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DIELECTRIC AND OPTICAL PROPERTIES OF POLAR AND NONPOLAR LIQUIDS AT DIFFERENT TEMPERATURES

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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

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KEYWORDS

Dielectric constant, density, refractive index, excess property.

I. INTRODUCTION

One of the most urgent needs of our society is the development of technological systems that allow continuous progress while respecting the environment. Design of chemical products and processes more environmentally benign is necessary; thus the "greening" of industry has been the aim of prioritized research over the last decade. 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]. Knowledge of the physicochemical and thermodynamic properties of binary liquid mixtures formed by one or two components associated through hydrogen bonds is important from both theoretical and process design aspects. Excess properties, which depend on the composition and/or temperature, are of great importance for the characterisation of the interaction between 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 [8-12]. These properties have been used to study the structure and solvent-solvent interaction of binary mixtures. Solvent structure determines the nature of interactions between the like and unlike molecules of a liquid binary mixture.

When a binary mixture is formed, the refractive index, thermodynamic parameters and dielectric parameters do not vary linearly. The deviation from linearity of these parameters is termed as excess parameters and is helpful to understand the nature of bonding between the two liquids. Recently several workers [13-17] have studied the excess parameters in liquid mixtures.

II. EXPERIMENTAL DETAILS:

The chemicals Benzene 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 refractometer with accuracy 0.001units.Water was circulated in to the prism of the refractometer by a circulation pump connected to an external thermostated water bath. Calibration was performed by measuring the refractive indices of doubly distilled water and Methyl Acetate at defined temperatures within 0.01 K. The sample mixture was directly injected in to the prism assembly of the instrument using a syringe.

Density of pure components and their mixtures were measured pyknometer having a bulb volume approximately 3 cm^3 and internal diameter of the capillary tube of about 0.275 mm with the precision of density measurements was 10^{-5} g cm^{-3}.

Dielectric constant is measured by indigenouslly designed instrument in our laboratory with accuracy 0.0001.

III. THEORETICAL ASPECTS:

Dielectric constant of the pure and their binary mixtures were measured using the indigenously designed instrument with derived equation for dielectric constant in terms of the pulse width [18] 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' called sample holding device constant (SHD) to be determined experimentally over large range for the dielectric constants which has the dimension of time.

The information related to solute-solvent interaction can be obtained by excess properties [19] related to the dielectric constant, density and refractive index in the mixture. 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 densities or excess molar volume etc, A_1, A_2 and A_{mix} represent the refractive index or density or molar volume of pure liquids 1, 2 and mixture respectively. The X_1 & X_2 represents the mole fraction of component 1and 2 of the mixtures
The computed results of excess properties have been fitted to a Redlich-Kister type polynomial equation. The estimated coefficient along with standard deviation is listed in table 3.

Table 3

aj coefficients of excess dielectric constant, excess refractive index, excess molar volume (cm mole^{-1}), excess molar polarization (cm mole^{-1}), and standard deviation (σ) of Benzene+ Methyl Acetate system

Parameters/a_j	a_0	a_1	a_2	a_3	σ
			288 K		
ε_s^E	2.45639	-2.18046	1.67469	0.45654	0.02454
n_D^E	-0.07171	0.01592	-0.01851	0.00058	0.00042
V_m^E	2.84103	-1.02118	-0.02832	-0.39462	0.03582
P_m^E	34.93161	-25.80190	25.78558	-14.69213	0.21483
			298 K		
ε_s^E	2.03152	-2.33042	0.74521	0.68564	0.03824
n_D^E	-0.06944	0.01383	-0.00223	-0.00138	0.00065
V_m^E	2.66387	-1.51692	-0.07356	0.97432	0.02062
P_m^E	32.60379	-27.94658	18.15794	-2.93727	0.24754
			308 K		
ε_s^E	1.56150	-2.16803	1.00142	0.80918	0.03867
n_D^E	-0.06741	0.02007	-0.00757	-0.01938	0.00068
V_m^E	2.30402	-1.12128	-0.56133	1.15518	0.01789
P_m^E	29.49929	-26.41960	18.15162	-0.77622	0.31543

			318 K		
ε_s^E	1.36827	-1.99942	0.15531	1.58949	0.03811
n_D^E	-0.06292	0.02189	-0.01018	-0.02989	0.00040
V_m^E	2.16470	-0.93712	-0.59208	0.54563	0.01289
P_m^E	33.04336	-29.42840	11.99155	10.20830	0.40732

IV. RESULTS AND DISCUSSION

It is observed that static dielectric constant (ε_s) increases with increase in mole fraction of Methyl Acetate in the mixture but decreases with increase in temperatures. The values of the static dielectric constant (ε_s) are tabulated in table1.

Table1

Static dielectric constant and Density (10^2Kg/m^3) of Benzene- Methyl Acetate binary system

Mole fraction of Methyl acetate	288 K		298 K		308 K		318 K	
	ε_s	ρ	ε_s	ρ	ε_s	ρ	ε_s	ρ
0.0000	2.44	0.88614	2.44	0.87182	2.44	0.85931	2.12	0.85090
0.0899	3.24	0.88694	3.06	0.87438	3.00	0.86265	2.58	0.85388
0.1818	3.83	0.88929	3.72	0.87635	3.64	0.86533	3.21	0.85521
0.2758	4.27	0.89290	4.15	0.88091	3.99	0.86941	3.61	0.85783
0.3720	4.65	0.89803	4.49	0.88565	4.28	0.87473	3.93	0.86286
0.4705	5.02	0.90398	4.73	0.89165	4.60	0.88201	4.28	0.86864
0.5714	5.24	0.91182	5.08	0.90041	4.84	0.89007	4.55	0.87511
0.6746	5.55	0.92046	5.35	0.90939	5.16	0.89986	4.84	0.88271
0.7804	5.88	0.92958	5.61	0.91838	5.45	0.90821	5.21	0.88927
0.8889	6.20	0.93826	5.95	0.92696	5.79	0.91652	5.53	0.89582
1.0000	6.44	0.94889	6.28	0.93680	6.12	0.92593	5.92	0.90246

Table2

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	$\propto$	n_D	$\propto$	n_D	$\propto$	n_D	$\propto$
0.00000	1.504	3.0799	1.496	3.0883	1.489	3.0956	1.483	3.0935
0.08958	1.488	2.9801	1.481	2.9859	1.474	2.9888	1.469	2.9921
0.18126	1.474	2.8854	1.467	2.8909	1.461	2.8953	1.456	2.9022
0.27512	1.459	2.7817	1.452	2.7824	1.447	2.7922	1.442	2.8024
0.37122	1.445	2.6791	1.438	2.6794	1.433	2.6859	1.427	2.6899
0.46966	1.431	2.5751	1.424	2.5736	1.419	2.5748	1.413	2.5816
0.57051	1.417	2.4670	1.411	2.4666	1.406	2.4685	1.401	2.4834
0.67388	1.403	2.3584	1.397	2.3556	1.393	2.3593	1.388	2.3780
0.77985	1.389	2.2504	1.383	2.2466	1.379	2.2506	1.374	2.2715
0.88852	1.376	2.1505	1.371	2.1508	1.367	2.1543	1.361	2.1718
1.00000	1.364	2.0531	1.358	2.0488	1.354	2.0520	1.348	2.0732

In view of the current interest on dielectric constant values of the mixed solvents, a comparative dielectric study of Benzene mixture with widely used Methyl Acetate solvents over the entire mixing range have been executed to probe the formation of solvent–cosolvent complexes. In liquid binary mixtures there is a wide range of possible interactions between the constituents such as molecular associations, dipole–dipole, and dipole-induced dipole interactions.

The different strength of solvent–cosolvent interactions and the net dipolar alignments is responsible for the magnitude and divergent signs of ε_s^E as shown in figure 1(a) in the mixture. The maximum value position on the mole fraction scale of Methyl Acetate for Benzene- Methyl Acetate, mixture leads to a long range parallel dipolar ordering in Benzene- Methyl Acetate complex system. Positive values of excess dielectric constant indicates that the constituents of the binary mixture interact in such a way that they act with parallel dipolar alignment in the same direction, which results in increase of effective number of aligned dipoles contributing to the mixture dielectric polarization.

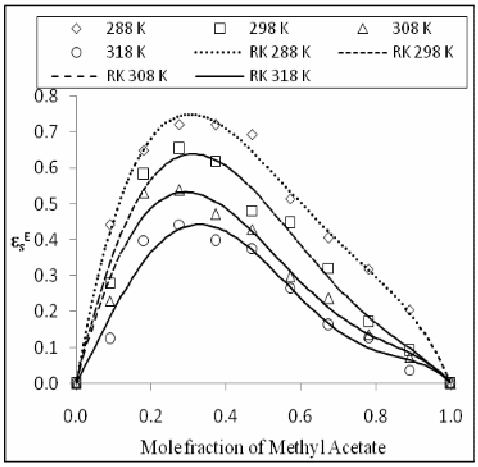


Figure 1

(a) Excess dielectric constant

The values of excess refractive index were negative over the entire range of mole fraction shown in figure 1(b). It can be summarized that excess values may be due to the specific forces between molecules, such as charge transfer complexes, bringing negative excess values. The second factor is the physical intermolecular forces, including electrostatic forces between charged particles and between a permanent dipole and so on induction forces between a permanent dipole and an induced dipole and forces of attraction and repulsion between non polar molecules. Excess refractive indices values are negative over the complete mole fraction range for binary mixtures indicative of weak intermolecular interactions related to increase in molar volume.

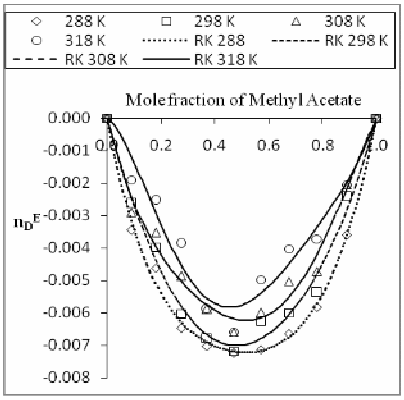
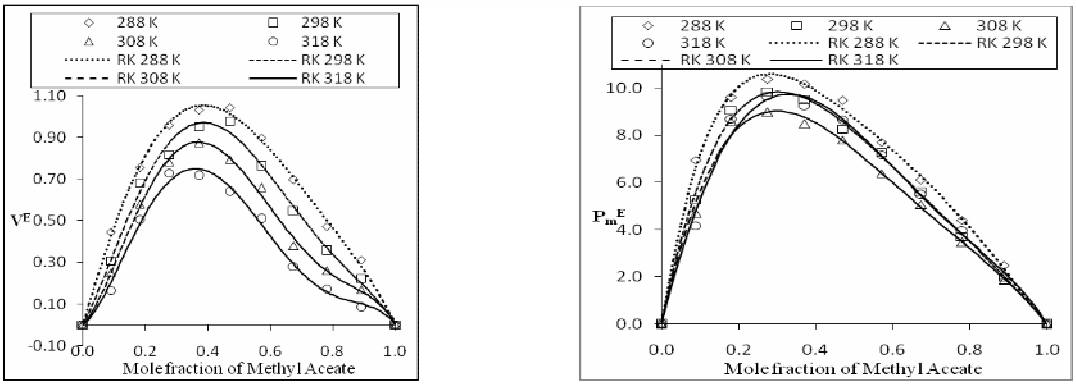


Figure 1

(b) excess refractive index of Benzene-Methyl Acetate binary system

The excess molar volume of Benzene-Methyl Acetate mixture is shown in figure 2(a).The positive values for excess volume of Benzene-Methyl Acetate mixture arises from weakening the structural effects that causes expansion of mixture in comparison with pure components [20, 21]. The positive values for excess molar volume indicate that Physical interaction mainly consisting of dispersion forces or weak dipole−dipole interaction and making a positive contribution.



a b

Figure 2
(a) Excess molar volume refractive index
(b) excess molar polarization of Benzene-Methyl Acetate binary system

The polarizability expresses the ease with which the molecule's electrons can be displaced by an electric field. If refractive index is measured in the optical region, orientation effects do not contribute to $\propto$, regardless of the permanent electric dipole moment of the substance. This is due to the longer relaxation time of the dipoles as compared with the period of oscillation of light [22, 23].Thus, only deformation occurs and the higher $\propto$ is, the more easily the molecule deforms and the stronger are the dispersion forces. Since R_m is proportional to $\propto$, the molar refraction in the optical region is related to the strength of the dispersion forces.The higher the permanent electric dipole moment of molecules, the more important are the orientational effects. Since we measured the refractive indexes in the optical region, the polarizability should not include orientational effects. Therefore the molar refraction should not depend on temperature T over a small temperature range, as can be seen in figure 3(a).This shows that R_m values can, in fact, be associated with electronic polarizability.

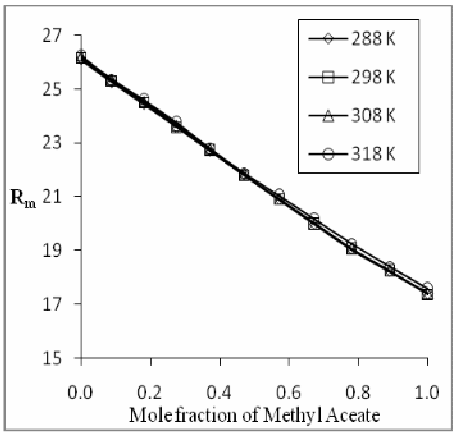


Figure 3
(a) Molar refraction (m^3mole^{-1})

The molar polarization of substances that allows electron polarizability of molecules in various states of aggregation (gaseous, liquid, and solid) to be determined. It is necessary for calculating the dipole moment of the complex from the experimental data. Higher value in the system may be due to the effect of hydrogen bonding in a mixed solvent [24]. Excess molar polarization is the only relation that recognizes the short range interaction between the dissimilar molecules and similar molecules in the mixtures taking molecular properties of the polar and non-polar liquids in the mixture into consideration [25].Excess molar polarization remains positive in associated rich region This is most probably due to the fact that the parallel alignment of molecular dipoles is the dominant factor in the associated rich region where the long range electrostatic interaction plays a vital role for polarization [26].

The inter-ionic distance in the crystalline state is not exactly additive for the radii of the constituent ions, it can be explains it in terms of polarization. It gives the information of orientation polarizability of the dipole [27].

The variation of molecular radius Benzene-Methyl Acetate binary system is shown in figure 3(b). It is observed that molecular radius is decreases as the concentration of Methyl Acetate increases and it increases as temperature increases. This phenomenon is particularly 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 [28].

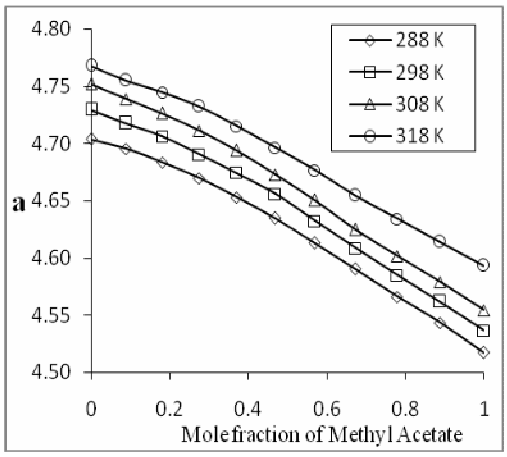


Figure 3
(b) Molecular radius (10^{-10}m) of Benzene-Methyl Acetate binary system

Figure 4 shows the plot of Bruggeman factor vs. volume fraction of Methyl Acetate. In this system, it is observed that the value of Bruggeman factor f_B deviates from linear one. The nonlinearity of the curve indicates hetero-interaction, which may arise due to the formation of complex [29] between Benzene and Methyl Acetate. These values deviate more in equal concentration of both solutions, indicating significant intermolecular interaction in this region.

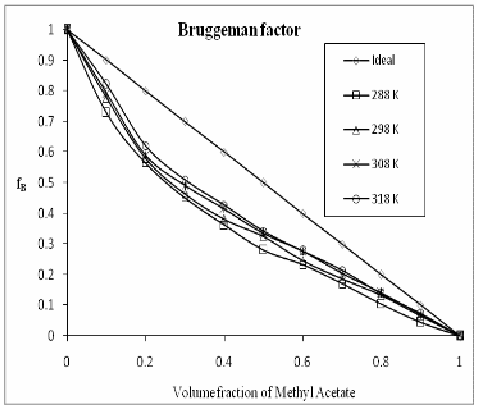


Figure 4
Bruggeman factor (f_B) of Benzene-Methyl Acetate binary system

5. CONCLUSIONS

The dielectric study of binary mixtures of Benzene with Methyl Acetate solvents confirms the formation of hetero-molecular interactions over the entire concentration range. The excess dielectric constant values evaluated from mole-fraction mixture conclude that these mixtures have mixing behaviour. The strength of hetero-molecular interactions in binary mixtures is strongly governed by the values of dielectric constant and excess parameters.

The values of V_m^E are found negative indicating the presence of specific donor–acceptor (charge-transfer) interactions between Benzene and Methyl Acetate molecules, which decrease with increase in temperature. From the dielectric and optical study of Benzene with Methyl Acetate we get some structural information which will be helpful in medical and industrial applications.

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