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# DIELECTRIC CONSTANT, DENSITY AND REFRACTIVE INDEX STUDY ON MIXING PROPERTIES OF BINARY LIQUID MIXTURE

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## ABSTRACT

The present paper reports the study of binary mixtures and their properties over the entire range of composition at temperatures 288, 298, 308 and 318 K. Excess dielectric constant, excess molar volume, excess refractive index, molar refraction and excess molar refraction at different temperatures have been computed from the experimentally measured values of the aforesaid parameters and fitted to the Redlich-Kister equation. Excess dielectric constant, excess refractive indices are positive whereas excess molar volume is negative over entire composition range of Methyl Acetate for all temperatures. The results are discussed in the light of intermolecular interactions occurring in the binary mixture. Estimated coefficients of the Redlich-Kister polynomials and the standard error along with the coefficients are also reported.

**KEYWORDS:** **Dielectric constant, density, refractive index, excess property.**

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# 1. INTRODUCTION

Study of dielectric behavior of polar and non-polar molecules and their mixtures [1-4] under varying conditions of compositions and temperatures has evoked considerable interest. There have been several investigations on the dielectric behavior of solvent mixtures in which dielectric spectra were used to examine molecular orientations, hydrogen bonded networks and microdynamics of these systems [5-8]. Excess properties depend on the composition and temperature, are of great importance for the study of the interaction between mixing components. Refractive index and density measurements of solvent mixtures are expected to shed some light on the solvent-solvent interaction and configuration of their mixtures [8-10]. Very few attempts have been made to study Carbon Tetrachloride and Methyl Acetate [11, 12]. Carbon tetrachloride is used as cleaning solvent, refrigerant etc. Methyl Acetate is used as solvent, in nail polish etc. When a binary mixture is formed, the excess properties like refractive index and dielectric parameters do not vary linearly with composition. The deviation from linearity of these parameters is termed as excess parameters and is helpful to understand the nature of intermolecular interactions and bonding between the two liquids. As a result many workers [13-16] have studied the excess parameters in liquid mixtures.

### *2. Experimental details*

The Carbon Tetrachloride ($CCl_4$) and Methyl Acetate are obtained from Qualigens fine chemicals and Kemphasol, Mumbai. These chemicals were used without further purification as the supplier claims their purity is more than 99%. The solutions are prepared at eleven different volume fractions of respective chemicals from 0 to 1 in step of 0.1. These volume fractions are converted to mole fractions for further calculations. Refractive indices were measured using thermostatically controlled Abbe's refractometer with an accuracy of ± 0.001. Calibration was performed by measuring the refractive indices of doubly distilled water and Acetone at defined temperatures within ± 0.01 K. The sample mixture was directly injected into the prism assembly of the instrument using a syringe. Densities of pure components and their mixtures were measured by using Pycknometer having a bulb volume approximately 3 $cm^3$ and internal diameter of the capillary tube of about 0.275 cm with the precision of density measurements about ± $10^{-5}$ $g.cm^{-3}$. Dielectric constant is measured by indigenously designed instrument in our laboratory with an accuracy of ± 0.1 %.

### *3. Theoretical aspects*

Dielectric constant of the pure and their binary mixtures were measured using the indigenously built monostable multivibrator instrument in which the pulse width varied according to the dielectric constant of a desired liquid in a cell with derived equation for the dielectric constant in terms of pulse width[17] as,

$$\varepsilon_r = \left( \frac{T_2 - T_1}{A} \right) + 1$$

where $T_1$ be the pulse width without liquid, $T_2$ is the pulse width with liquid and 'A' is called as Geometric cell constant which is determined experimentally over large range of the dielectric constants, which has the dimension of time. The information related to solute-solvent interaction can be obtained by excess properties [18] related to the dielectric constant, density and refractive index in the mixtures. The excess properties of the

mixtures were calculated using the following equation.

$$A^E = A_{mix} - \left(A_1 X_1 + A_2 X_2\right)$$

where $A^E$ represents the refractive index deviation, excess dielectric constant, excess molar volume etc. $A_1$, $A_2$ and $A_{mix}$ represent the refractive index or dielectric constant or molar volume of pure liquids 1, 2 and mixture respectively. The $X_1$ and $X_2$ represents the mole fraction of component 1and 2 of the mixtures. The excess parameters were fitted to a Redlich-Kister (RK) polynomial equation for determination of $a_j$ coefficients. The estimated $a_j$ coefficients along with standard deviation are listed in table 3.

**Table1**

***Static dielectric constant and Density ($10^3 Kg/m^3$) of $CCl_4$- Methyl Acetate binary system***

| Mole fraction of Methyl acetate | 288 K | | 298 K | | 308 K | | 318 K | |
|---|---|---|---|---|---|---|---|---|
| | $\varepsilon_s$ | $\rho$ | $\varepsilon_s$ | $\rho$ | $\varepsilon_s$ | $\rho$ | $\varepsilon_s$ | $\rho$ |
| 0.0000 | 2.3291 | 1.60296 | 2.1689 | 1.58272 | 2.0729 | 1.56498 | 1.9127 | 1.54039 |
| 0.0833 | 3.0496 | 1.53922 | 2.7614 | 1.51720 | 2.7294 | 1.49744 | 2.5212 | 1.47575 |
| 0.1697 | 3.7542 | 1.47335 | 3.4019 | 1.45137 | 3.2418 | 1.43280 | 3.0657 | 1.40525 |
| 0.2595 | 4.4267 | 1.40008 | 4.1225 | 1.38084 | 3.9624 | 1.36287 | 3.6741 | 1.34048 |
| 0.3528 | 5.0032 | 1.33587 | 4.6669 | 1.31918 | 4.4908 | 1.30056 | 4.2666 | 1.27649 |
| 0.4498 | 5.5637 | 1.27127 | 5.2754 | 1.25551 | 5.0512 | 1.23786 | 4.8110 | 1.21264 |
| 0.5509 | 5.8679 | 1.20518 | 5.5476 | 1.18991 | 5.3715 | 1.17402 | 5.1153 | 1.15220 |
| 0.6561 | 6.0120 | 1.13814 | 5.7718 | 1.12407 | 5.5957 | 1.10871 | 5.3715 | 1.08824 |
| 0.7658 | 6.2522 | 1.07193 | 5.9319 | 1.05945 | 5.7558 | 1.04602 | 5.5156 | 1.02746 |
| 0.8804 | 6.3163 | 1.00788 | 6.0440 | 0.99872 | 5.8999 | 0.98498 | 5.6597 | 0.97032 |
| 1.0000 | 6.4444 | 0.94401 | 6.2042 | 0.93503 | 6.0921 | 0.92670 | 5.9159 | 0.91131 |

## 4. RESULTS AND DISCUSSION

The values of the static dielectric constant ($\varepsilon_s$) of mixtures are tabulated in table1. It is observed that static dielectric constant ($\varepsilon_s$) increases with increase in mole fraction of Methyl Acetate in the mixture but decreases with increase in temperatures. In view of the current interest on dielectric constant values of the mixed solvents, a comparative dielectric study of $CCl_4$ mixtures with Methyl Acetate solvents over the entire mixing range have been studied to probe the formation of solvent–cosolvent H-bonded complexes. In binary liquid mixtures there is a possibility of interactions between the constituents such as hydrogen bonding, molecular associations, dipole–dipole, and dipole-induced dipole interactions [19, 20]. The variation of excess dielectric constant with mole fraction scale of Methyl Acetate is shown in figure 1. It was observed that the Methyl Acetate molecules are built in via H-bonding into the $CCl_4$ structure and vice-versa, which results the strengthening of H-bonds and leads to a long range parallel dipolar ordering in $CCl_4$-Methyl Acetate complex system. There is a substitution of $CCl_4$ molecules by Methyl Acetate in the hydrogen bonds, which results into the formation of a common hydrogen bond network of the $CCl_4$-Methyl Acetate system that favours the parallel ordering of H-bonded of $CCl_4$ Methyl Acetate cluster. Hence, there is increase in net dielectric constant values versus mole fraction of the $CCl_4$ -Methyl Acetate mixture. The same conclusions were

also drawn on the formation of $CCl_4$ -Methyl Acetate clusters from the thermodynamics [21, 22].

The values of excess refractive index ($n_D^E$) were negative over the entire range of mole fraction of Methyl Acetate as shown in figure 2. This may be due to specific forces between molecules, such as hydrogen bonds, charge transfer complexes and complexes bringing negative excess values. Negative values of $n_D^E$ for $CCl_4$-Methyl Acetate binary mixtures are indication of weak intermolecular interactions related to increase in molar volume [23, 24]. The excess molar volume ($V^E$) values of $CCl_4$-Methyl Acetate binary mixture are negative over the entire range of composition as shown in figure 3. The $V^E$ curves are shifted in a regular way with increasing temperature. However, the excess refractive index deviation values are positive. This is due to the behaviour of the refractive index which is not too non-linear between pure components [25]. The observed negative $V^E$ values for $CCl_4$-Methyl Acetate mixtures indicate the formation of hydrogen bonding between unlike molecules. Negative contribution to $V^E$ comes from the geometrical fitting of unlike molecules into each other's structures due to difference in size and shape of the molecules. The negative $V^E$ values indicate that there is a volume contraction on mixing. This negative excess molar volume $V^E$ is an indication of strong heteromolecular interaction in the liquid mixtures and is attributed to charge-transfer, dipole–dipole interactions between the unlike molecules. In the present investigation, the $CCl_4$- Methyl Acetate mixture gave a negative magnitude of $V^E$, and they depict the presence of hetero-molecular interaction [26, 27].

The polarizability of $CCl_4$-Methyl Acetate binary liquid mixtures versus mole fraction is tabulated in table 2. It is observed that polarizability decreases as concentration of Methyl Acetate increases but increases with temperature. Thus deformation occurs and higher the polarizability, the more easily the molecule deforms and the stronger are the dispersion forces. The molar refraction should not depend on temperature over a small temperature range, as can be seen in figure 4. This shows that molar refraction ($R_M$) values can, be associated with electronic polarizabilities. These values are indicate the electronic perturbation of the individual molecules during mixing and therefore these values depends very much on the nature of the mixing components [28].The nature of excess molar polarization is shown in figure 5.The observed values of excess molar polarization remain positive in $CCl_4$ associated rich region, and is most probably due to the fact that the parallel alignment of molecular dipoles is the dominant factor in the $CCl_4$ associated rich region where the long range electrostatic interaction plays a vital role for polarization [29].

The variation of molecular radius $CCl_4$-Methyl Acetate binary system is shown in figure 6. It is observed that molecular radius decreases as the concentration of Methyl Acetate increases and it increases as temperature increases. Conscientious factor for a change in the intermolecular radius on replacement of hydrogen forming the hydrogen bond by Methyl Acetate, in case where the density of the steric arrangement of the atoms is low, may increase with disordering. This is probable for molecular liquids in which the formation of a lattice or another form of order is apparently associated with an increase in the deviation from the closest packing of the molecules and hence with some volume expansion [30, 31].

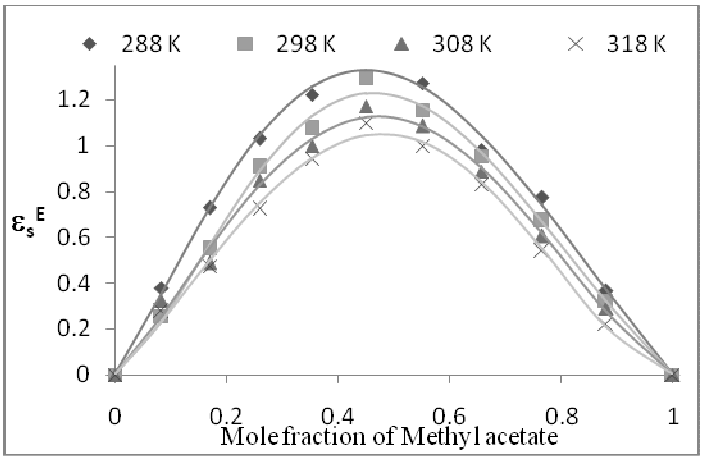


**Figure 1**
***Excess dielectric constant of $CCL_4$- Methyl Acetate binary system***

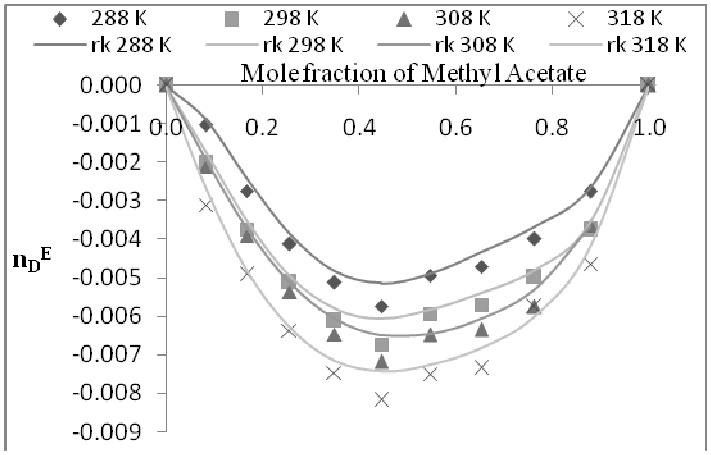


**Figure 2**
***Excess refractive index of $CCL_4$- Methyl Acetate binary system***

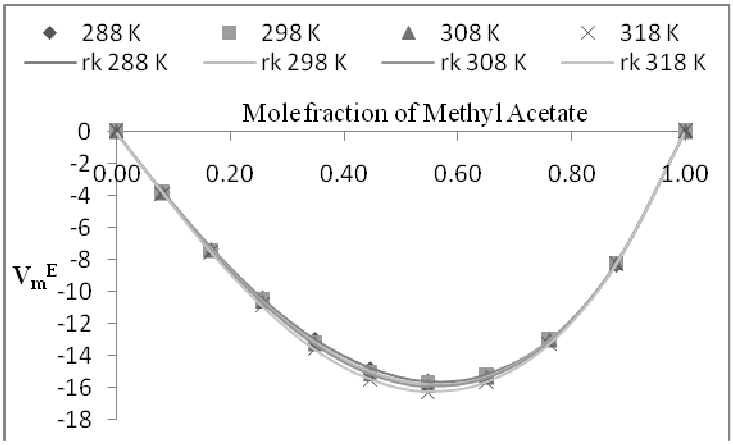


**Figure 3**
***Excess molar volume of $CCL_4$- Methyl Acetate binary system***

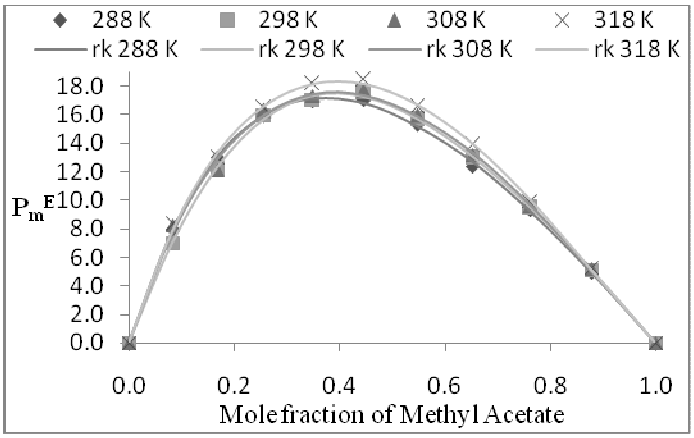


**Figure 4**
***Excess molar polarization of $CCL_4$- Methyl Acetate binary system***

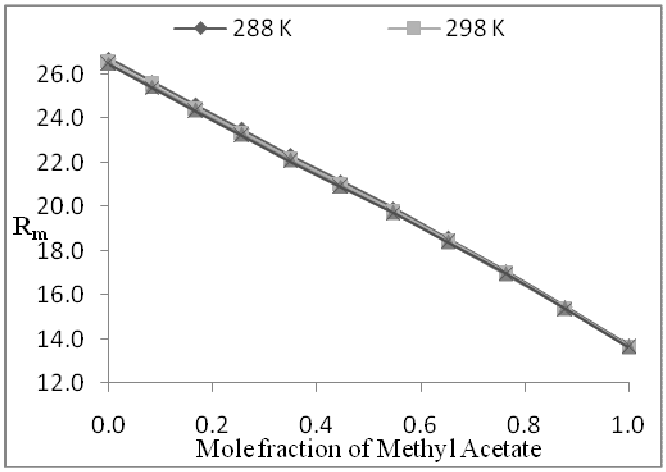


**Figure 5**
***Molar refraction of $CCL_4$- Methyl Acetate binary system***

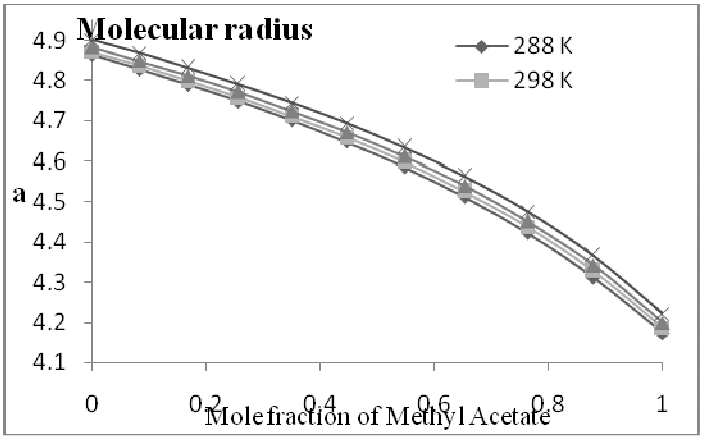


**Figure 6**
***Molecular radius ($10^{-10}$ m) of $CCL_4$- Methyl Acetate binary system***

**Table 2**

***Refractive index and Polarizability ($10^{-25}$ m /molecule) of $CCl_4$- Methyl Acetate binary system***

| Mole fraction of Methyl acetate | 288 K | | 298 K | | 308 K | | 318 K | |
|---|---|---|---|---|---|---|---|---|
| | $n_D$ | ∝ | $n_D$ | ∝ | $n_D$ | ∝ | $n_D$ | ∝ |
| 0.0000 | 1.461 | 3.1561 | 1.456 | 3.1395 | 1.450 | 3.1254 | 1.444 | 3.1236 |
| 0.0833 | 1.452 | 3.0326 | 1.446 | 3.0143 | 1.440 | 3.0023 | 1.433 | 2.9984 |
| 0.1697 | 1.442 | 2.9041 | 1.436 | 2.8869 | 1.430 | 2.8760 | 1.423 | 2.8702 |
| 0.2595 | 1.432 | 2.7743 | 1.426 | 2.7559 | 1.420 | 2.7458 | 1.413 | 2.7395 |
| 0.3528 | 1.422 | 2.6386 | 1.416 | 2.6208 | 1.410 | 2.6089 | 1.403 | 2.6035 |
| 0.4498 | 1.412 | 2.4964 | 1.406 | 2.4815 | 1.400 | 2.4690 | 1.393 | 2.4646 |
| 0.5509 | 1.403 | 2.3527 | 1.397 | 2.3404 | 1.391 | 2.3293 | 1.384 | 2.3251 |
| 0.6561 | 1.393 | 2.1915 | 1.387 | 2.1814 | 1.381 | 2.1712 | 1.374 | 2.1696 |
| 0.7658 | 1.383 | 2.0179 | 1.377 | 2.0085 | 1.371 | 1.9991 | 1.365 | 2.0032 |
| 0.8804 | 1.373 | 1.8260 | 1.367 | 1.8196 | 1.362 | 1.8141 | 1.355 | 1.8126 |
| 1.0000 | 1.364 | 1.6181 | 1.359 | 1.6135 | 1.354 | 1.6076 | 1.348 | 1.6097 |

**Table 3**

***aj coefficients of excess dielectric constant, excess refractive index, excess molar volume ($10^{-2}$ m $mole^{-1}$), excess molar polarization ($10^{-2}$ m $mole^{-1}$) and standard deviation (σ) of $CCl_4$ +Methyl Acetate system***

| Parameters/$a_j$ | $a_0$ | $a_1$ | $a_2$ | $a_3$ | σ |
|---|---|---|---|---|---|
| | | | 288 K | | |
| $\varepsilon_s^E$ | 5.24310 | -1.46202 | -1.78248 | 0.91507 | 0.03834 |
| $n_D^E$ | -0.02024 | 0.00535 | 0.00078 | -0.02122 | 0.00016 |
| $V_m^E$ | -61.40063 | -16.18942 | -6.20385 | -2.51179 | 0.02507 |
| $P_m^E$ | 64.32204 | -31.73945 | 14.25723 | -5.09238 | 0.16386 |
| | | | 298 K | | |
| $\varepsilon_s^E$ | 4.87982 | -1.10362 | -2.76188 | 1.33818 | 0.03449 |
| $n_D^E$ | -0.02390 | 0.00475 | -0.00826 | -0.01905 | 0.00019 |
| $V_m^E$ | -62.32628 | -15.66920 | -4.29082 | -1.85052 | 0.02616 |
| $P_m^E$ | 66.45826 | -32.22792 | 5.11044 | 7.32276 | 0.18493 |
| | | | 308 K | | |
| $\varepsilon_s^E$ | 4.48947 | -0.77752 | -2.39480 | 0.14312 | 0.04216 |
| $n_D^E$ | -0.02603 | 0.00110 | -0.00738 | -0.01172 | 0.00021 |
| $V_m^E$ | -62.82960 | -15.39496 | -3.30536 | -2.16605 | 0.02831 |
| $P_m^E$ | 67.01243 | -29.18832 | 8.96489 | -5.71434 | 0.38984 |
| | | | 318 K | | |
| $\varepsilon_s^E$ | 4.19563 | -0.58462 | -2.73449 | -0.45411 | 0.03024 |
| $n_D^E$ | -0.02954 | 0.00333 | -0.01323 | -0.01128 | 0.00032 |
| $V_m^E$ | -64.28431 | -14.85061 | -2.29029 | -3.14207 | 0.01669 |
| $P_m^E$ | 70.02241 | -29.61026 | 7.35731 | -7.75766 | 0.25722 |

## 5. CONCLUSIONS

The dielectric study of binary mixtures $CCl_4$-Methyl Acetate confirms the formation of heteromolecular interactions over the entire concentration and temperature. The dielectric parameter shows systematic change with concentration and temperature. The excess dielectric constant values evaluated from mole-fraction mixture conclude that these mixtures have intermolecular interactions. The values of $V_m^E$ are found negative indicating the presence of specific donor–acceptor (charge-transfer) interactions between $CCl_4$ and Methyl Acetate molecules. From the dielectric and optical study of $CCl_4$ with Methyl Acetate we get some structural information which may be helpful to medical and industrial applications.

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