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다른 온도에서 유전 특성을 통한 사이클로헥산-메틸 아세테이드 바이너리 시스템의 상호관계

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Interaction of Cyclohexane-Methyl Acetate Binary System through Dielectric Properties at Different Temperatures

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요 약. 본 논문은288, 298, 308, 318 K에서 구성 요소의 전체 영역에서 이성분 혼합물과 그 특징을 발표하였다. 각각의 다른 온도에서 초과유전상수, 초과 몰 부피, 초과 굴절률, 몰 굴절, 초과 몰 굴절은 실험적으로 측정된 이전의 파라미터 값으로부터 계산되었고 Redlich-Kister 식으로 확인했다. 초과 유전상수, 초과 몰 부피, 초과 몰 편광은 음수인 반면에 초과 굴절률은 모든 온도에 대해 메틸 아세테이드의 전체 몰 분율에서 양수이다. 본 결과는 이성분 혼합물에서 발생하는 분자 사이의 상호작용을 고려하여 논의 되었다. Redlich-Kister 다항식의 예측된 계수와 계수에 따른 표준오차 또한 보고되었다.
주제어: 유전 상수, 밀도, 굴절률, 초과 특징

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 molar volume excess molar polarizations are negative whereas excess refractive indices are positive over entire mole fraction of methyl acetate for all temperatures. The results are discussed in light of intermolecular interactions occurring in the binary mixture. Estimated coefficients of the Redlich-Kister polynomials and the standard error along the coefficients are also reported.
Keywords: Dielectric constant, Density, Refractive index, Excess property

INTRODUCTION

The dielectric study of liquids gives important information about molecular structures, molecular interactions between components of solutions, dynamics and kinetics of the solution. The static dielectric constant of a solvent is a relative measure of its polarity. Dielectric characterization has great potential in studying the H-bond interactions; dipolar alignments and stoichiometric ratio of stable adduct formation in mixed solvents.[1-5] In liquid binary mixtures there is a range of possible interactions between the constituents such as hydrogen bonding, molecular associations, dipole-dipole, and dipole-induced dipole interactions.[6-9]

Very few attempts have been made to study cyclohexane and methyl acetate binary mixtures. Methyl acetate is used as a volatile low toxicity solvent in paints, glues, and nail polish removers. It is also a solvent for waste film in the production of cellulosic adhesives. It is a perfume solvent and reaction solvent in dye production. Heat treating equipment manufacturer surface combustion uses cyclohexane as a carbon carrying gas in their high purity vacuum carburizing furnaces. It is also used for calibration of differential scanning calorimetry (DSC) instruments, because of a convenient crystal-crystal transition. Because of such wide applications of the cyclohexane and methyl acetate therefore it will be interesting to study dielectric and optical properties of their binary liquid mixtures.

EXPERIMENTAL DETAILS

The chemicals cyclohexane 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 accuracy ± 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 pyknometer 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} gm-cm^{-3}.

Dielectric constant is measured by indigenously designed instrument in our laboratory with accuracy ± 0.1%.

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 as[10]

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

Where, T_1 be the pulse width without liquid, T_2 is the pulse width with liquid and 'A' called Geometric cell constant 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[11] related to the dielectric constant, density and refractive index in the mixtures.

The excess properties of the mixtures were calculated using the following equation.

$$A^E = A_{mix} - (A_1X_1 + A_2X_2)$$

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 estimated results of excess properties have been fitted to a Redlich-Kister (RK) type polynomial equation.

***Table* 1.** aj coefficients of excess dielectric constant, excess refractive index, excess molar volume, excess molar polarization, and standard deviation (σ) of Cyclohexane + Methyl Acetate system

Parameters/a_j	a_0	a_1	a_2	a_3	σ
			288 K		
ε_s^E	-3.19939	-1.53415	1.74010	2.39489	0.04148
n_D^E	0.06159	0.03442	0.01018	-0.00576	0.00024
V_m^E	-65.78184	-37.41394	-33.77144	-24.41085	0.19998
P_m^E	-41.34725	-25.32517	-9.78755	-6.83705	0.26859
			298 K		
ε_s^E	-3.93430	-1.15302	1.89848	1.52617	0.03185
n_D^E	0.05964	0.03952	0.00890	-0.04721	0.00052
V_m^E	-66.56261	-36.00654	-20.15324	-15.44983	0.11291
P_m^E	-45.91022	-20.44740	-0.49425	-5.55506	0.16807
			308 K		
ε_s^E	-4.73424	-0.89854	1.42190	1.05476	0.02561
n_D^E	0.05633	0.04612	-0.00684	-0.05870	0.00061
V_m^E	-65.44223	-31.71617	-17.38393	-17.43963	0.21277
P_m^E	-52.10816	-12.80787	-1.06840	-9.67591	0.16904
			318 K		
ε_s^E	-5.29140	-1.79643	1.00972	1.17898	0.03938
n_D^E	0.05187	0.04693	-0.01879	-0.06264	0.00079
V_m^E	-63.33329	-40.99023	-11.77589	17.20741	0.19508
P_m^E	-57.28897	-20.75864	3.88039	10.49429	0.29390

The estimated coefficients along with standard deviation are listed in *Table* 1.

RESULTS AND DISCUSSION

Table 2 shows that static dielectric constant (ε_s) increases with increase in mole fraction of methyl acetate in the mixture but decreases with increase in temperature. In liquid binary mixtures there is a range of possible interactions between the constituents such as molecular associations, dipole-dipole, and dipole-induced dipole interactions.[9,12]

The density increases and refractive index of the system decreases as the concentration of methyl acetate increase but decrease with increase in the temperature. The nonlinear behaviour of the density and refractive index with concentration of Methyl Acetate indicates intermolecular interactions in the system which is shown *Table* 3 and 4 respectively.

***Table* 2.** Dielectric constant (ε_s) of Cyclohexane-Methyl Acetate binary system

Mole fraction of Methyl Acetate	288 K	298 K	308 K	318 K
0.0000	2.28	1.96	1.91	1.64
0.1627	2.68	2.28	2.08	1.80
0.3042	2.98	2.53	2.28	1.96
0.4284	3.40	2.88	2.60	2.28
0.5383	3.67	3.24	3.00	2.60
0.6362	4.12	3.72	3.4	3.00
0.7240	4.60	4.20	3.96	3.56
0.8032	5.21	4.84	4.60	4.23
0.8749	5.67	5.35	5.16	4.76
0.9403	6.06	5.77	5.64	5.32
1.0000	6.44	6.20	6.12	5.91

***Table* 3.** Density of Cyclohexane-Methyl Acetate binary system

Mole fraction of Methyl Acetate	288 K	298 K	308 K	318 K
0.00000	0.77471	0.77346	0.76381	0.75230
0.07429	0.80044	0.79398	0.79091	0.78316
0.15294	0.81960	0.81479	0.81145	0.81018
0.23637	0.85175	0.84494	0.84210	0.83786
0.32501	0.87848	0.87477	0.87123	0.86449
0.41936	0.89200	0.89049	0.88537	0.88438
0.52001	0.90549	0.90129	0.89929	0.89530
0.62759	0.91745	0.91315	0.90965	0.90545
0.74286	0.92171	0.91745	0.91668	0.91285
0.86667	0.93251	0.92391	0.92302	0.91666
1.00000	0.94405	0.93507	0.92676	0.91140

***Table* 4.** Refractive index of Cyclohexane-Methyl Acetate binary system

Mole fraction of Methyl Acetate	288 K	298 K	308 K	318 K
0.0000	1.461	1.456	1.454	1.444
0.1627	1.451	1.447	1.443	1.432
0.3042	1.442	1.437	1.433	1.423
0.4284	1.433	1.428	1.424	1.414
0.5383	1.424	1.419	1.415	1.405
0.6362	1.415	1.41	1.406	1.397
0.7240	1.406	1.401	1.397	1.388
0.8032	1.396	1.391	1.386	1.377
0.8749	1.385	1.379	1.374	1.365
0.9403	1.374	1.368	1.363	1.355
1.0000	1.363	1.359	1.355	1.348

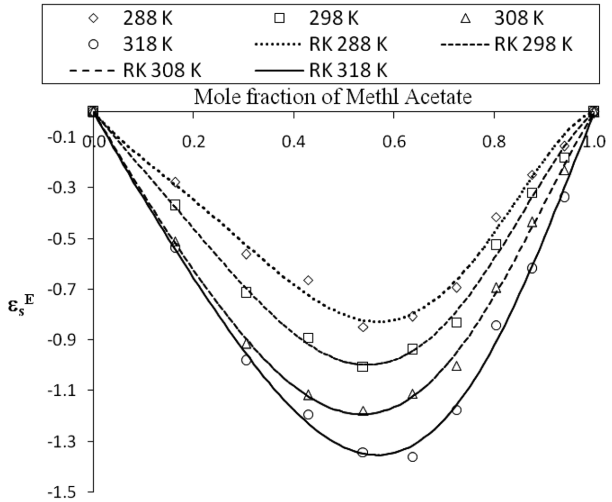

***Fig*. 1.** Excess dielectric constant of Cyclohexane-Methyl Acetate system.

The maximum value position of excess dielectric constant on the mole fraction scale of methyl acetate for cyclohexane-methyl acetate mixtures is shown in *Fig.* 1. Negative values of excess dielectric constant favors the anti-parallel ordering of cyclohexane-methyl acetate structures.[13]

The values of excess refractive index were positive over the entire range of mole fraction of methyl acetate is shown in *Fig.* 2. This is due to the specific forces between molecules, such as charge transfer complexes, intermolecular forces bringing positive excess values. Another aspect responsible for the values is the structural characteristics of the component arising from geometrical fitting of one component into other structure due to the differences in shape and size of the components and free volume. Excess refractive indices values are positive over the

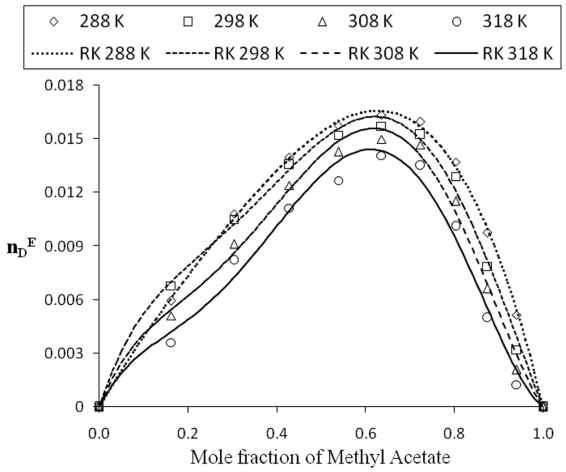

***Fig.* 2.** Excess refractive index of Cyclohexane-Methyl Acetate binary system.

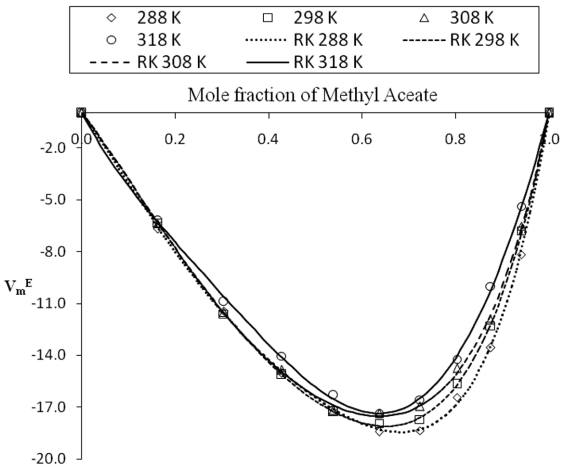

***Fig.* 3.** Excess molar volume of Cyclohexane-Methyl Acetate binary system.

complete mole fraction range for binary mixtures indicative of intermolecular interactions related to decrease in molar volume.[14,15]

Fig. 3 shows the nature of the excess molar volume versus mole fraction of methyl acetate. This nature may be due to physical contributions, which are nonspecific interactions between the real species present in the mixture, contributing to excess molar volume. The excess molar volume results can be analyzed using the Prigogine-Flory-Patterson theory.[16-18] The chemical or specific intermolecular interactions result in a volume decrease, this effect contributes negative values to excess molar volume. The negative value for excess molar volume of cyclohexane-methyl acetate mixture arises from structural effects that cause contraction of mixture in comparison with pure components.[19]

***Table* 5.** Polarizability (10^{-23} cm/molecule) of Cyclohexane-Methyl Acetate binary system

Mole fraction of Methyl Acetate	288 K	298 K	308 K	318 K
0.0000	1.7153	1.7083	1.7160	1.6977
0.1627	1.7134	1.7302	1.7355	1.7284
0.3042	1.7403	1.7421	1.7561	1.7698
0.4284	1.7715	1.7804	1.8035	1.8242
0.5383	1.8228	1.8308	1.8508	1.8737
0.6362	1.8695	1.8999	1.9340	1.9359
0.7240	1.9364	1.9715	2.0104	2.0231
0.8032	2.0286	2.0662	2.1034	2.1173
0.8749	2.1202	2.1636	2.1845	2.2295
0.9403	2.2539	2.2970	2.3136	2.3399
1.0000	2.4310	2.4502	2.4644	2.4671

The polarizability values are tabulated in *Table* 5. The nature of the values is due to the longer relaxation time of the dipoles as compared with the period of oscillation of light.[20] Thus deformation occurs and the higher polarizability, more easily the molecule deforms and the stronger are the dispersion forces. Molar refraction in the optical region is related to the strength of the dispersion forces. Since we measured the refractive indices in the optical region, the polarizability should not include orientational effects. Therefore the molar refraction should not depend on T over a small temperature range, as can be seen in *Fig.* 4. This shows that molar refraction values can, in fact, be associated with electronic polarizabilities. It gives the information of orientation polarizability of the dipole.[21]

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.[22] Values of excess molar

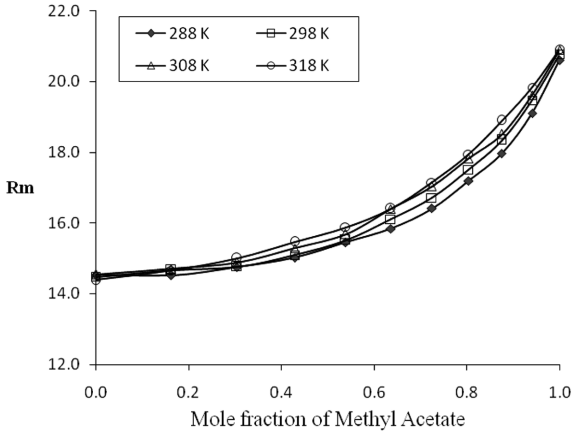

***Fig.* 4.** Molar refraction of Cyclohexane-Methyl Acetate binary system.

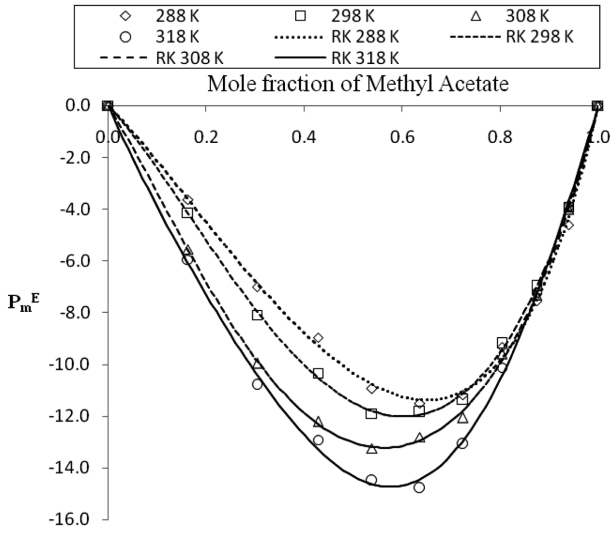

***Fig*. 5.** Excess molar polarization of Cyclohexane-Methyl Acetate binary system.

polarization are negative for all temperatures and all concentrations for cyclohexane-methyl acetate system as shown in *Fig.* 5. This is most likely due to the fact that the anti-parallel alignment of molecular dipole predominates in the region where non-associated liquid is in excess.[23]

Fig. 6 shows the plot of Bruggeman factor versus volume fraction of methyl acetate. In this system, it is observed that the value of Bruggeman factor deviates from linear one. The nonlinearity of the curve indicates hetero-interaction, which may arise due to the formation of complex between cyclohexane and methyl acetate. These values deviate more in equal concentration of both solutions, indicating significant intermolecular interaction in this region.[24,25]

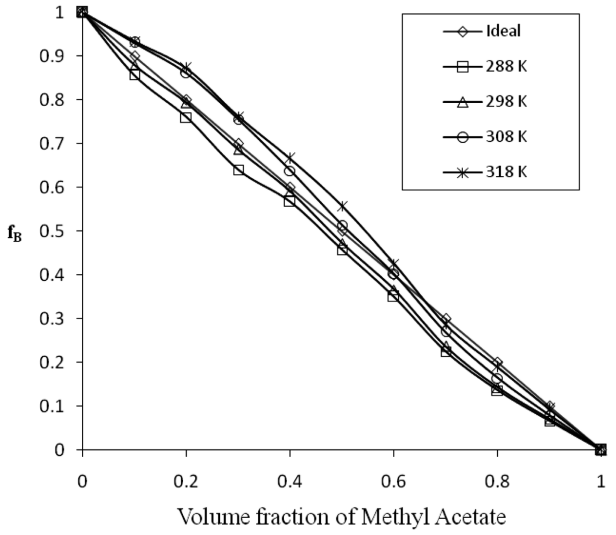

***Fig*. 7.** Molecular radius (10-10 m) of Cyclohexane-Methyl Acetate binary system.

The molecular radius of cyclohexane- methyl acetate binary system is shown in *Fig.* 7. It is observed that molecular radius is increases as the concentration of methyl acetate increases and it decreases with increase in temperature. 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.[26]

CONCLUSION

Cyclohexane has the ring structure i.e. it has no stable pi bond so there is no scope for Hydrogen bonding with other molecules. In this case there is possible interaction are dipole-dipole, dipole-induced dipole interaction.

The negative values of excess dielectric constant indicates that one of the mixture constituents acts self-associated structures with orientation of some of the neighboring dipoles in an anti-parallel direction. The values of excess molar volume are found negative indicating the presence of specific donor-acceptor (charge-transfer) interactions between cyclohexane and methyl acetate molecules, which decrease with increase in temperature. From the dielectric and optical study of cyclohexane with methyl acetate we get some structural information which will be helpful in medical and industrial applications.

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