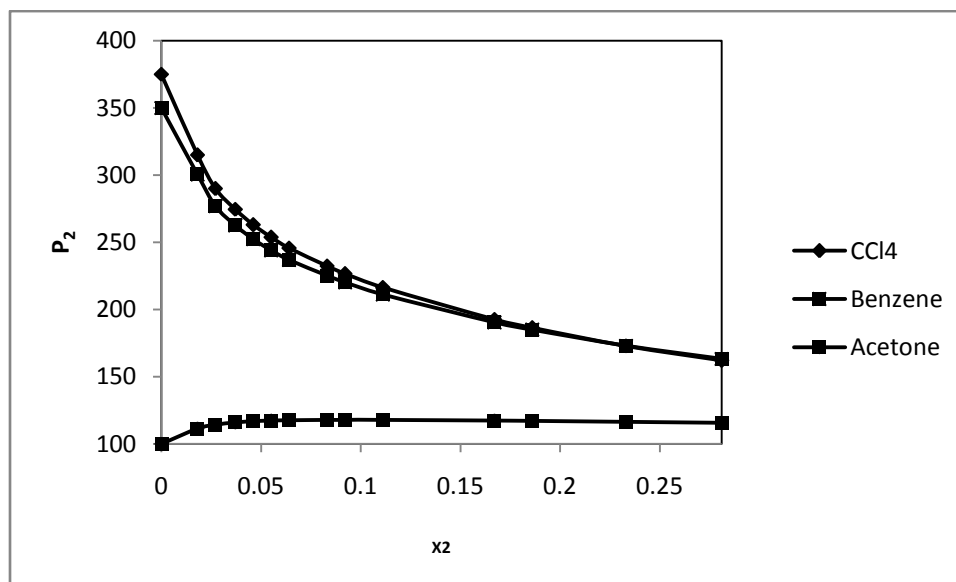
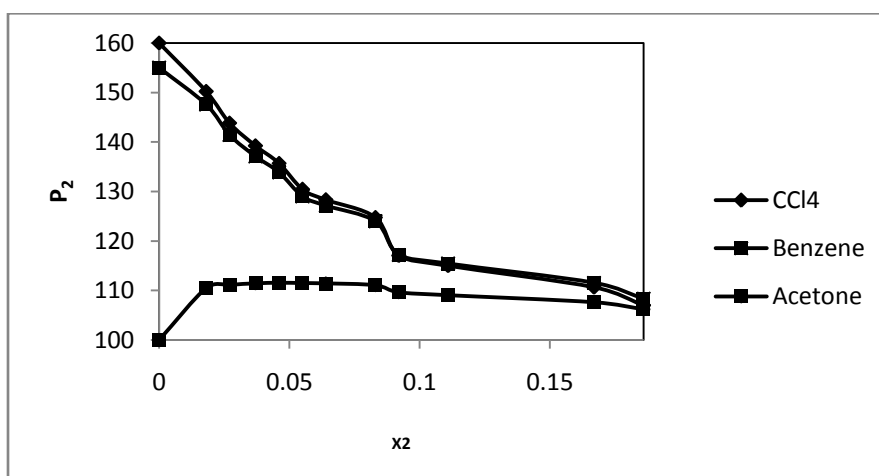


Fig 6 - Plots of polarization (P_2) vs Concentration of p-chlorobenzaldehydesystem



Polarization of solute (P_2) vs molefraction in dilute solutions of carbon tetrachloride , benzene shows that P_2 follows the similar behavior as Kirkwood correlation factor 'g' with mole fraction. But acetone behave differently polarization of polar-polar solute cannot find the Debye theory. P_2 values are higher in acetone than that for other solvents suggesting the presence of hydrogen bonding between the solute molecules under investigation and similar results were obtained the other workers [14-21].

CONCLUSION

The extent of solute – solvent interaction in different molecules varies with concentration comparatively higher inter and intra hydrogen bonding found in o-

chlorobenzaldehyde in dilute solution of acetone. The order of interactions of the solvents are carbon tetrachloride<benzene<acetone.

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