Dielectric Characteristics Studies of Esters (Amyl Acetate, Isoamyl Acetate) with Solvents (Carbon Tetrachloride, Benzene, Acetone)

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Abstract: The Kirkwood correlation factor (g) of binary mixtures of amyl acetate and isoamyl acetate with in benzene, carbon tetrachloride and acetone were obtained from a measurement of dielectric constant, density and refractive index at 301 K. The fluid structure of amyl acetate and isoamyl acetate is discussed. In amyl acetate and isoamyl acetate in carbon tetrachloride, benzene and acetone, a dimeric linear chain with the individual dipoles more or less parallel orientation is preferred. In amyl acetate, with increase of concentration, the value of g tending to unity indicates the parallel orientation.

Keywords: Amyl acetate, Kirkwood correlation factor, Dielectric constant, Refractive index

Introduction

The studies of molecular interactions interesting one to provide valuable information regarding dipole-dipole, dipole-induced dipole interactions and these in turn help to understand the molecular structure of the polar solutes[1-5].

The Kirkwood theory[6-8] of dipolar liquids defines the short range dipolar interactions through a dimensionless parameter g. Kirkwood correlation factor of dielectric polarization is a measure of the short range intermolecular forces that leads to dipole orientation in solutions. The g factor varies with concentration, temperature and solute environment done by many authors[9-17]. Fluid structure detected by a measurement of concentration dependence of Kirkwood correlation factor for the esters. An increase in g is expected on linear or cyclic. The clarification of the structure of chains in a solvent environment is very important in the context of biological systems. Hence we have taken up the study of Kirkwood correlation factor and the related parameters of two amyl acetate and isoamyl acetate substitutes in the solution state in solvent carbon tetrachloride, benzene and acetone.

Experimental

Dielectric constant and refractive index was measured using Toshniwal RL09 type dipole meter at 300 KHz with accuracy of ±0.0002 and Abbe's refractometer with accuracy of

±0.002 for sodium *D*-line respectively at temperature 301 K. The densities were obtained by a 25 ml specific gravity bottle with accuracy of 0.0001 gcm^{-3}. The solutes and solvents of AR grade were used without further purification having 99% of purity. The high dielectric permittivity taken as $\varepsilon_{\infty \text{ due}}$ to atomic polarization over electronic polarization of the solute

THEORY

Limiting Polarization method (PM)

The polarization of the solution P_{12} is find form the dielectric measurements is

$$P_{12} = \left[\frac{\varepsilon_{12} - 1}{\varepsilon_{12} + 2} \right] \left[\frac{m_1 x_1 + m_2 x_2}{d_{12}} \right] \tag{1}$$

ε_{12} is the dielectric constant of the solution, m1 and m2 are the molecular weight of the component, d_{12} is the density of the component P_{12} is the sum of the polarization contributions of the two components.

$$P_{12} = P_1 X_1 + P_2 X_2 \tag{2}$$

Where P_1 and P_2 are the molar polarization of the solvent and solute respectively. P_2 is determined using the above relation P_2 plotted against x_2 and the resultant curve may be extrapolated to $X_2 = 0$ to obtain the polarization at infinite dilution $P_2\infty$. This value of $P_2\infty$ includes the contribution of electronic and atomic polarizations also which taken into consideration gives the orientation polarization of the solute molecule and thereby the value of the dipole moment from the following relation.

$$\mu_2 = \left[\frac{9KT}{4\pi N} P_2 \mu T \right]^{1/2} \tag{3}$$

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

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

Insertion of the appropriate values for the constants leads to

$$\mu_2 = 0.01281 X 10^{-18} \left[P_2 \mu T \right]^{1/2} \tag{5}$$

Kirkwood correlation factor

The Kirkwood–Froehlich correlation factor of dielectric polarization g is an important parameter which provides some insight into short range intermolecular forces that arise due to dipole-dipole interactions and hence gives some information regarding local ordering of polar solute molecules in solutions. By considering each kind of multimers as a separate entity and assuming that the total dipole moment of the cluster of one type multimers has no specific correlation with that of the other types, the extended Kirkwood–Froehlich's expression for solutions can be written as for pure liquids and solution.

The structural information about the liquids from the dielectric parameters may be obtained using the Kirkwood correlation factor g^f this factor is also a parameter for obtaining information regarding orientation of electric dipoles in polar liquids. The g for pure liquid can be obtained from the following expression.

$$\frac{4\pi N \mu^2 \rho}{9KTM} g = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0 (\varepsilon_\infty + 2)^2} \tag{6}$$

A modified form of this equation has been used to study the orientation of electric dipoles in binary mixtures. For the mixtures of two polar liquids, say 1 and 2, equation (1) is modified by assuming that g^{eff} has become the effective correlation factor in the mixture. The Kirkwood equation for the mixture can be expressed as follows

$$\frac{4\pi N}{9KT}\left(\frac{\mu_1^2 \rho_1}{M_1} X_1 + \frac{\mu_2^2 \rho_2}{M_2} X_2\right) g^{eff} = \frac{(\varepsilon_{12} - \varepsilon_{\infty 12})(2\varepsilon_{12} + \varepsilon_{\infty 12})}{\varepsilon_{12}(\varepsilon_{\infty 12} + 2)^2} \tag{7}$$

Where g^{eff} is the effective Kirkwood correlation factor for a binary mixture with X_1 and X_2 as mole fractions of liquids 1 and 2 respectively. N is Avogadro's number, where ε_{12} represents the dielectric constant of the components, ε_∞ is the high dielectric Permittivity, Due to induced polarization of the polar component in the pure solute and finally μ_i is the dipole moment components.

We also assume that correlation factors of solute molecules are affected by the same amount g^f in the mixture. The Kirkwood– Frohlich equation for the mixture can be written as

$$\frac{4\pi N}{9KT}\left(\frac{\mu_1^2 \rho_1 g_1}{M_1} X_1 + \frac{\mu_2^2 \rho_2 g_2}{M_2} X_2\right) g^f = \frac{(\varepsilon_{12} - \varepsilon_{\infty 12})(2\varepsilon_{12} + \varepsilon_{\infty 12})}{\varepsilon_{12}(\varepsilon_{\infty 12} + 2)^2} \tag{8}$$

The Kirkwood correlation factors g_1, g_2 for individual species are modified by assuming for solute-solvent mixture that two kinds of intermolecular hydrogen bonds exist. One is the hydrogen bond between the solute-solvent molecules. The plots of g^f *vs.* x_2 are shown in Figure 3 and 4.

Excess permittivity (ε^E)

For the detection of the cooperative domains in the mixture it is useful to compute the excess permittivity ε^E which may be further used to study dynamics of the mixture due to molecular interactions. The excess permittivity ε^E is defined as

$$\varepsilon^E = (\varepsilon_{12} - n_{12}^2) - \left[(\varepsilon_1 - n_1^2)x_1 + (\varepsilon_2 - n_2^2)x_2\right] \tag{9}$$

Where X– mole fraction and suffices 12, 1, 2 represents mixture, liquid 1 and liquid 2 respectively. The excess permittivity provides qualitative information about structural aspects of the mixture.

If $\varepsilon^E = 0$ indicates the liquid 1 and 2 do not interact at all. If $\varepsilon^E < 0$ indicates the liquid 1 and 2 interaction in such a way that the total effective dipole gets reduced. This suggests that the liquid 1 and 2 may form multimers leading to less effective dipoles or in other words there is a tendency of dipole to align in antiparallel direction. If $\varepsilon^E > 0$ indicates the liquid 1 and 2 interaction in such a way that the total effective dipole moment increases. There is a tendency of dipole aligned in parallel direction.

Results and Discussion

The experimental values of dielectric constant (ε_{12}), density (kg/m^3), refractive index (n_{12}), are given in Table 1 to 6 also given the predicted values of polarization (P_{12}) and linear correlation factor (g^{eff}) with the concentration of amyl acetate and isoamyl acetate with

carbon tetrachloride, benzene and acetone at 301 K. The dipole moments were determined from the experimental values by the method of polarization given Table 7.

Table 1. Amyl acetate with carbon tetrachloride

x_2	ε_{12}	ρ_{12} kg/m^3	n_{12}	P_{12}	g^{eff}
0.017	2.358	1.586	1.469	30.130	3.972
0.026	2.387	1.579	1.468	30.660	3.062
0.034	2.416	1.572	1.468	31.190	2.574
0.043	2.445	1.565	1.467	31.720	2.305
0.051	2.474	1.557	1.466	32.240	2.125
0.06	2.503	1.550	1.466	32.760	1.977
0.077	2.561	1.536	1.465	33.800	1.792
0.086	2.590	1.529	1.464	34.310	1.733
0.103	2.648	1.515	1.463	35.340	1.632
0.157	2.822	1.472	1.459	38.390	1.466
0.175	2.880	1.458	1.458	39.390	1.429
0.22	3.025	1.423	1.455	41.900	1.362
0.266	3.170	1.387	1.452	44.400	1.316

Table 2. Amyl acetate with benzene system

x_2	ε_{12}	ρ_{12}	n_{12}	P_{12}	g^{eff}
0.033	2.417	0.870	1.508	29.17	2.706
0.049	2.445	0.871	1.507	29.75	2.195
0.065	2.474	0.871	1.506	30.33	1.938
0.081	2.502	0.871	1.505	30.92	1.783
0.096	2.530	0.871	1.504	31.50	1.678
0.111	2.559	0.871	1.503	32.08	1.603
0.142	2.616	0.872	1.501	33.24	1.501
0.156	2.644	0.872	1.500	33.82	1.465
0.185	2.701	0.872	1.498	34.99	1.409
0.268	2.871	0.874	1.492	38.47	1.312
0.294	2.928	0.874	1.490	39.63	1.291
0.357	3.070	0.875	1.485	42.52	1.252
0.417	3.212	0.876	1.480	45.41	1.225

Table 3. Amyl acetate with acetone system

x_2	ε_{12}	ρ_{12}	n_{12}	P_{12}	g^{eff}
0.044	21.664	0.802	1.361	64.82	1.241
0.065	21.496	0.803	1.362	65.47	1.241
0.085	21.328	0.804	1.362	66.11	1.240
0.106	21.160	0.805	1.363	66.74	1.239
0.125	20.992	0.805	1.363	67.37	1.238
0.144	20.824	0.806	1.364	68.00	1.237
0.181	20.488	0.808	1.365	69.24	1.236
0.199	20.320	0.809	1.365	69.86	1.235
0.234	19.984	0.811	1.366	71.07	1.234
0.330	18.976	0.816	1.369	74.61	1.229
0.359	18.640	0.818	1.370	75.75	1.227
0.428	17.800	0.823	1.373	78.51	1.224
0.490	16.960	0.827	1.375	81.14	1.220

Table 4. Isoamyl acetate with carbon tetrachloride system

x_2	ε_{12}	ρ_{12}	n_{12}	P_{12}	g^{eff}
0.017	2.372	1.599	1.469	30.10	4.242
0.026	2.408	1.599	1.469	30.60	3.288
0.034	2.444	1.598	1.468	31.09	2.840
0.043	2.480	1.598	1.468	31.57	2.544
0.051	2.516	1.597	1.468	32.04	2.344
0.060	2.552	1.597	1.467	32.50	2.219
0.077	2.624	1.596	1.466	33.39	2.035
0.086	2.660	1.595	1.466	33.83	1.962
0.103	2.732	1.594	1.465	34.67	1.863
0.157	2.948	1.591	1.463	37.01	1.680
0.175	3.020	1.590	1.462	37.73	1.644
0.220	3.200	1.588	1.460	39.42	1.572
0.266	3.380	1.585	1.458	40.95	1.521

Table 5. Isoamyl acetate with benzene system

| x_2	ε_{12}	ρ_{12}	n_{12}	P_{12}	g^{eff}
0.033	2.431	0.884	1.508	28.93	2.942
0.049	2.466	0.890	1.508	29.37	2.429
0.065	2.502	0.897	1.507	29.82	2.170
0.081	2.537	0.904	1.506	30.25	2.013
0.096	2.572	0.911	1.505	30.67	1.906
0.111	2.608	0.918	1.504	31.09	1.829
0.142	2.679	0.931	1.503	31.90	1.724
0.156	2.714	0.938	1.502	32.30	1.686
0.185	2.785	0.952	1.500	33.07	1.627
0.268	2.997	0.992	1.496	35.23	1.522
0.294	3.068	1.006	1.494	35.91	1.499
0.357	3.245	1.040	1.490	37.51	1.455
0.417	3.422	1.074	1.486	38.99	1.423

Table 6. Isoamyl acetate with acetone system

x_2	ε_{12}	ρ_{12}	n_{12}	P_{12}	g^{eff}
0.044	21.678	0.815	1.361	63.78	1.242
0.065	21.517	0.823	1.362	63.90	1.241
0.085	21.356	0.830	1.363	64.02	1.240
0.106	21.195	0.838	1.364	64.13	1.239
0.125	21.034	0.845	1.364	64.24	1.239
0.144	20.873	0.853	1.365	64.34	1.238
0.181	20.551	0.868	1.366	64.53	1.237
0.199	20.390	0.875	1.367	64.62	1.236
0.234	20.068	0.890	1.368	64.79	1.235
0.330	19.102	0.935	1.373	65.20	1.231
0.359	18.780	0.950	1.374	65.30	1.230
0.428	17.975	0.988	1.378	65.50	1.227
0.490	17.170	1.025	1.381	65.60	1.225

Table 7. Dipole moments of solute with solvent systems

S.No.	Solute	Solvent	$P_2 \mu$	μ
1	Amyl acetate	CCl_4	29	2.48
		Benzene	17	2.48
		Acetone	94	1.98
2	Isoamyl acetate	CCl_4	47	2.48
		Benzene	37	2.43
		Acetone	37	1.13

From the Figure 1 and 2 for the mixture of carbon tetrachloride, benzene, polarization decreases but acetone mixture increases. Polarization variation depends on the polarization of pure liquids. Acetone is more polarization in the pure states so increasing the concentration acetone than increasing the polarization, but in carbon tetrachloride and benzene smoothly decrease. It is solute-solvent interaction taking place. From the polarization at infinite dilution $P2\infty$ and R_D find the value obtained $P_2\mu$. From this value dipole moment of the pure liquids are given Table 7 with literature value.
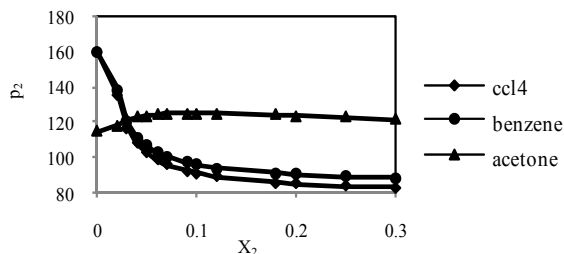
Figure 1. Plots P_2 with the mole fraction of amyl acetate
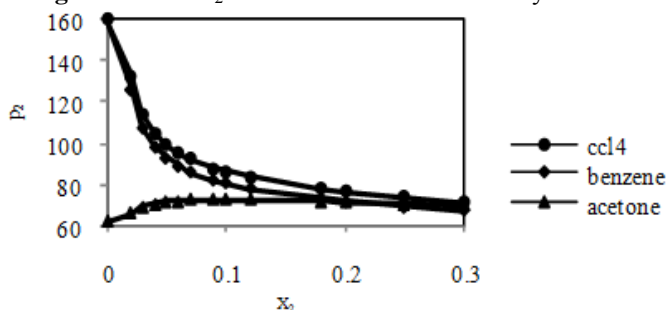
Figure 2. Plots of P_2 with the mole fraction of isoamyl acetate
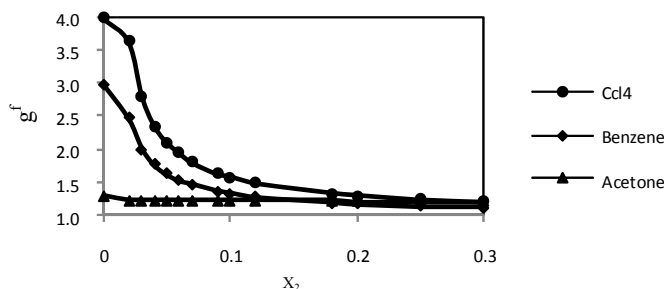
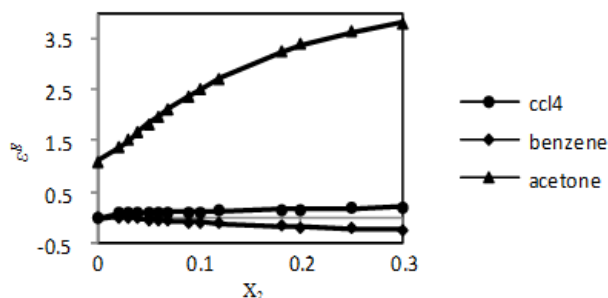**Figure 3.** Plots g^f with the mole fraction of amyl acetate
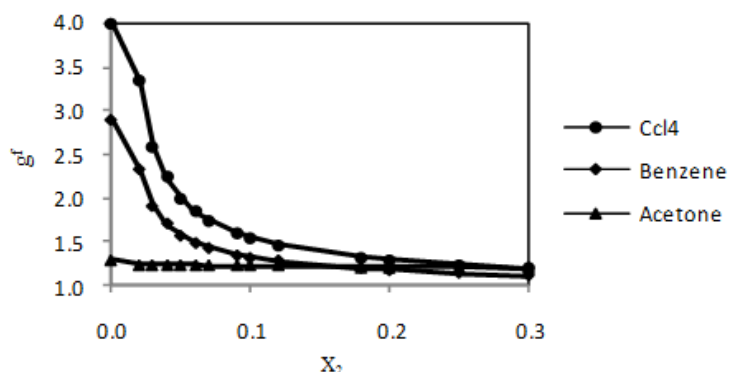
Figure 4. Plots of g^f with the mole fraction of isoamyl acetate

The value of g is directly related to the correlation between the directions of a particular molecule under consideration with the molecules in its neighborhood in solution. The dipoles whose dipole-dipole interaction lead to a positive correlation, parallel orientation gives g>1 are called α-multimers. The dipoles whose dipole-dipole interaction lead to a negative correlation, anti-parallel orientation gives g<1 are called β – multimers.

From Figure 1 and 2, the Kirkwood correlation factor of dielectric polarization of amyl acetate and isoamyl acetate in carbon tetrachloride, benzene gradually increases with increasing concentration of the solute which clearly indicates more and more β –multimers get converted into α – multimers. This behaviour can be attributed to the interaction of the lone pair electrons with the solvent or hyper conjugation effect of the acetate group which is present in solution.

The amyl acetate and isoamyl acetate with an acetone investigated. It can be observed from the Figure 1 and 2; the g values are almost around unity which clearly indicates the strong of solute-solute interactions and also solute-solvent interactions and the idealistic behaviour of polar solvent.

The Figure 5 showed the plots of ε^E for the binary mixture of amyl acetate and isoamyl acetate with carbon tetrachloride, benzene and acetone. In the solvent benzene ε^E is negative. It is total effective dipole get reduced. The liquid mixture may for multimer leads to less effective dipole or dipole to align anti parallel orientation. In the solvent carbon tetrachloride and acetone ε^E is positive. It is total effective dipole get increased then increasing dipole moment then aligned dipole in parallel orientation. As similar results observe in the case of isoamyl acetate as shown in Figure 6. The order of solute solvent interactions are benzene < carbon tetrachloride < benzene.

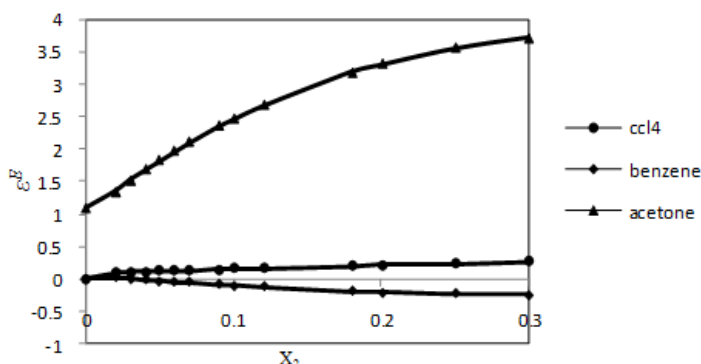**Figure 5.** Plots of ε^E with the mole fraction of amyl acetate

Figure 6. Plots of ε^E with the mole fraction of isoamyl acetate

Conclusion

The polarization of the solution, Kirkwood correlation factors of dielectric polarization and excess permittivity of two acetates dissolved in carbon tetrachloride, benzene and acetone of various concentrations have been reported. The gradually increasing value of g with the increasing concentration of solute in the solvent clearly indicates more g^{eff} variation. Different g^{eff} values for amyl acetate and isoamyl acetate in carbon tetrachloride, benzene attributed to the idealistic behavior of the solvent and two acetates in acetone attributed to the non idealistic behavior of the solvent. From the polarization, linear correlation factor and excess permittivity is in the order of benzene < carbon tetrachloride < acetone amyl acetate / isoamyl acetate as one of the components.

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