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Relative Permittivity Behaviour of $CH_3COCH_2CH_3$ (2-Butanone) with CH_2Cl_2 , $CH_2Cl.CH_2Cl$ and CCl_2CCl_2

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ABSTRACT

The experimental data for $\boldsymbol{\varepsilon}$ (relative permittivities) and $\boldsymbol{n}$ (refractive indices), were measured for mixtures of 2-butanone (BN) ($CH_3COCH_2CH_3$) with dichloromethane (CH_2Cl_2), 1,2-dichIoroethane ($CH_2Cl.CH_2Cl$) and tetrachloroethene (CCl_2CCl_2) at the temperature 308.15 K. The values of $\Delta\varepsilon$ which represent the departures of the ε for the mixtures from the quantities occuring from the law achieved from mole fraction mixture, have been obtained. Calculated values of $\Delta\varepsilon$ shows positive sign for BN with CH_2Cl_2 and $CH_2Cl.CH_2Cl$, whereas it is negative in the case of BN with CCl_2CCl_2. With the help of the values of ε and n, the Kirkwood correlation parameter, g, have been calculated for mixtures of BN with CH_2Cl_2 and $CH_2Cl.CH_2Cl$. The values of g indicate that BN forms intermolecular complexes with these compounds. The Equilibrium constant K_f, for the creation of complexes (1:1) of BN with $CH_2Cl.CH_2Cl$ and CH_2Cl_2, have also been obtained with the experimental data for ε.

Keywords: 2-butanone, Relative Permittivity, Dichloromethane, Hydrogen Bonding, Dekameter

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1. INTRODUCTION

The studies of mixtures of 2-butanone with CH_2Cl_2 and $CH_2Cl.CH_2Cl$ and tetrachloroethene (CCl_2CCl_2) helps to reveal its structural arrangements. A literature investigation disclosed that in depth readings concerning the properties of such types of systems haven't been created. Relative permittivities measurements (1-2) are familiar to offer reliable information regarding the occurence of specific interactions. The particular interaction of $CH_3COC_2H_5$ with the aforesaid compounds are because of the presence of non-bonding pair of electrons on the oxygen atom of $CH_3COC_2H_5$, thus it will perform as n-donor toward these chloro-compounds. $CC1_2CC1_2$ will perform as σ -type acceptors in the direction of 2-butanone, whereas CH_2C1_2 and CH_2ClCH_2C1 will also perform as σ-acceptors toward, and be concerned within the creation of H- bond with, 2-butanone. Since, the values of refractive indices, is too an investigative of the degree of association of molecules in their mixtures, and thus give some information on the character of the particular interaction between the elements. So as to analyze the molecular orientations and interactions occurring in contrast to species of the binary mixture, relative permittivity measurements of mixtures of $CH_3COC_2H_5$ with CH_2C1_2, CH_2ClCH_2C1 and $CC1_2CC1_2$ have been made at 308.15 K. Since the values of n, of $CH_3COC_2H_5$, CH_2C1_2 and CH_2ClCH_2C1 and mixtures of $CH_3COC_2H_5$ with CH_2C1_2 and CH_2ClCH_2C1 were required to obtain g values (3) of $CH_3COC_2H_5$ with CH_2C1_2 and CH_2ClCH_2C1, determinations of refractive indices for these mixtures have conjointly been created at 308.15 K and the obtained data are discussed in this article.

2. EXPERIMENTAL DETAILS

$CH_3COC_2H_5$ was distilled over potassium permanganate, dried over K_2CO_3 and then made fractional distillation. Methylene dichloride was shaken with water and sodium carbonate solution, dried over Calcium Chloride and then purified by fractional distillation. 1,2-Dichloroethane was shaken with dilute KOH and water, dried over $CaCl_2$ and obtained through fractional distillation. Tetrachloroethene (CCl_2CCl_2) was purified as given elsewhere (4). The densities of purified samples were measured at 308.15K with a densimeter (5). The observed values of density for all these compounds are in excellent concurrence with the literature data (6).

3. METHOD

Experimental procedures for Measurements of the relative permittivities and refractive indices are given elsewhere (2).

3. RESULT AND DISCUSSION

The experimental values of n for 2-butanone, CH_2CI_2, CH_2ClCH_2Cl and CCl_2CCl_2 at 308.15 K were found to be 1.3740, 1.4170, 1.4710, and 1.5000 respectively. The obtained values, for refractive indices, n12, for different mixtures at 308.15 K, have been fitted by using the equation

$$n_{12} = a + bx_1 + c\, x_1{}^2 \qquad (1)$$

where "x_1 " represents the mole fraction of 2-butanone. The constants values a, b and c together with the standard deviations $\partial\ (\ n\ )$ in the measuring values of *n* from the values calculated from eqn (l), are collected in Table 1 for the different systems.

The measured values of ε, for the uncontaminated liquids of BN, CH_2Cl_2, CH_2Cl. CH_2Cl and tetrachloroethene (CCl_2CCl_2) and for binary mixtures of BN with CH_2Cl_2 and $CH_2Cl.CH_2Cl$ and tetrachloroethene (CCl_2CCl_2) at 308.15 K are collected in Table 2, where ***x1*** represents the mole fraction of BN. The measured values of ε obtained for CH_2Cl_2 $CH_2Cl.CH_2Cl$ and tetrachloroethene (CCl_2CCl_2) are 8.622,10.078 and 2.294 respectively, in close agreement with the available literature data (7-8). The value for ε for 2-butanone was found to be 17.65 which is based on the available literature data (7).

The values of ε for the different systems are utilized for calculating the parameter Δε, which is the departure of ε of the mixture from ideality by using the equation

$$\Delta\varepsilon\ = \varepsilon_{12} - \varepsilon_1 x_1 - \varepsilon_2 x_2 \qquad (2)$$

where ε_1 and ε_2 are the dielectric constants (Relative permittivities) of the two uncontaminated components, and ε_{12}, is the dielectric constant of the mixture. A plot between Δε and x1 is plotted in Figure 1, it can be seen that positive deviation is observed for the system BN+ CH_2Cl_2 and + $CH_2Cl.CH_2Cl$, and negative for BN+ CCl_2CCl_2 system in the liquid state. The negative deviation for the system BN+CCl_2CCl_2 can be pointed out because of a decline in the degree of coalition of the dipoles with changing composition. The negative values of Δε arise in the mixtures having molecules, which are unlike in shape as well as size, thus such type of deviations reveal presence of geometric effects. The creation of a complex species, for negative Δε will be at the minima of Figure 1. Therefore, the minimum in the Δε is an indication of a greatest in the structuredness between unlike components in the mixture as in the case of BN+ CCl_2CCl_2 system in the liquid state.

The interaction between BN+ CCl_2CCl_2 can be thought of due to a presence of charge-transfer complex formation of CCl_2CCl_2 with the nonbonding electrons of BN. The complexation of CH_2Cl_2 and $CH_2Cl.CH_2Cl$ are due to H atom of these compounds with the nonbonding electrons on O atom of BN, which results high positive values of Δε values in the liquid state. Also there is formation of charge transfer complex between BN and CH_2Cl_2 or $CH_2Cl.CH_2Cl$ because of interaction of Cl atom via O atom. The positive values of Δε, indicates strong interactions. The chief part to the deviation from ideal mixtures is because of the specific interactions, interaction due to the dipole-dipole, H-bond formation trend between components.

The Kirkwood correlation parameter, g, represents the degree of association of molecules. In order to get information that 2-butanone forms strong molecular complex with CH_2Cl_2 and + $CH_2Cl.CH_2Cl$, the g values have been obtained with the help of Frohlich's equation:

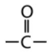
$$\frac{g4\pi\mu N_0}{9\kappa TV\varepsilon_0}=\frac{(\varepsilon-n^2)(2\varepsilon+n^2)}{\varepsilon(n^2+2)^2} \qquad (3)$$

where k is the values of Boltzmann constant and N_0 Avogadro's number, ε_0 refers to the permittivity(free space), V is used for the volume (molar), T is the Kelvin scale temperature, and μ represents dipole moment in the gas phase. The values of μ for CH_2ClCH_2Cl and CH_2Cl_2 were 1.44 and 1.631 Debye, as reported by McClellan, 1965(8), the value 2.53D of μ for 2-butanone was calculated by means of the formula given elsewhere (9). For mixtures the values of μ were calculated with the help of following equation (10)

$$\mu_{12} = x_1\mu_1 + x_2\mu_2 \qquad (4)$$

$\mu_1 and\, \mu_2$ represents the dipole moments(gas phase) of the components one and two, respectively. The density values of the individual components were taken from the literature (6-7) and the values of excess volumes (4) for binary mixtures were taken for calculating the values of V for individual components and their mixtures, which were used in equation 3. The values of g for 2-butanone, CH_2ClCH_2Cl and CH_2Cl_2 as obtained from equation 4 are 1.551, 2.042 and 1.114 D respectively.

When the value of g factor is one, it match ups at right angles orientation. Since the values of μ for 2-butanone, CH_2ClCH_2Cl and CH_2Cl_2 are 2.53, 1.44 and 1.631D respectively, the larger or lesser order in the equivalent association of the molecules of 2-butanone, cannot be due to dipole involvement , but it is because of the specific interaction of 2-butanone molecules with CH_2ClCH_2Cl and CH_2Cl_2. The value of μ makes use of only a slight effect on the creation of the local order in mixtures. The g values are more than one during the whole range of composition for the mixtures of BN+ methylene chloride and + CH_2ClCH_2Cl can be thought of being due to the formation of molecular complexes.

There are two types of forces operating in these systems, i.e. attractive forces(long range) from multipole interactions or repulsive forces (short range)arising because of steric interactions. The local order in liquid $CH_3COCH_2CH_3$ is assessed by interactions (steric) between the $–CH_3$ or $–C_2H_5$ groups. The relative orientation of adjacent molecules becomes stable by means of weak H- bonds between the H atom of the $–CH_3$ or $–C_2H_5$ group and the O atom of the  $-\overset{O}{\overset{\|}{C}}-$ group. The g-factor is accountable for the angles occurring between the dipole moments of compounds. Its value represents the presence of direction relationship between 2-butanone. All C=O bonds are directed towards the interior side of sphere and most of BN molecules are present at 90^0 to each other. This association of the C=O bond leads to the observed gathering of the short O-O distances. The perpendicular orientation of, which overlaps with the C=O bond axes, gives justification of the value of g (1.551).

Since a perpendicular orientation of μ was found largest, which means that dipolar forces play only a slight role in creation of the restricted order in liquid BN , as bulky CH_3 or C_2H_5 groups keep away from association of the dipole moments .

When the BN molecules mix with the CH_2ClCH_2Cl or CH_2Cl_2 molecules, the value of μ of the 2-butanone molecule has a weak consequence on the relative orientation of adjacent molecules. In the structure of the BN, the C=O group, is responsible for μ, is screened by bulky CH_3 or C_2H_5 group. Thus the creation of mainly energetically favourable orientations of adjacent dipoles, i.e. a equivalent or antiparallel association seem to be obstructed, therefore BN molecules are associated through specific interaction in the binary mixtures of BN + CH_2ClCH_2Cl or +CH_2Cl_2.

For getting further information on the creation of complexes of BN with CH_2ClCH_2Cl and CH_2Cl_2, calculations were made for getting the entire molar polarizations *(P)* for BN, CH_2ClCH_2Cl and CH_2Cl_2. and also for its binary mixtures of BN with CH2ClCH2Cl and CH2C12 , by means of the Kirkwood-Frohlich equation (10)

$$P = \frac{(\epsilon - n^2)(2\epsilon + n^2)V}{9\epsilon} \qquad (5)$$

As described earlier, the values of molar volume (*V*) and refractive index (*n*) for unadulterated components and for the different mixtures have been calculated.

The whole molar polarizations were utilized to obtain the apparent molar polarisation, P_1, of BN at various concentrations in CH_2ClCH_2Cl and CH_2Cl_2, in the same manner as given by Rastogi and Nath, 1967(11). The values of *p1,* were found to raise with decreasing x1 of BN for the mixtures of BN- CH_2ClCH_2Cl and BN-CH_2C1_2.

Figure 2 depicts the fluctuation of P1 for the BN - CH_2ClCH_2Cl system with mole fraction x1 of BN. P1 behaves in this way, implying that BN forms strong complexes with CH_2ClCH_2Cl and CH_2C1_2. With the help of Earp and Glasstone's (12) technique, the molar polarisation, P12, was produced by forming a 1:1 molecular complex (donor-acceptor) between BN (1-donor) and the chloro-compound (2-acceptor). P12 values of 591 and 541 cm^3 mol-1 were reported for the 1:l complexes of BN with CH2ClCH2Cl and CH_2C1_2, respectively.

Furthermore, the equilibrium constant, K_f, for the creation of 1:1 complexes for mixtures of BN with CH_2ClCH_2Cl and CH_2C1_2, were obtained from the $\boldsymbol{\varepsilon}$ **(**relative permittivities) data. The data show that the values of K_f vary significantly with mixture composition for the systems BN- CH_2ClCH_2Cl and CH_2C1_2. Rivail and Thiebaut (13), have also obtained that for the pure binary system $CHCl_3$-C_5H_5N, the values of K_f, show a noteworthy deviation with the composition of the mixture. As given by Rivail and Thiebaut, 1974, a theory, which is based on the electrostatic interactions of the solute with the liquid, shows a straight line by plotting log of K_f, with the quantity $f(\varepsilon)$

$$f(\varepsilon) = \frac{(\varepsilon - 1)(\varepsilon_\infty - 1)}{3(2\varepsilon + \varepsilon_\infty)} \qquad (6)$$

where ε_∞ to the infinite-frequency values of ε of the mixture. For calculation of $f(\varepsilon)$ from eqn (6), we used $\varepsilon_\infty = n^2$. Figure 3 shows a linear variation of log K_f, against the values of $f(\varepsilon)$, *for* BN- CH_2ClCH_2Cl and BN- CH_2C1_2. This implies that the values of K_f are consistent with the same theory (13-14).

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Table 1: Experimental values of Relative permittivities, ε, deviation of Relative permittivities, Δε and the Kirkwood correlation parameter g, for the various mixtures of 2-Butanone at 308.15 K
2-butanone + methylene chloride

X1	ε	Δε	g
0.0000	8.622		1.114
0.0941	9.619	0.182	1.167
0.1621	10.443	0.411	1.199
0.1987	11.089	0.609	1.213
0.2543	11.912	0.861	1.264
0.3458	12.911	1.161	1.298
0.4321	13.959	1.382	1.323
0.5598	15.132	1.38	1.378
0.6002	15.439	1.302	1.387
0.6753	15.811	1.151	1.413

0.7821	16.401	0.702	1.468
0.7984	16.502	0.581	1.497
0.8112	16.571	0.511	1.511
0.8562	16.918	0.303	1.534
0.8991	16.953	0.191	1.544
0.9552	17.407	0.019	1.548
0.9799	17.561	0.009	1.549
1.0000	17.653		1.551

2-butanone +CH_2ClCH_2Cl

X1	**ε**	Δ**ε**	**g**
0.0000	10.078		2.042
0.0812	10.849	0.109	2.012
0.1087	11.112	0.181	2.009
0.1612	11.574	0.302	1.995
0.2087	12.202	0.511	1.877
0.2612	12.731	0.712	1.843
0.2771	12.562	0.761	1.834
0.3098	13.441	0.991	1.765
0.4167	14.777	1.492	1.732
0.4662	15.152	1.614	1.719
0.5121	15.672	1.732	1.687
0.6012	16.392	1.762	1.632
0.6687	16.790	1.551	1.596
0.6912	16.821	1.511	1.581
0.7065	16.897	1.396	1.574
0.8188	17.021	0.711	1.568
0.9412	17.244	0.091	1.559
1.0000	17.653		1.551

2-butanone +CCl_2CCl_2

X1	**ε**	Δ**ε**	
0.0000	2.294		
0.0705	3.114	-0.069	
0.1094	3.819	-0.169	
0.1903	4.321	-0.392	
0.2619	5.532	-0.721	
0.3111	6.254	-1.029	
0.4111	7.109	-1.399	
0.4502	7.615	-1.558	
0.5112	8.294	-1.709	
0.5563	9.238	-1.762	
0.6232	9.849	-1.739	
0.6786	10.922	-1.601	
0.7221	11.681	-1.441	
0.8112	13.918	-0.798	
0.8602	14.902	-0.499	
0.8912	16.051	-0.189	
0.9343	16.731	-0.061	
1.0000	17.653		

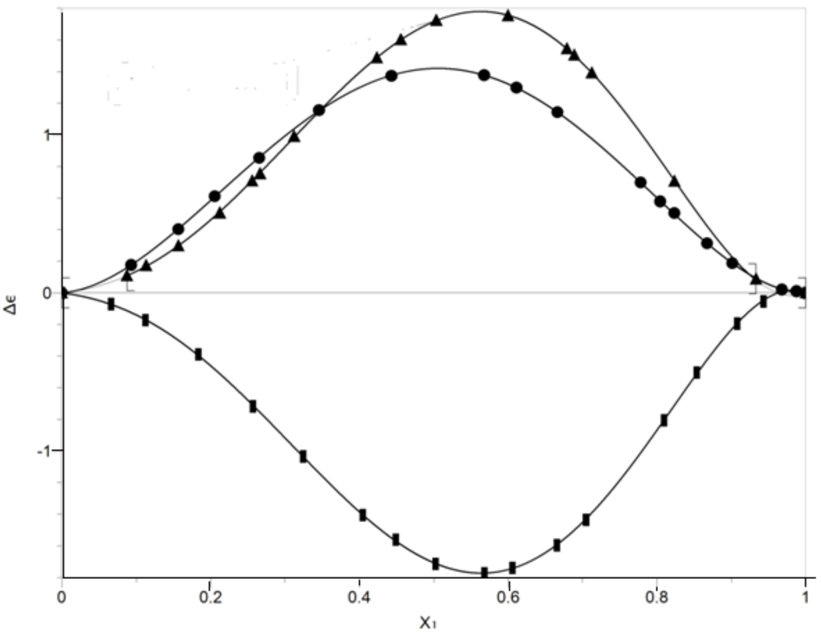

Figure 1: Plot of Δε vs mole fraction of 2-butanone, x_1, for the various Systems●, 2-butanone-CH2C12, ; ▲, 2-butanone-CH2C1 CH2C1; ▮2-butanone-CCl2CC12 at 308.15 K.

Table 2: Values of the constants a, b and c of eqn (1), and the standard deviations *∂(n)*, for the various systems of BN at 308.15 K

System	**A_0**	**A_1**	**A_2**	**∂(n)**
2-butanone(1) CH_2Cl_2 (2)	1.416	-0.0576	0.015	0.002
2-butanone(1) + $CH_2Cl.CH_2Cl$ (2)	1.474	-0.224	0.13	0.002
2-butanone(1) + CCl_2CCl_2 (2)	**1.499**	**-0.126**	**-0.011**	**0.003**

Table 3: Least Squares Coefficients of Eq 5 for the Δε, and the standard deviations, σ, of 2-butanone(1) + methylene Chloride (2), or + $CH_2Cl.CH_2Cl$(2), or + CCl_2CCl_2 (2), at 308.15K

System	**A_0**	**A_1**	**A_2**	A_3	σ/ (J mol^{-1})
2-butanone(1) CH_2Cl_2 (2)	5.676	0.2568	-5.476	-0.4484	0.004
2-butanone(1) + $CH_2Cl.CH_2Cl$(2)	6.861	3.978	-7.513	-5.156	0.0045
2-butanone(1) + CCl_2CCl_2 (2)	-6.828	-4.030	7.438	5.284	0.005

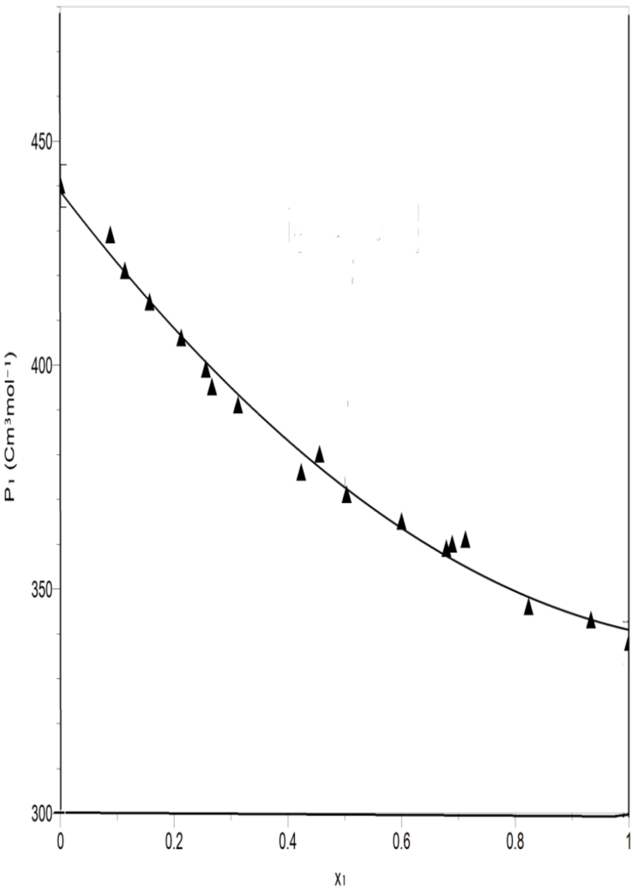

Figure 2: Plot of the apparent molar polarisation, *P1*, against mole fraction of 2-butanone, x_1, for the system BN-CH2ClCH2Cl at 308.15 K

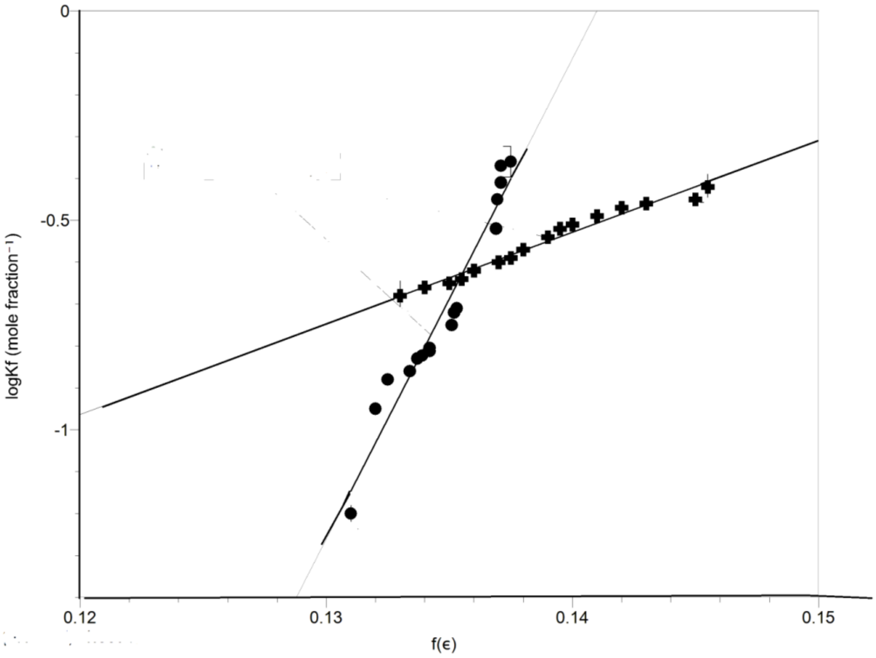

Figure 3: Plot of log [Kf, (mole fraction)$^{-1}$ against the quantity f(ε) for the various systems at **308.15** K: ✚ , *BN*-CH2ClCH2Cl; ●, BN-CH2Cl2.

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