

Dielectric Behaviour of 2-Butanone with Dichloromethane, 1, 2-Dichloroethane and Tetrachloroethene

Abstract

The experimental data for ϵ (relative permittivities) and n (refractive indices), were measured for mixtures of 2-butanone (BN) ($\text{CH}_3\text{COCH}_2\text{CH}_3$) with dichloromethane (CH_2Cl_2), 1,2-dichloroethane ($\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$) and tetrachloroethene (CCl_2CCl_2) at the temperature 308.15 K. The values of $\Delta\epsilon$ which represent the departures of the ϵ for the mixtures from the quantities occurring from the law achieved from mole fraction mixture, have been obtained. Calculated values of $\Delta\epsilon$ shows positive sign for BN with CH_2Cl_2 and $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$, whereas it is negative in the case of BN with CCl_2CCl_2 .

Keywords: 2-butanone, relative permittivity, dichloromethane, hydrogen bonding, dekameter

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Introduction

The studies of mixtures of 2-butanone with CH_2Cl_2 and $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$ and tetrachloroethene (CCl_2CCl_2) helps to make clear its structural arrangements at the molecular level. A literature investigation unconcealed that in depth readings regarding the properties of these systems haven't been created. Relative permittivities measurements (Nath J et.al,1984, 1985,1989) are familiar to offer reliable information regarding the occurrence of specific interactions. The particular interaction of $\text{CH}_3\text{COCH}_2\text{CH}_3$, with these are because of the presence of non-bonding pair of electrons on the O atom of $\text{CH}_3\text{COCH}_2\text{CH}_3$, thus it will perform as n-donor toward these chloro-compounds. CCl_2CCl_2 will perform as σ -type acceptors in the direction of 2-butanone, whereas CH_2Cl_2 and $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$ will also perform as σ -acceptors toward, and be concerned within the creation of H-bond with, 2-butanone. Since, the values of n , is also 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 mixtures, relative permittivity measurements of mixtures of $\text{CH}_3\text{COC}_2\text{H}_5$ with CH_2Cl_2 , $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$ and CCl_2CCl_2 have been made at 308.15 K. The results are interpreted in this article.

Experimental Details

$\text{CH}_3\text{COC}_2\text{H}_5$ 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(Nath J,Saini R,1989). The densities of purified samples were measured at 308.15K with a densimeter

(Patil KR et.al.1990) . The observed values of density for all these compounds are in excellent concurrence with the literature data(Riddick & Bunger,1970).

Method

Experimental procedures for Measurements of the relative permittivity are given elsewhere(Nath J,Tripathi AD.1984). The measured values of ϵ , for the uncontaminated liquids of BN, CH_2Cl_2 , $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$ and tetrachloroethene (CCl_2CCl_2) and for binary mixtures of BN with CH_2Cl_2 and $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$ and tetrachloroethene (CCl_2CCl_2) at 30°C are collected in Table 2, where x_1 represents the mole fraction of BN. The measured values of ϵ obtained for CH_2Cl_2 , $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$ and tetrachloroethene (CCl_2CCl_2) are 8.622, 10.078 and 2.294 respectively, in close agreement with the available literature data (Timmermans,1950;McClellan,1965). The value for ϵ for 2-butanone was found to be 17.65 which is based on the available literature data (Timmermans,1950).

Results and Discussion

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

$$\Delta\epsilon = \epsilon_{12} - \epsilon_1x_1 - \epsilon_2x_2 \text{-----(1)}$$

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 $\Delta\epsilon$ and x_1 is plotted in Fig.1, it can be seen that positive deviation is observed for the system BN+ CH_2Cl_2 and + $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$, 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 $\Delta\epsilon$ 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 $\Delta\epsilon$ will be at the minima of Fig.1. Therefore, the minima in the $\Delta\epsilon$ 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 $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$ are due to H atom of these compounds with the nonbonding electrons on O atom of BN, which results high positive values of $\Delta\epsilon$ values in the liquid state.

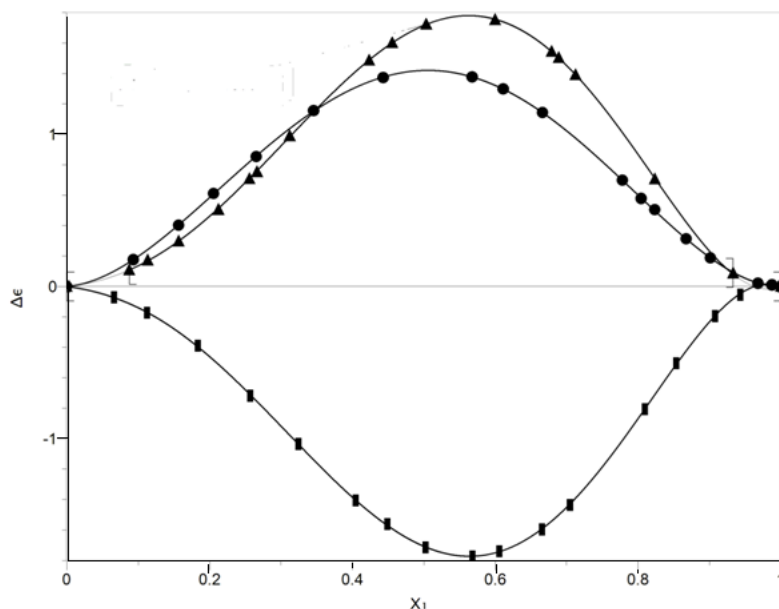


Fig. 1. Plot of $\Delta\epsilon$ vs mole fraction of 2-butanone, x_1 , for the various Systems \bullet , 2-butanone- CH_2Cl_2 ; \blacktriangle , 2-butanone- $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$; \blacksquare 2-butanone- CCl_2CCl_2 at 308.15 K.

Also there is formation of charge transfer complex between BN and CH_2Cl_2 or $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ because of interaction of Cl atom via O atom. The positive values of $\Delta\epsilon$, 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.

Table 1. Experimental values of Relative permittivities, ϵ , deviation of relative Permittivities, $\Delta\epsilon$, for the various mixtures of 2-Butanone at 308.15 K

2-butanone + CH_2Cl_2			2-butanone + $\text{CH}_2\text{ClCH}_2\text{Cl}$			2-butanone + CCl_2CCl_2		
X1	ϵ	$\Delta\epsilon$	X1	ϵ	$\Delta\epsilon$	X1	ϵ	$\Delta\epsilon$
0.0000	8.622		0.0000	10.078		0.0000	2.294	
0.0932	9.641	0.176	0.0874	10.851	0.11	0.0662	3.24	-0.071
0.1567	10.441	0.403	0.1132	11.109	0.174	0.1122	3.845	-0.172
0.2056	11.091	0.611	0.1567	11.563	0.298	0.1834	4.723	-0.388
0.2654	11.872	0.853	0.2122	12.191	0.506	0.2567	5.521	-0.717
0.3458	12.901	1.156	0.2557	12.724	0.709	0.3244	6.242	-1.034
0.4432	13.998	1.373	0.2665	12.557	0.754	0.4044	7.111	-1.405
0.5678	15.126	1.376	0.3122	13.432	0.989	0.4487	7.626	-1.560
0.6112	15.44	1.298	0.4234	14.768	1.487	0.5022	8.293	-1.714

0.6663	15.782	1.143	0.4555	15.131	1.603	0.5678	9.241	-1.774
0.7782	16.348	0.698	0.5034	15.614	1.723	0.6054	9.852	-1.740
0.8045	16.465	0.578	0.5998	16.375	1.754	0.6654	10.918	-1.596
0.8234	16.563	0.505	0.6789	16.775	1.545	0.7045	11.679	-1.435
0.8675	16.908	0.313	0.6889	16.801	1.505	0.8095	13.922	-0.805
0.9013	16.949	0.187	0.7123	16.872	1.392	0.8533	14.897	-0.503
0.9678	17.383	0.021	0.8234	17.022	0.707	0.9078	16.043	-0.194
0.9876	17.551	0.010	0.9331	17.235	0.089	0.9432	16.727	-0.054
1.0000	17.653		1.0000	17.653		1.0000	17.653	

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