STUDY OF EFFECT OF CARBON CHAIN LENGTH OF KETONE ON INTERMOLECULAR INTERACTION BETWEEN ALLYL BROMIDE AND KETONE AT TEMPERATURE 283 ^{0}K

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Abstract: Dielectric measurement on binary mixtures of Allyl bromide (AB) with 2-Butanone (2-BU), 2-Pentanone (2-PE) and 2-Hexanone were studied by using Time Domain Reflectometry Technique in microwave frequency range 10 MHz to 10 GHz at temperature 283 K. The density and refractive index are also measured. We discuss the composition dependent dynamical structures of mixture in terms of Bruggeman factor (f_B), Kirkwood correlation factor, excess dielectric constant(ε_s^E), excess molar volume (V^E) and excess molar refraction (R_m^E). It was found that positive values of ε_s^E , V^E and R_m^E of binary systems in AB rich region and negative in ketone rich region. The study reveals that the tendency of parallel alignment of dipoles increases with increase in carbon chain length of ketone. Bruggeman factor also shows that volume expansion of mixture in AB rich region and contraction in ketone rich region.

Keyword: Static dielectric constant, density, refractive index, Kirkwood correlation factor, Bruggeman factor

I. INTRODUCTION

The study of physical and chemical properties of material in liquid state is a very challenging task as compared to solid and gaseous state. The physical properties such as density and refractive index of pure liquids and there mixtures are helpful to understanding their thermodynamic and transport properties as well as chemical engineering field [1]-[4]. Their excess properties play vital role to access information about interaction between molecules in mixture particularly when polar liquid concerned. The dielectric constant of solvent mixture can be related to drug solubility[5].The study of homologous series useful to insight into the relationship of biological activity and properties with chemical changes (or intermolecular interaction) that only involve number of alkyl group[6],[7]. Dielectric measurements, Kirkwood correlation factor of mixtures are useful to understanding rearrangement of dipoles in presence of external time varying electric field [8]-[11]. Among the polar liquids, Allyl bromide used in synthesis of polymers, pharmaceuticals etc. The properties of ketones determined by carbonyl group and are central importance to organic chemistry and biochemistry. In both class of liquids, spatial correlation between molecules may appear through dipole-dipole interaction. Thus hydrogen bonding is less possible as concern molecular structure of AB and ketones (2-BU, 2-PE and 2-HE).

Few researchers [6], [12]-[14] reported the dielectric study of pure ketone and in binary mixture with other liquids. Dielectric properties of Allyl halide with Dimethylformamide, alcohol [8], [9] and in dilute solution of Benzene [15] in microwave frequency range reported. Density and excess molar volume of ketone with 1-3 Dioxane and1-4 Dioxane [2], Amine and Aniline [3], Diethyl Carbonate are reported [4].

No attempt, so, far seems to have been made to study the physical properties of binary mixtures of AB with ketones (2-BU, 2-PE and 2-HE). In the present paper, dielectric constant, density and refractive index of AB with ketones at temperature 283 K carried out to confirm complex formation through dipole-dipole interactions between AB and ketones. The objective of the present paper is to report the experimental dielectric, density and refractive index for AB+2-BU, AB+2-PE and AB+2-HE mixtures, and determine molecule's structural properties through the experimental data.

II. EXPERIMENTAL SECTION

A. Chemicals

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

B. Experimental method

The Hewlett Packard HP54750A sampling oscilloscope with HP54754A TDR plug-in module has been used for experimental dielectric measurements. The experimental details and data analysis are same as reported earlier [7]-[9], [16],[17].

The density is measured by using simple pycnometer while refractive index is measured by Abbe's refractometer.

III. THEORY

The excess 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 [18] for pure polar liquid is modified for mixture is known as effective Kirkwood correlation factor [19] 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 AB, 2-BU, 2-PE and 2-HE is 1.90, 2.78, 2.70 and 2.66 D [20] used to determine values of Kirkwood correlation factor(g), the values of g is 0.79, 1.28, 1.35 and 1.41 respectively.

The corrective Kirkwood correlation factor is determined by considering effective correlation between dipole contributed in proportion from pure g_A and g_B.

$$\frac{4\pi N}{9kT}\left(\frac{\mu_A^2 \rho_A g_A}{M_A} v_A + \frac{\mu_B^2 \rho_B g_B}{M_B} v_B\right) g_f = \frac{(\varepsilon_{sm} - \varepsilon_{\infty m})(2\varepsilon_{sm} + \varepsilon_{\infty m})}{\varepsilon_{sm}(\varepsilon_{\infty m} + 2)^2} \quad (3)$$

The excess molar volume and excess molar refraction of mixture are determined by using equation (4) and (5) respectively,

$$V^E = \left[\frac{x_A M_A + x_B M_B}{\rho}\right] - \left[\frac{x_A M_A}{\rho_A} + \frac{x_B M_B}{\rho_B}\right] \quad (4)$$

$$R_m^E = R_m - \left(X_A R_m^A + X_B R_m^B\right) \quad (5)$$

The Bruggeman factor (f_B) [21] parameter which may be used as an indicator of solute-solvent interactions and is given by,

$$f_B = \left(\frac{\varepsilon_m - \varepsilon_B}{\varepsilon_A - \varepsilon_B}\right)\left(\frac{\varepsilon_A}{\varepsilon_m}\right)^{(1/3)} = 1 - V \qquad (6)$$

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

IV RESULT AND DISCUSSION

Table 1: Static dielectric constant, density and refractive index of Allyl bromide with ketones system at temperature 283 K

$X_{2\text{-BU}}$	AB+2-BU			$X_{2\text{-PE}}$	AB+2-PE			$X_{2\text{-HE}}$	ALB+2-HE		
	ε_s	ρ (g/cm^3)	n_D		ε_s	ρ (g/cm^3)	n_D		ε_s	ρ (g/cm^3)	n_D
0	7.46	1.4162	1.473	0	7.46	1.416	1.473	0	7.46	1.416	1.473
0.0969	8.91	1.3445	1.461	0.0828	8.83	1.351	1.463	0.0722	8.61	1.354	1.464
0.1945	9.94	1.2737	1.450	0.1688	9.77	1.276	1.452	0.149	9.35	1.276	1.456
0.2927	10.8	1.2067	1.440	0.2582	10.44	1.207	1.444	0.2308	9.87	1.207	1.449
0.3917	11.69	1.1665	1.433	0.3513	10.9	1.166	1.438	0.3183	10.34	1.169	1.443
0.4913	12.66	1.124	1.427	0.4482	11.33	1.130	1.433	0.4119	10.8	1.133	1.438
0.5916	13.69	1.0816	1.422	0.5492	11.78	1.086	1.428	0.5123	11.22	1.091	1.434
0.6926	14.8	1.0414	1.416	0.6546	12.47	1.045	1.422	0.6203	11.70	1.046	1.429
0.7944	15.96	0.9707	1.407	0.7647	13.31	0.983	1.415	0.7369	12.11	0.987	1.422
0.8968	17.35	0.8924	1.396	0.8797	14.55	0.902	1.405	0.8631	13.13	0.905	1.413
1	19.03	0.8164	1.383	1	16.37	0.818	1.393	1	14.76	0.82	1.404

The linear variation of physical parameters with one of mixture constituent indicated ideal mixture of non interacting solute and solvent. From table 1, the non-linear variation of physical parameters (static dielectric constant, density and refractive index) of real mixture under study confirms the dipole-dipole complex formation between AB and ketone (2-Bu, 2-PE and 2-HE). The intermolecular association take place through dipole-dipole interaction between bromine (-Br) group of AB and carbonyl group (C=O) of ketones. Increasing static dielectric constant with mole fraction of ketones indicates that effective dipole moment increases [17]. While it decreases in order AB+2-BU> AB+2-PE>AB+2-HE, it indicates effective dipole moment decreases with carbon chain length of ketone in mixture and is an expected in view of static dielectric constant depends some extent on carbon chain length[10]. The density and refractive index are decreases with increase in mole fraction of ketones ($X_{2\text{-BU}}$, $X_{2\text{-PE}}$ &$X_{2\text{-HE}}$). It is also noticed that density increase along with decrease in refractive index wisth increase in carbon chain length of ketones in mixture.

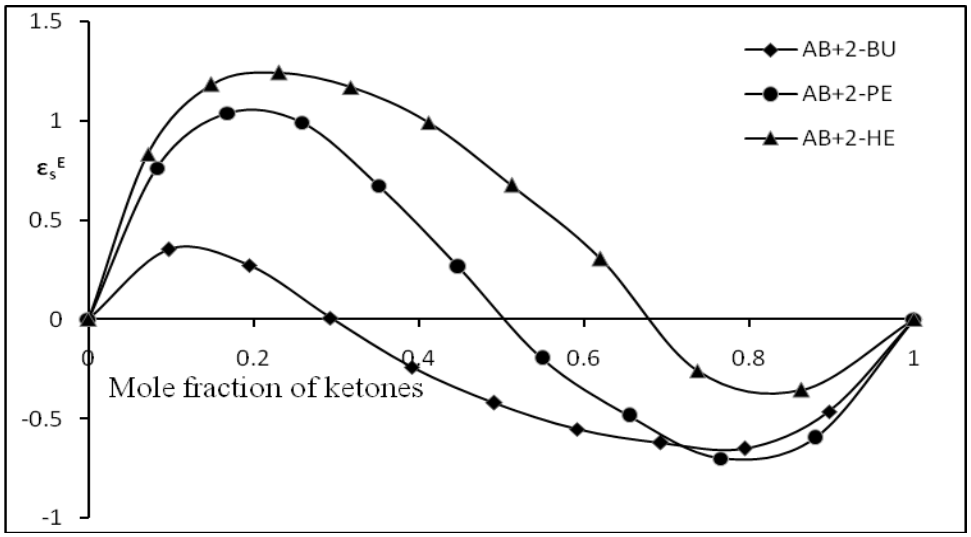

Fig. 1: Plot of ε_s^E against mole fraction of ketones (2-BU, 2-PE, 2-HE) at temperature 283 K

The positive values of ε_s^E (Figure 1) in AB rich region indicates dipole moment per unit volume increases with parallel alignment of dipoles which contribute to increases in dielectric polarization while negative values in ketone rich region indicates dipole moment per unit volume decreases with antiparallel alignment which contribute to decreases in dielectric polarization[10],[17]. The magnitude ε_s^E increases in order of AB+2-HE > AB+2-PE > AB+2-BU. The positive to negative intercept of ε_s^E shifted to higher mole fraction of ketones in mixture from AB+2-BU to AB+2-HE. This indicates tendency of parallel alignment of dipoles increases from AB+2-BU to AB+2-HE. This is confirmed by effective Kirkwood correlation factor which gives type of orientation of dipoles in mixture.

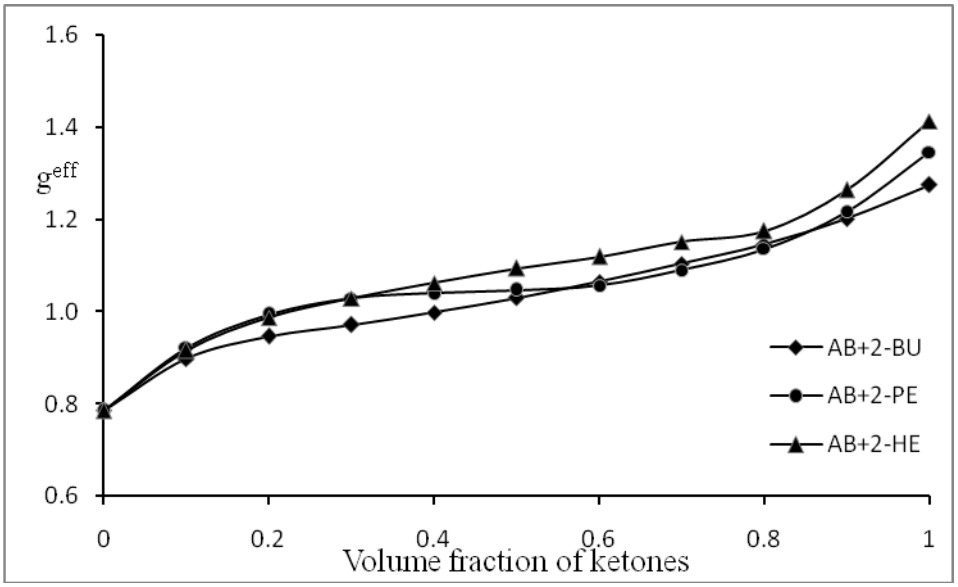

Fig. 2: Plot of g^{eff} against volume fraction of ketones(2-BU, 2-PE, 2-HE) at temperature 283 K

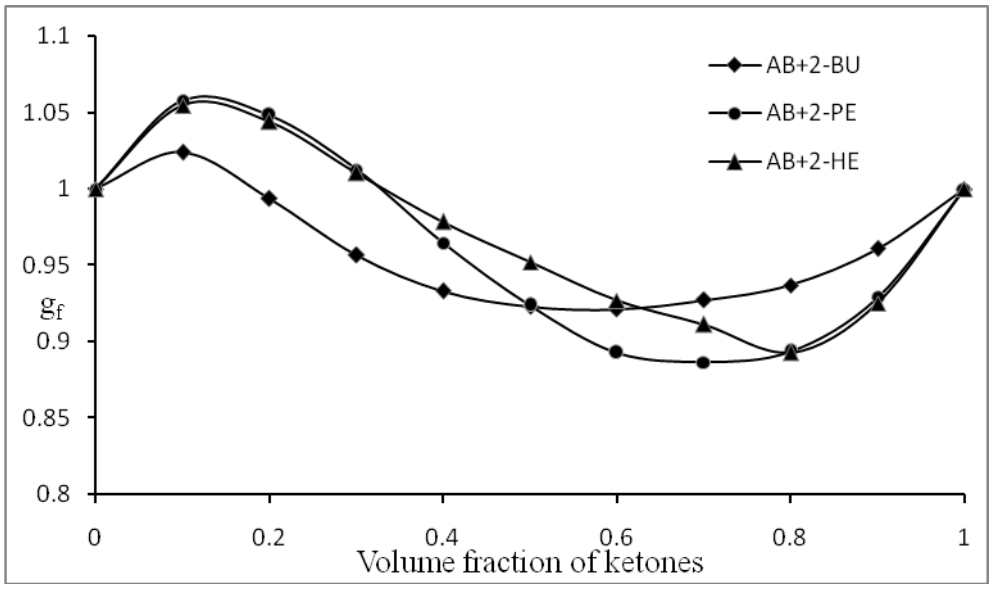

Fig. 3: Plot of g_f against volume fraction of ketones(2-BU, 2-PE, 2-HE) at temperature 283 K

The g values of AB are less than unity indicates dipoles have tendency in antiparallel alignment while greater than unity in ketone indicates dipole have tendency in parallel orientation of dipole [18]. When these two opposite behaviour liquids mixed, effective Kirkwood correlation factor increases from g value of AB to g values of ketones as shown in Figure 2. This indicates correlation between neighbouring dipoles increases with parallel orientation of alignment.

The deviation of corrective Kirkwood correlation factor (g_f) from unity (g_f =1 for ideal mixture) indicate interaction between solute and solvent. The deviation of g_f from unity in Figure 3 indicates that change in dipolar orientation due to change in dipole-dipole interaction [11], [22]. For three system AB+2-BU, AB+2-PE and AB+2-HE values of g_f greater than unity in AB rich region mainly contributed from change in dipole ordering of AB due to self associated ketones (g>1 for 2-BU, 2-PE and 2-HE) structure. The values of g_f less than unity in ketone rich region mainly arises from change in dipole ordering of ketone due to non-self associated AB structure(g<1).

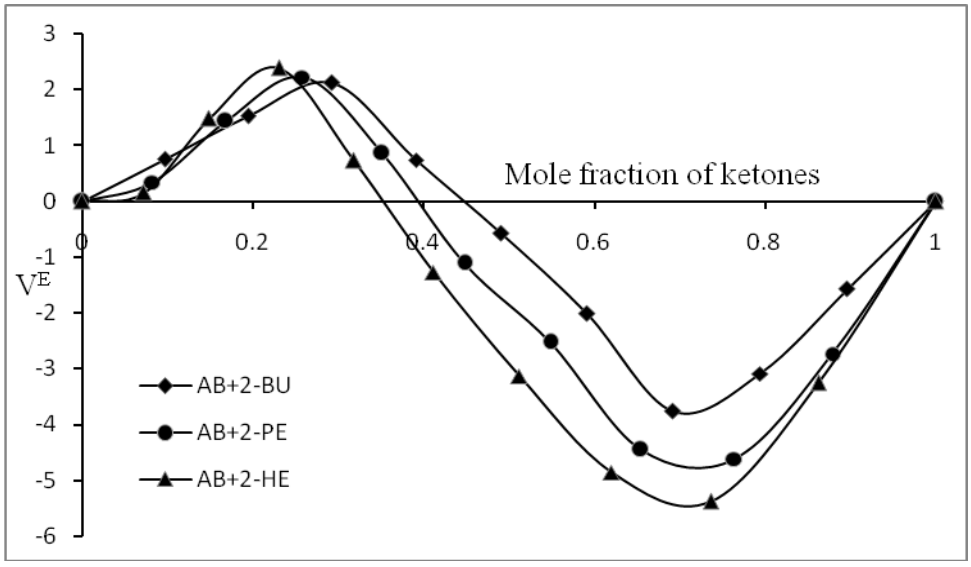

Fig. 4: Plot of V^E against mole fraction of ketones(2-BU, 2-PE, 2-HE) at temperature 283 K

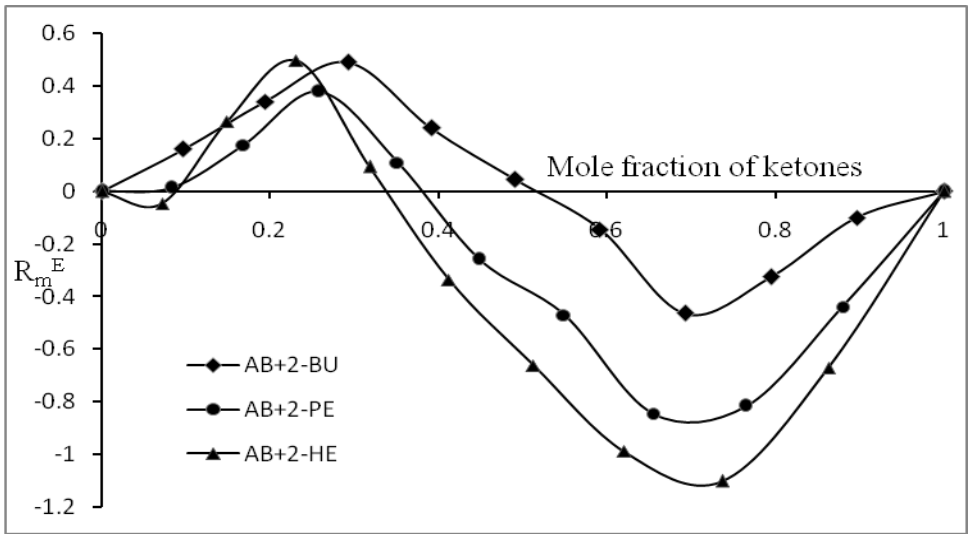

Fig. 5: Plot of R_m^E against mole fraction of ketones (2-BU, 2-PE, 2-HE) at temperature 283 K

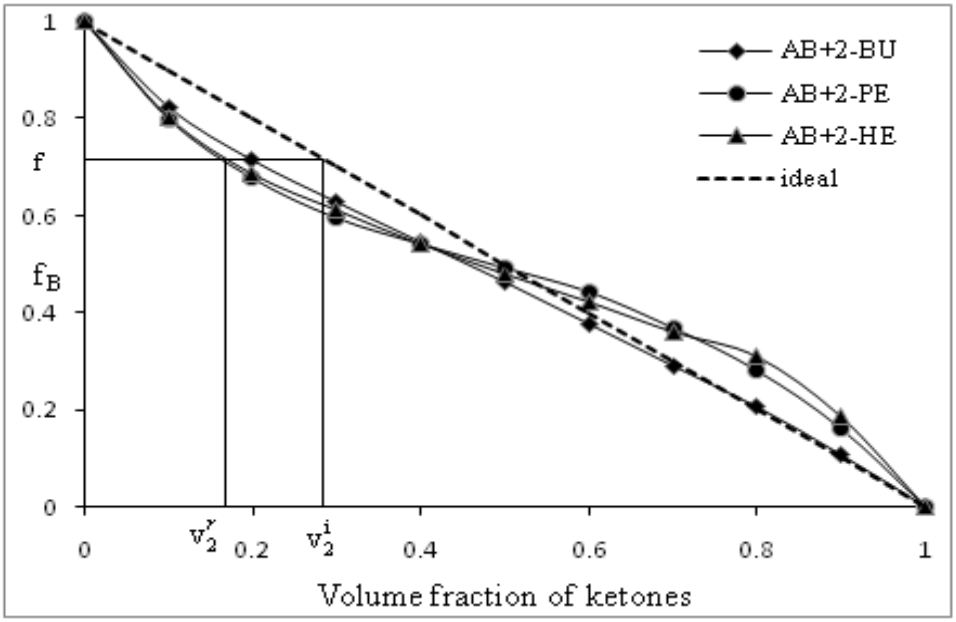

Fig. 6: Plot of f_B against volume fraction of ketones(2-BU, 2-PE, 2-HE) at temperature 283 K

The plots of V^E and R_m^E of AB+2-BU, AB+2-PE, AB+2-HE binary mixtures are–shown in figures 4 and 5 respectively. The positive values of V^E and R_m^E in AB rich indicates weak intermolecular interaction between solute and solvent while negative values in ketones rich region indicates strong intermolecular interaction[1],[2],[17]. The magnitude of negative values of V^E and R_m^E is increases in order AB+2-BU<AB+2-PE<AB+2-HE. This indicates strength of intermolecular interaction increases with increases in carbon chain length of ketones.

Many researchers [16], [17], [22], [23] reported Bruggeman factor (f_B), deviation of f_B from ideal line indicates intermolecular interaction take place during complex formation between solute and solvent. Bruggeman factor not only indicates presence or absence of intermolecular interaction between solute and solvent, but also useful to access the modified volume of mixture due to intermolecular interaction.

Figure 6 illustrates 'f_B' of AB+2-BU, AB+2-PE and AB+2-HE with volume fraction of ketones. From Figure 6 if 'f' is Bruggeman factor for particular mixture, if mixture of AB and ketones acts as an ideal behaviour then it is corresponding to v_2^i volume fraction of ketones.

$$v_2^i = \frac{v_1}{v_1 + v_2}$$

But real mixture shows that, 'f' is corresponding to v_2^r.

$$v_2^r = \frac{v_1}{v_1 + v_2}$$

Thus from Figure 6,

$$v_2^r < v_2^i \qquad (7)$$

Any particular mixture added volume of two liquid (v_1 and v_2) are constant. So above equation (7) is satisfied only when resultant volume ($v^r = v_1 + v_2$) of mixture increases. This suggests that volume expansion take place in mixture due to intermolecular interaction between AB and ketones. This is supported by trend of V^E as shown in Figure 4. Thus, there is volume expansion of mixture in AB rich region and contraction in ketone rich region.

V. Conclusion

This paper reported the static dielectric constant, density, and refractive index of AB with 2-BU, 2-PE and 2-HE binary mixture at temperature 283 K. The excess plot of dielectric constant, molar volume and molar refraction indicates dipole-dipole interaction between bromine group of AB and carbonyl group of ketone. The Kirkwood correlation factor indicates that there is change in dipolar ordering in mixture with change in concentration of ketones in mixture. The Bruggeman factor indicates volume modification take place due to intermolecular interaction.

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References:

[1] M. Gupta, I. Vibhu, J. P. Shukla," Refractive index, molar refraction deviation and excess molar volume of binary mixtures of 1,4-dioxane with carboxylic acids" *Phy. Chem. Liq.* Vol. 48 pp.415-427, 2010.

[2] M. Nath Roy, B. Sinha and V. Kumar Dakua, "Excess Molar Volumes and Viscosity Deviations of Binary Liquid Mixtures of 1,3-Dioxolane and 1,4-Dioxane with Butyl Acetate, Butyric Acid, Butylamine, and 2-Butanone at 298.15 K" *J. Chem. Eng. Data*, vol. 51, pp.590-594, 2006

[3] Alonso, I. Mozo, I. G. De La Fuente, J. A. Gonzalez and J. C. Cobos, "Thermodynamics of ketone+amine mixtures 7. Volumetric and speed of sound data at (293.15, 298.15 and 303.15) K for 2-pentanone+aniline, +N-methylaniline, or +pyridine systems " *J. Mol. Liq.*vol. 160,pp.180-186, 2011.

[4] Fabio-Comelli and Romolo Francesconi, "Densities and Excess Molar Volumes of Binary Mixtures Containing Diethyl Carbonate + Linear or Cyclic Ketones at 298.15 K " *J. Chem. Eng. Data* vol. 40, pp. 25-27, 1995.

[5] A. Martin, P. Bustmante and A. H. C. Chun, Physical Pharmacy 4th ed. B. I. Waverty, Pvt. Ltd. New Delhi, 1993.

[6] V. Madhurima, B. Viswanathan and V. R. K. Murthy, "Effect of steric hindrance of ketones in the dielectric relaxation of methanol +ketone systems "*Phys. Chem. Liq.*vol. 44, pp.563-569, 2006.

[7] P. Sivagrunathan, K. Dharmalingam, K. Ramchandran, P. B. Undre, P. W. Khirade and S. C. Mehrotra, "Dielectric relaxation study of mixtures of alkyl methacrylates and 1-alcohols using time-domain reflectometry" *Phil. Mag. Lett*. Vol. 86,pp.291-300, 2006.

[8] G. M. Dharne, A. P. Maharolkar, S. S. Patil, P. W. Khirade and S. C. Mehrotra. "Study Of Solute Solvent Interaction Through Dielectric Properties Of Allyl Chloride With Dimethyl Formamide Using Time Domain Reflectometry Technique. " *International J. Pharma and Bio Sciences* vol. 1, pp.1-9, 2010.

[9] Y. S. Sudake, S. P. Kamble A. P. Maharolkar, S. S. Patil, P. W. Khirade and S. C. Mehrotra, "Dielectric Study of Allyl Chloride with 2-Pentanone and 2-Hexanopne in microwave frequency range" *Bull. of the Korean Chem. Society*, vol. 33(10),pp.3423-3426,2012.

[10] R. J. Sengwa, S. Sonkhla and V. Khatri, "Dielectric characterization and molecular interaction behaviour in binary mixtures of amides with dimethylsulphoxide and 1,4-dioxane " *J. Mol. Liq.* Vol. 151, pp. 17-22, 2010.

[11] R.J. Sengwa, S. Sankhla and V. Khatri, "Static dielectric constants of the binary mixtures of N-methylformamide with water, ethyl alcohol, ethylene glycol, dimethylsulphoxide, acetone and 1,4-dioxane" *Phil. Mag. Lett*. Vol. 90, pp.463-470, 2010.

[12] Buta singh, "Dielectric relaxation of some Aliphatic Ketones in dilute solution" *Bull. Chem. Soc. Japan* vol. 57, pp. 2337-2338, 1984

[13] John Crossley, "Dielectric Relaxation and Intramolecular Rotation in Aliphatic Ketones" *Can. J. Chem.* Vol. 51, pp.2671-2675, 1973.
[14] R. Ghosh and R. K. Datta, "Relaxation Times and Free Energies of Activation of Some Ketone Molecules in the Ultrahigh Frequency Region"*J. Phys. Soc. Japan* vol. 51,pp.1449-1452, 1982.
[15] M. Jeyaraj and J. Sobhanadri, "Dielectric relaxation studies IV-allyl bromide and allyl ethers in dilute solutions"*J. Phys D: Appl. Phys*.vol. 13, pp.1925-1931, 1980.
[16] S. B. Sayyad, P. B. Undre, P. Yannewar, S. S. Patil, P. W. Khirade and S. C. Mehrotra, "Investigations Of Intermolecular Interactions Between 2-Methoxyethanol And Nitrobenzene Through Dielectric Relaxation Study " *Lith. J. Phys*.vol. 51, pp. 29-37, 2011.
[17] Y. S. Sudake, S. P. Kamble, S. S. Patil, P. W. Khirade and S. C. Mehrotra, "Study of Dynamics of Allyl Chloride-2-Butanone Binary System Using Time Domain Reflectometry, "*J. Korean Chem.. Society* vol. 56, pp.20-27, 2012.
[18] G. Oster and J. G. Kirkwood, "The Influence of Hindered Molecular Rotation on the Dielectric Constants of water, Alcohols and other Polar Liquids " *J. Chem. Phys*. vol.11pp.175. 1943.
[19] A.C. Kumbharkhane, S.M. Puranik and S. C. Mehrotra, "Dielectric relaxation studies of aqueous N,N-dimethylformamide using a picosecond time domain technique" *J. Sol. Chem.* 22, pp. 219-229, 1993.
[20] Lide, David R; CRC Handbook of Chemistry and Physics 87th Edition 2006-07.
[21] D. A. G. Bruggeman, *Ann. Phys. (Leopz)* 5, pp. 636-664, 1935.
[22] G. Parthipan and T. Thenappan, "Dielectric and thermodynamic behaviour of binary mixtures of anisole with *o*-chlorophenol and with *o*-cresol" *Phil. Mag. Lett*. 89, pp.282-293, 2009.
[23] S. P. Kamble, Y. S. Sudake, S. S. Patil, P. W. Khirade and S. C. Mehrotra, "Interaction of Cyclohexane-Methyl Acetate Binary System through Dielectric Properties at Different Temperatures," *J. Korean Chem. Society* 55, p.373-378, 2011.