IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

An International Open Access, Peer-reviewed, Refereed Journal

Dielectric Study Of Binary Mixture Of Allyl Bromide With 2-Pentanone And 2-Hexanone In Microwave Frequency Range

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Abstract:

Dielectric measurement of a binary mixture of Allyl Bromide with 2-Pentanone and 2-Hexanone was carried out over the entire concentration range using a Time-domain Reflectometer (TDR) at temperatures 293.15K, 303.15K, and 313.15K in microwave frequency range 10 MHz to 10 GHz. The static dielectric constant(ε_s) and relaxation time(τ) of binary mixture were determined which are further used to study excess static dielectric constant(ε_s^E), excess inverse relaxation time$(\frac{1}{\tau})^E$, effective Kirkwood correlation factor(g^{eff}), and Bruggeman factor(f_B). These parameters are used to study intermolecular interaction between Allyl Bromide (ALB) and the carbonyl group of 2-Pentone (2-PE) and 2-Hexanone (2-HE). Intermolecular interaction of Allyl Bromide with 2-Pentanone and 2-Hexanone occurs through dipole-dipole interaction. The excess static dielectric constant and excess inverse relaxation time are fitted to Redlich-Kister equation.

Keyword: Static dielectric constant, Effective Kirkwood correlation factor, Relaxation time

Introduction:

Dielectric spectroscopy is a nice probe for accessing information about molecular structure, dynamics, and kinematics of binary mixtures of solute-solvent, especially in polar solvents. The study of dielectric properties of liquid is necessary not only to understand the molecular structures but also to provide technical data to use in industries, science, medicine and engineering. For the last three decades, the microwave technique has been extensively employed for better understanding the dielectric properties of a binary mixture of polar-polar and polar-nonpolar liquids [1]. Allyl Bromide is a highly versatile product due to its dual reactive sites at the double bond and its presence of electronegativity at bromine. It is used in many syntheses of polymer, and pharmaceutical alloys. It has wide applications in pharmaceutical medicine.

2-PE and 2-HE are carbonyl groups of ketones that have many applications in science and industry. Both are aprotic solvents having carbonyl groups attached to different alkyl groups. Dharne et.al [2] reported dielectric relaxation measurements of Allyl Chloride with Dimethylformamide and alcohol using the Time Domain Reflectometry. M. Jeyaraj et.al [3] studied the dielectric relaxation of Allyl Bromide and Allyl ether in a dilute solution of Benzene in the microwave frequency region at different temperature. Madhurima et.al [4,5] studied the steric hindrance of ketone in the dielectric relaxation of ketone with methanol. Gilani et.al [6] reported the non-linear variation of the dielectric constant of 2 Butanone with 2-Butanol and Cyclohexane. We reported the dielectric and thermodynamics study of Allyl Chloride with Ketone [7-9]. As part of our continuous research work, in this paper, we reported a dielectric study of ALB with 2-PE and 2-HE at temperatures 293.15K, 303.15K, and 313.15 K. There are many techniques employed in the dielectric study of binary mixture. Among these techniques, the Time domain Reflectometry technique is used for present work because their precise, reproducibility varies with a wide frequency range.

Experimental section

Chemical:

The AR grade chemicals used in the present work are ALB, 2-PE, and 2-HE with a purity of 99% and are used without further purification. The solutions were prepared at eleven different volume percentages of adding ketone (2-PE, 2-HE) in ALB starting from 0% to 100% in steps of 10%, by micropipette with an accuracy of ±0.0006ml.

Experimental method:

The Hewlett Packard HP54750A Sampling Oscilloscope with HP54754ATDR plug-in module has been used for experimental measurement of complex permittivity data of the sample. A fast-rising voltage pulse of about 39 picoseconds rise time generated by the tunnel diode is propagated through a flexible coaxial cable with an impedance of 50Ω. The sample is placed at the end of the coaxial cable in a standard military application (SMA) coaxial cell. The data acquisition of eleven concentration samples at temperatures 293.15K, 303.15K, and 313.15 K. The details of the experimental setup, procedure, and data analysis are explained earlier [1, 7-8,10].

Theory

The excess static dielectric constant (ε_s^E) of mixtures is given by,

$$\varepsilon_s^E = \varepsilon_{sm} - (\varepsilon_{sA} x_A + \varepsilon_{sB} x_B) \quad (1)$$

Where x is mole fraction and suffixes m, A, B represent mixture, liquid A and liquid B respectively.

The Kirkwood correlation factor (g) equation [11] for pure polar liquid is modified for mixture is known as effective Kirkwood correlation factor [12] and is given by,

$$\frac{4\pi N}{9KT}\left(\frac{\mu_A^2 \rho_A}{M_A}\Phi_A + \frac{\mu_B^2 \rho_B}{M_B}\Phi_B\right) g^{eff} = \frac{(\varepsilon_{sm} - \varepsilon_{\infty m})(2\varepsilon_{sm} + \varepsilon_{\infty m})}{\varepsilon_{sm}(\varepsilon_{\infty m} + 2)^2} \quad (2)$$

Where symbols has usual meaning, 'Φ_A' and 'Φ_B' be the volume fractions of liquid 'A' and 'B' respectively. Dipole moment (μ) of ALB, 2-PE and 2-HE is 1.90, 2.70 and 2.66 D [13] are used to determine values of Kirkwood correlation factor (g) of pure liquids.

The Bruggeman factor (f_B) parameter which may be used as an confirmation of solute-solvent interactions and is given by[14],

$$f_B = \left(\frac{\varepsilon_m - \varepsilon_B}{\varepsilon_A - \varepsilon_B}\right)\left(\frac{\varepsilon_A}{\varepsilon_m}\right)^{(1/3)} = 1 - V \quad (3)$$

Where V is volume fraction, which is a qualitative measure of volume of the solute in the mixture.

Result and Discussion:

The static dielectric constant (ε_s) and relaxation time (τ) of ALB+2-PE and ALB+2-HE are obtained by fitting experimental data with the Debye equation [15] and tabulated in Tables 1 and 2 respectively. This represents the nonlinear behaviour of ε_s and τ with variation of mole fraction of 2-PE and 2-HE in ALB+2-PE and ALB+2-HE system respectively. This nature confirms intermolecular interaction takes place between solute and solvent because of the presence of the electronegative of Br in ALB and the carbonyl group of 2-PE and 2-HE. The prominent dipole-dipole interaction takes place between ALB and 2-PE in the ALB+2-PE system and ALB and 2-HE in the ALB+2-HE system. 2-HE has a longer hydrocarbon chain than 2-PE, it exhibits stronger dispersion forces, making its interaction with ALB slightly stronger than 2-PE. Both Static dielectric constant and relaxation time decrease with increasing temperature. The values of relaxation time of mixtures in general different from the averaged value because of changes in the molecular environment and the size of rotating molecular entities [10].

Table 1: Static dielectric constant and Relaxation Time of ALB+2-PE binary system

Mole fraction of 2-PE	293.15 K		303.15 K		313.15 K	
	ε_s	τ(ps)	ε_s	τ(ps)	ε_s	τ(ps)
0	7.14	13.20	6.74	12.24	6.54	11.39
0.0828	8.29	19.99	7.84	18.64	7.63	18.33
0.1688	9.19	24.78	8.73	23.71	8.43	22.85
0.2582	9.69	27.81	9.30	25.58	8.94	25.59
0.3513	10.08	31.75	9.73	28.98	9.42	28.16
0.4482	10.53	34.59	10.17	31.79	9.82	30.74
0.5492	10.99	35.33	10.62	34.83	10.28	33.09
0.6546	11.61	39.66	11.19	38.03	10.81	36.98
0.7647	12.45	44.35	12.00	41.25	11.52	39.93
0.8797	13.66	50.22	13.16	47.66	12.74	46.61
1	15.37	59.43	15.11	57.60	14.59	56.02

Table 2: Static dielectric constant and Relaxation time of ALB+2-HE binary system

Mole fraction of 2-HE	293.15 K		303.15 K		313.15 K	
	ε_s	τ(ps)	ε_s	τ(ps)	ε_s	τ(ps)
0	7.14	13.20	6.74	12.24	6.54	11.39
0.0722	7.88	18.95	7.60	18.98	7.31	19.15
0.1490	8.70	26.30	8.41	26.69	8.08	25.67
0.2308	9.52	33.43	8.92	31.71	8.59	30.11
0.3183	10.01	37.20	9.35	33.83	9.07	32.33
0.4119	10.57	43.33	9.86	37.12	9.46	36.08
0.5123	10.94	45.42	10.34	41.97	9.84	40.21
0.6203	11.44	49.13	10.86	46.11	10.29	43.29
0.7369	11.87	51.95	11.34	50.27	10.94	46.63
0.8631	12.92	61.45	12.29	57.10	11.97	55.04
1	14.55	72.37	14.01	70.82	13.66	67.38

The effective Kirkwood correlation factor (g^{eff}) [11] of system ALB+2-PE and ALB+2-HE are listed in Table 3 and Table 4 respectively. The g^{eff} values of pure ALB are less than unity attributed to a high degree of the antiparallel molecular association while g^{eff} values of 2-PE and 2-HE are greater than unity which would be expected to ascertain the presence of parallel association. These two opposing tendencies of molecules mix with different molecular concentrations. They aim to change other compounds' inclination toward collective to individual. This shows that g^{eff} values in both systems ALB+2-PE and ALB+2-HE increase accordingly in the proportionate concentration of 2-PE and 2-HE. The g^{eff} does not have significant changes as an increase in temperature of pure component, in binary combination its values decrease concerning temperature.

Table 3: Effective Kirkwood correlation factor of ALB+2-PE binary system

Volume fraction of 2-PE	293.15K	303.15K	313.15K
0	0.77	0.74	0.73
0.1	0.88	0.85	0.85
0.2	0.96	0.93	0.92
0.3	0.98	0.96	0.95
0.4	0.98	0.98	0.97
0.5	1.00	0.99	0.98
0.6	1.01	1.01	1.00
0.7	1.04	1.03	1.03
0.8	1.09	1.08	1.07
0.9	1.18	1.17	1.16
1	1.30	1.32	1.31

Table 4: Effective Kirkwood correlation factor of ALB+2-HE binary system

Volume fraction of 2-HE	293.15K	303.15K	313.15K
0	0.77	0.74	0.73
0.1	0.85	0.84	0.83
0.2	0.94	0.93	0.91
0.3	1.02	0.98	0.96
0.4	1.06	1.01	1.01
0.5	1.10	1.05	1.04
0.6	1.13	1.09	1.06
0.7	1.16	1.13	1.10
0.8	1.19	1.17	1.16
0.9	1.29	1.26	1.26
1	1.44	1.43	1.44

The excess static dielectric constant (ε_S^E) of ALB+2-PE and ALB-2-HE are plotted in Fig. 1 and Fig. 2 respectively. Experimental proof of complex formation and strength of attraction of unlike molecules is provided by the non-zero values of ε_S^E of both systems over the whole concentration range [16]. While the negative value of ε_S^E in 2-PE and 2-HE rich region attributes dipole moment per unit volume falls, the positive value of ε_S^E in ALB rich region shows dipole moment per unit volume decreases. The change in the sign of ε_S^E from a positive to negative trend was observed at a higher molecular concentration of 2-HE in ALB+2-HE as compared to 2-PE in the ALB+2-PE system. This may be due to an increase in carbon chain length in 2-HE [9].

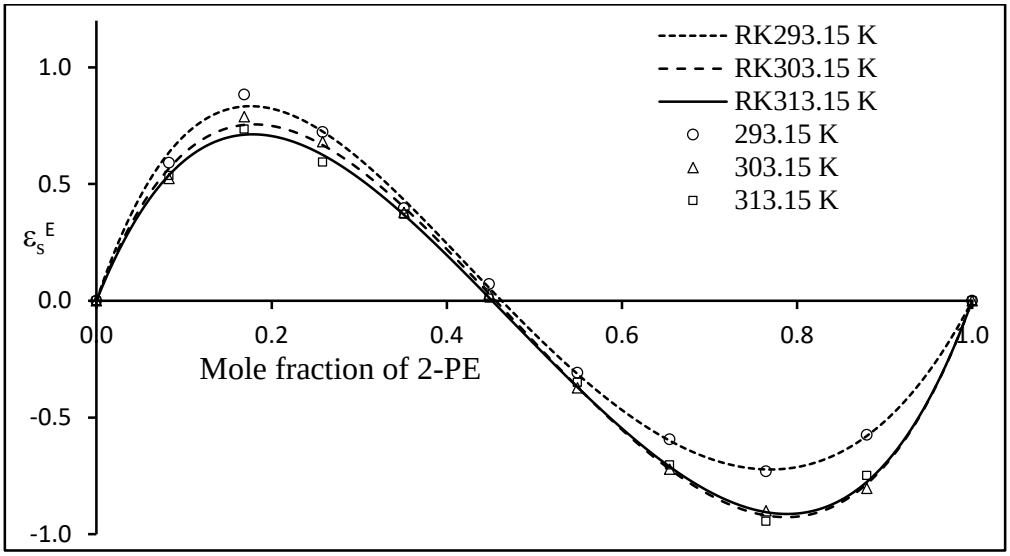

Figure 1: Excess static dielectric constant $(\varepsilon_s^E)$of ALB+2-PE binary system

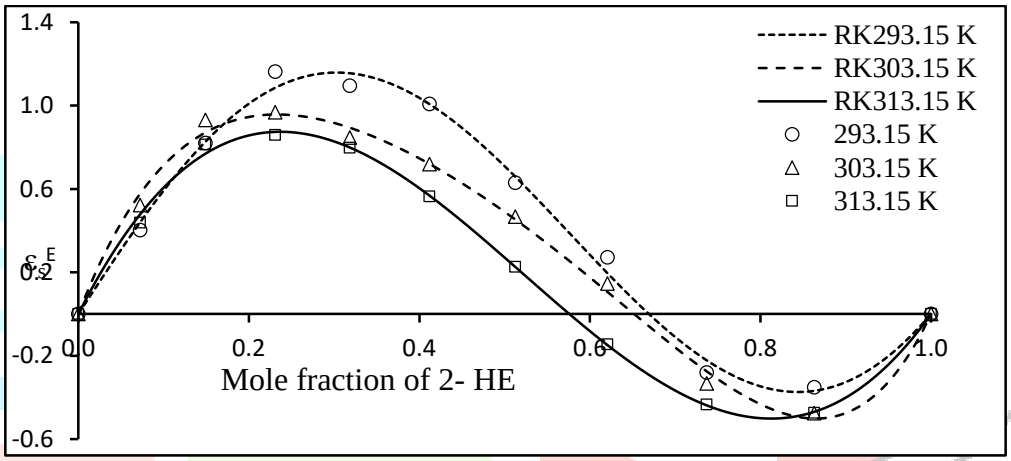

Figure 2: Excess static dielectric constant (ε_s^E) of ALB+2-HE binary system

The excess inverse relaxation time of ALB+2-PE and ALB+2-HE are plotted in Fig. 3 and Fig. 4 respectively. The negative values of excess inverse relaxation time in both systems suggests that the reorientation of dipoles in both systems is hindered by the effective field produced by dipole-dipole interaction between ALB and Ketone (2-PE, 2-HE). A similar interpretation was made by Sivagurunathan et.al [17] when studied the molecular association of alkyl methacrylates and alcohols in a non-polar solvent. From the figure, it is also noticed that the reorientation of dipoles in the ALB+2-HE mixture is more hindered than in the ALB+2-PE mixture. This is due to an increase in carbon chain length in 2-HE than 2-PE.

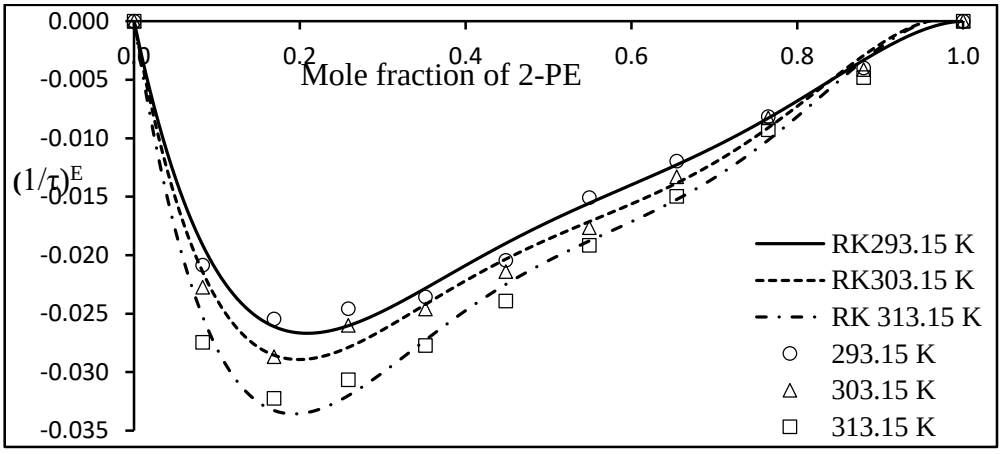

Figure 3: Excess inverse relaxation time$(1/\tau)^E$ of ALB+2-HE binary system

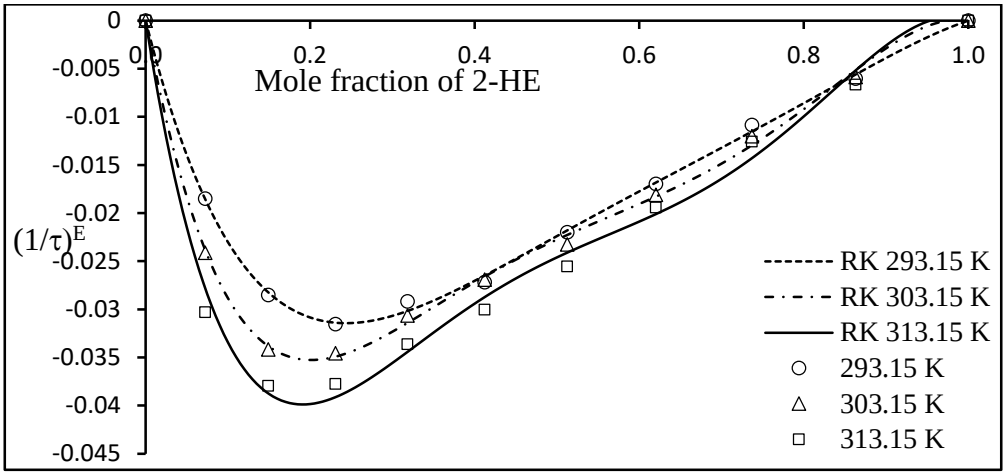

Figure 4: Excess inverse relaxation time$(1/\tau)^E$ of ALB+ 2-HE binary system

The excess static dielectric constant and excess inverse relaxation time fitted to Redlich-Kister equation and determined a_j coefficient and standard deviation for binary mixture are tabulated in table 5.

Table 5: a_j coefficient and standard deviation (σ) of excess parameters

System	parameter	a_0	a_1	a_2	a_3	σ
	293.15K					
ALB+2-PE	ε_s^E	-0.5618	-7.3575	2.5241	-1.7668	0.0295
	$(1/\tau)^E$	-0.0687	0.0679	-0.1000	0.0985	0.0011
ALB+2-HE	ε_s^E	2.8342	-7.9433	-2.1371	2.4459	0.0548
	$(1/\tau)^E$	-0.0896	0.0944	-0.0935	0.0601	0.0006
	303.15K					
ALB+2-PE	ε_s^E	-0.7093	-7.9689	0.4387	-2.0803	0.0252
	$(1/\tau)^E$	-0.0745	0.0628	-0.1073	0.1388	0.0011
ALB+2-HE	ε_s^E	1.9615	-5.8042	-0.9945	-3.8324	0.0455
	$(1/\tau)^E$	-0.0910	0.0785	-0.1332	0.1588	0.0007
	313.15K					
ALB+2-PE	ε_s^E	-0.7408	-7.6416	0.2745	-2.1506	0.0248
	$(1/\tau)^E$	-0.0819	0.0724	-0.1346	0.1660	0.0013
ALB+2-HE	ε_s^E	1.0825	-7.1511	0.0939	0.2451	0.0230
	$(1/\tau)^E$	-0.0985	0.0804	-0.1590	0.2088	0.0016

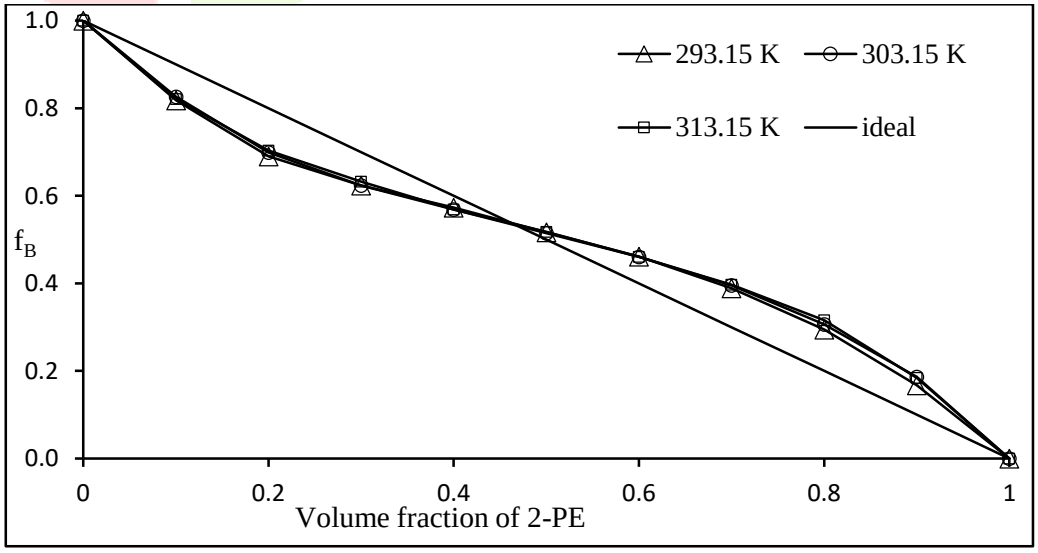

Figure 5: Bruggeman factor (f_B) of ALB+2-PE binary system

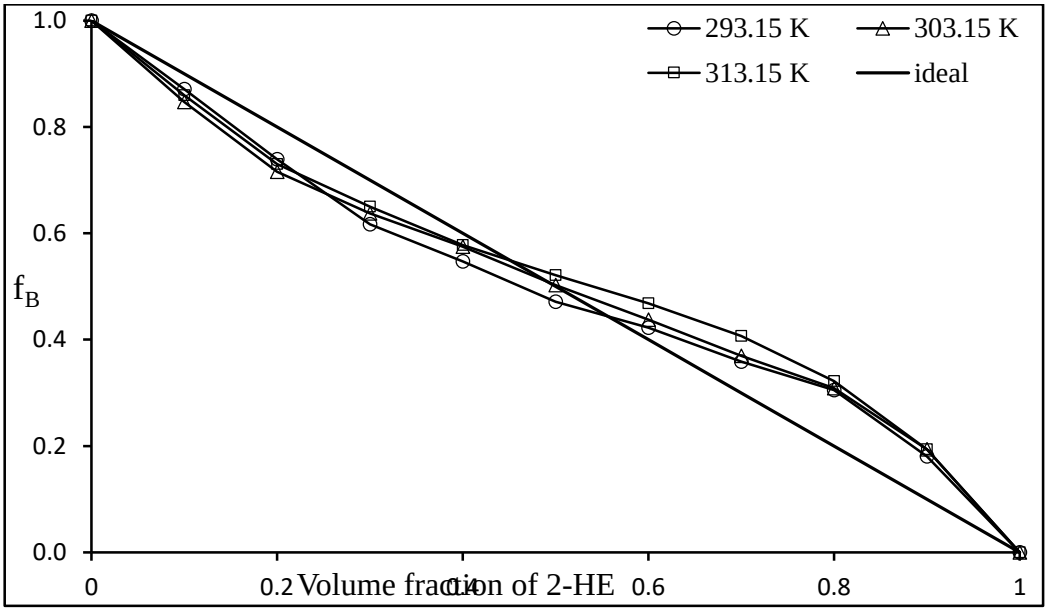

Figure 6: Bruggeman factor (f_B) of ALB+2-HE binary system

The Bruggeman factor of ALB+2-PE and ALB+2-HE systems are plotted in Fig. 5 and Fig.6 respectively. The deviation of the Bruggeman factor from the linear plot indicates that hetero-molecular interaction exists and leads to the formation of the complex. A similar interpretation is reported by s. Kumar et.al [18] for the study of Ketone with 2-Metoxyethanol and 2-butoxyethanol. It is also noticed that volume expansion of binary mixture in ALB rich region and contraction in 2-PE and 2-HE rich region [9, 11].

Conclusion:

The present paper successfully reported a dielectric study of both system ALB+2-PE and ALB +2-HE systems at temperatures 293.15K, 303.15K, and 313.15K in microwave frequency range 10MHz to 10 GHz. In both systems, excess static dielectric constant suggests that ALB and the carbonyl group of 2-PE and 2-HE have opposite tendencies regarding existing dipole moment in binary mixture. The value of the effective Kirkwood correlation factor of pure component supported to above interpretation. The excess inverse relaxation time of both systems shows dipole-dipole interaction between solute and solvent produce field hindered rotations of dipoles. It is also observed that static dielectric constant and relaxation time decreases as temperature increases from 293.15 K to 313.15K. The excess values and effective Kirkwood correlation factor strongly suggest that there are intermolecular interaction takes place between ALB and 2-PE and also in between ALB and 2-HE.

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