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Study the dielectric behavior of Allyl Bromide with Acetone using Time Domain Reflectometry Technique

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ABSTRACT

Dielectric measurement of Allyl Bromide (ALB), Acetone (ACE) and their binary mixtures were carried out using time domain reflectometry technique in frequency range 10MHz to 10 GHz at four temperatures 283.15 K, 293.15 K, 303.15 K and 313.15 K. Values of density (ρ) and refractive index (n_D) of same system have also measured. Kirkwood factors are used to extract the information about the dipoles orientation in mixtures. Bruggeman factor, excess dielectric constant, excess inverse relaxation time, excess molar volume and excess molar refraction are also determined to study the intermolecular interaction. The excess parameters are fitted to Redlich-Kister equation.

Keywords: Dielectric relaxation, Time domain reflectometry, Kirkwood correlation factor, Bruggeman factor.

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INTRODUCTION

Dielectric relaxation studies on the binary mixtures (both polar–polar and polar–nonpolar) are important to extract the information regarding intermolecular interaction in the mixtures due to the dipole–dipole interactions and hydrogen bonding. In earlier, we reported the dielectric properties of Allyl Chloride with ketones at different temperature [1-3]. In this paper, we study the dielectric properties of Allyl Bromide (ALB) with Acetone. Density and Refractive index are fundamental properties which can be used to extract information about molecular interaction in binary liquids through excess molar volume and excess molar refraction respectively. Acetone is used as a polar aprotic solvent in variety of organic reactions, polymer, pharmaceutical industry and also used as cleaning agent. It contains in human body as one part of Ketone bodies [4].

ALB is an organic halide and alkylating agent, which is used in synthesis of polymers, pharmaceuticals, allyls and other organic compounds. It has wide applications in pharmaceutical medicine [5] such as Nalorphine, Nalline, Lathidrone norfin and Narcan etc.

M. Jeyaraj et al. [6] reported dielectric relaxation process of ALB and Ether in dilute solution of Benzene. The presence of double bond in ALB prevents the possibility of internal molecular modes of reorientation and molecule is relaxed in the way expected as rigid molecule. A. V. Celiano et al. [7] reported the dielectric constant of ACE with Ethanol; p-Dioxin at temperature 298 K. Sheo Prakash et al. [8] reported density, viscosity and sound velocity of mixture of Ketone with o-chlorophenol at temperature 298 K. The negative excess volume and deviation in isentropic compressibility of Ketone with o-chlorophenol indicates that the association between unlike molecules predominates over dissociation of o-chlorophenol aggregates.

Substantial works have been done on dielectric properties of ALB and ACE as individual systems. However, no work has been reported on the mixtures of ALB and ACE. Considering these facts the study of dielectric relaxation and thermodynamic properties of binary mixtures of ALB and ACE has been undertaken.

EXPERIMENTAL

Chemicals

The chemicals used in the present work are ALB and ACE of AR grade and are used without further purification. The solutions were prepared at eleven different volume percentages by adding ACE in 10 ml of ALB starting from 0% to 100% in steps of 10%, with accuracy ±0.0006ml

Experimental Section

The Hewlett Packard HP54750A sampling oscilloscope with HP54754A TDR plug-in module has been used. After observing TDR response for sample under study, the time window was kept to 5 ns and the SMA (standard military applications) sample cell with 1.35 mm effective pin length has been used. The sample cell holds the liquid under consideration. The physical dimensions of the sample cell are very important, so one must be careful while designing the sample cell. The impedance of the cell should be matched with coaxial transmission line to which cell is connected. If there is impedance mismatch then unwanted reflections may disturb the wave, thereby causing some errors in the measurements. The proper design of cell includes the inner conductor and outer conductor diameters. The length of the inner conductor is called as 'pin length' of the cell which is very important factor in analysis. The sample length must be enough to avoid unwanted reflections. In total reflection method, the sample length must be long enough to produce an adequate difference signal but short enough to keep less complication of resonance effects at frequencies above the range of interest. The characteristics impedance of a coaxial line is given by

$$Z = \frac{138.2}{\sqrt{\varepsilon}} \log_{10} \frac{b}{a} \qquad (1)$$

This impedance for our transmission line is frequently 50 Ω. Here 'a' is the diameter of inner conductor and 'b' is the inner diameter of outer conductor, ε is the relative permittivity of the dielectric

between the conductors. Using Teflon, air and taking appropriate 'a' and 'b', a cell can be designed to have a matching impedance of Z = 50 Ω (for air " = 1 and for Teflon " = 2.2). The SMA type cell has b = 3.5 mm. The inner conductor of SMA connector itself is considered as 'inner conductor' and hex-nut acts as an outer conductor. Since these SMA connectors have already been designed for precise impedance 50 Ω, a special design when used with high frequency is not required. The physical length of inner conductor can be changed. When cell is filled with sample above the physical length of inner conductor, the fringing effect [09, 10] takes place. Due to the fringing field the effective pin length [11] will not be equal to physical pin length. The effective electrical pin length will be more than the physical pin length. The accurate determination of effective pin length 'd' is very important for the accurate evaluation of dielectric parameters. It is found that for SMA type cell, effective pin length [11] is greater than actual physical length by 0.1–0.2 mm.

To reduce noise, time dependent response curve was averaged over 64 measurements taken and then stored in TDR oscilloscope memory with 1024 points per waveform. Firstly, the response waveform for empty cell is acquired and stored in memory, and then secondly, the response waveform for sample is acquired and stored in other memory. The empty cell waveform is used as reference waveform. Both the response waveforms are the reflected waveforms from the sample cell with open termination transmission line. The data acquisition is carried out for 11 concentrations at 283.15, 293.15, 303.15, and 313.15 K. The temperature of sample was maintained at desired value, within accuracy limit of $\pm 1^0$C, by circulating constant temperature water through heat insulating jacket surrounding sample cell.

At each time the response waveforms without sample and with sample were recorded. The time dependent response waveform without sample is referred to as $R_1(t)$ and with sample referred as $R_x(t)$.

Density of pure liquids and their binary mixtures were measured by using Pycnometer at temperatures 283.15 K, 293.15 K, 303.15 K and 313.15 K. The precision of density is 0.0001 gm/cm^3.

Refractive index was measured at sodium D line by using thermostatic Abbe's refractometer. The precision of the refractive index is 0.001 units. Constant temperature was maintained for density and refractive index measurement within the accuracy of $\pm 1^0$C.

Data analysis

The time dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ over a frequency range of 10 MHz to 10 GHz by using Fourier transform [12, 13]

$$\rho^*(\omega) = \left[\frac{c}{j\omega d}\right]\left[\frac{p(\omega)}{q(\omega)}\right] \tag{1}$$

where $p(\omega)$ and $q(\omega)$ are Fourier transforms of $[R_1(t)-R_x(t)]$ and $[R_1(t)+R_x(t)]$ respectively, c is the speed of light, ω is the angular frequency, d is effective pin length and $j=\sqrt{-1}$.

The complex permittivity spectra $\varepsilon^*(\omega)$ is obtained from reflection coefficient spectra $p^*(\omega)$ by applying a bilinear calibration method [14]. The complex permittivity spectra are fitted by the nonlinear least squares fit method to the Debye equation [15] to obtain various dielectric parameters.

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau} \tag{2}$$

Where, ε_s is the static permittivity, $\varepsilon_\infty = n_D{}^2$ is the high frequency limiting permittivity, ω is the angular frequency and τ is the relaxation time of the system.

THEORY

The excess permittivity ε_s^E of system can be defined as

$$\varepsilon_s{}^E = (\varepsilon_s)_m - [(\varepsilon_s)_A X_A + (\varepsilon_s)_B X_B] \tag{3}$$

Where, X– is mole fraction and suffices m, A, B represents mixture, ALB and ACE respectively

The excess inverse relaxation time of system is defined as

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_A X_A + (1/\tau)_B X_B] \tag{4}$$

Where, $(1/\tau)^E$ is the excess inverse relaxation time which represents the average broadening of dielectric spectra. The inverse relaxation time is analogy taken from spectral broadening in resonant spectroscopy [16].

Excess molar volume is determined by the following equation [17]

$$V^E = \left[\frac{X_A M_A + X_B M_B}{\rho}\right] - \left[\frac{X_A M_A}{\rho_A} + \frac{X_B M_B}{\rho_B}\right] \tag{5}$$

where, ρ is the density of the mixture, X_A, X_B, M_A, M_B and ρ_A and ρ_B are the mole fraction, molar mass and the density of pure ALB and ACE in composition respectively.

We have also investigated the molar refraction R_m defined by Lorentz-Lorentz [17] equation

$$R_m = \frac{n_D^2 - 1}{n_D^2 + 1} V_m \tag{6}$$

Where, V_m is the molar volume of liquids, n_D is refractive index of liquids.

Excess molar refraction is also important parameter for study the intermolecular interaction. It is determined by using equation

$$R_m^E = R_m - (X_A R^A{}_m + X_B R^B{}_m) \tag{7}$$

Where, $R^A{}_m$ and $R^B{}_m$ are molar refraction of the pure ALB and ACE respectively.

The excess or deviation properties were fitted to the Redlich-Kister equation [18] given by

$$Y^E = X(1 - X) \sum_{j=0}^{3} a_j (2X - 1)^j \tag{8}$$

and the standard deviation is obtained by the expression

$$\sigma = \sqrt{\frac{[\sum V^E{}_{cal} - V^E{}_{expt}]^2}{(n-1)}} \tag{9}$$

Where Y^E refers to be an excess or deviation parameter (ε_s^E , $\left(\frac{1}{\tau}\right)^E$, V^E and $R_m{}^E$) for binary mixture and X is mole fraction of ACE, (1-X) is the mole fraction of ALB, a_j represent the adjustable coefficients and n is the experimental data points.

The effective Kirkwood correlation factor [19, 20] is one of the important parameter for getting information regarding orientation of electric dipoles in liquids complex. The effective Kirkwood correlation factor for mixture is determined by equation

$$\frac{4\pi N}{9KT}\left[\frac{\mu^2_A \rho_A \varphi_A}{M_A} + \frac{\mu^2_B \rho_B \varphi_B}{M_B}\right] g^{eff} = \frac{(\varepsilon_{sm}-\varepsilon_{\infty m})(2\varepsilon_{sm}-\varepsilon_{\infty m})}{\varepsilon_{sm}(\varepsilon_{\infty m}+2)^2} \qquad (10)$$

Where, g^{eff} is the effective Kirkwood correlation factor for a binary mixture. M_A, Φ_A and M_B, Φ_B are molecular weight and volume fraction of liquid A and B, respectively, μ_A, ρ_A, and μ_B, ρ_B are dipole moment in gas phase and density of liquid A and liquid B respectively. ε_{sm} is static permittivity, K is Boltzmann constant and N is Avogadro's number, $\varepsilon_{\infty m}$ is high frequency limiting permittivity of mixture at optical frequency .

The effective volume of solute gets modified by solute–solvent interaction and is best illustrated by nonlinearity of Bruggeman equation.

$$f_B = \left(\frac{\varepsilon_m - \varepsilon_B}{\varepsilon_A - \varepsilon_B}\right)\left(\frac{\varepsilon_A}{\varepsilon_m}\right)^{(1/3)} = 1 - V \qquad (11)$$

Where, f_B-Bruggeman factor, V is Volume fraction of ACE, which is a qualitative measure of volume of the solute in the mixture. ε_m, ε_A and ε_B are the values of static dielectric constant of mixture, ALB and ACE respectively.

Thermodynamical energy parameters such as enthalpy, entropy are calculated by using Eyring equation [21] as

$$\tau = \frac{h}{KT}e^{\left(\frac{\Delta F_\tau}{RT}\right)} \qquad (12)$$

$$\Delta F_\tau = \Delta H_\tau - T\Delta S_\tau \qquad (13)$$

Where, τ is relaxation time, ΔH_τ is enthalpy; Δs_τ is entropy.

RESULT AND DISCUSSION

The physical parameters of pure liquids are reported in table 1 along with available literature values. It can be seen from table, the values determined from the method are in good agreement with the available literature values.

Table1: Physical parameters of ACE and ALB at 293.15 K and 303.15 K

Liquids	Temp	ε_s		ρ (gm/cm^3)		n_D	
		lit	Expt.	Lit	Expt.	lit	Expt.
ACE	293.15K	21.01[a]	20.73	0.7937[b]	0.7914	1.359[b]	1.358
						1.3540[c]	
	303.15K	-	19.66	0.7824[d]	0.7799	-	1.353
				0.77876[e]			
ALB	293.15K	7[a]	7.14	-	1.398	-	1.467
	303.15K	-	6.74	-	1.3813	-	1.46

[a]CRC handbook 87 ed., [b]Kurtz(1965), [c]J.Rheims(1997),[d]Pragati Jain(2004), [e]Liang-unLee(1997)

ε_s –static dielectric constant, ρ –density, n_D-refractive index

The values of the static dielectric constant and relaxation time of the binary mixtures are given in table 2. From the Tables 2, it can be seen that values of static dielectric constant of mixtures increases with increase of ACE concentration in the mixture. Values of density and refractive index of mixtures are reported in

table 3 and they vary in opposite trend. The variations with respect to temperature in these parameters have also got usual trend, i.e. static permittivity, relaxation time, density and refractive index all parameters decrease with increase of temperature.

Table 2: Dielectric constant and Relaxation time of ALB with ACE

Mole fraction of ACE	283.15 K		293.15 K		303.15 K		313.15 K	
	ε_s	τ (ps)	ε_s	τ (ps)	ε_s	τ (ps)	ε_s	τ (ps)
0	7.46	13.70	7.14	13.20	6.74	12.24	6.54	11.39
0.1158	9.80	15.13	9.26	14.64	8.57	13.64	8.32	12.77
0.2277	11.25	16.67	10.89	16.06	10.10	15.03	9.78	14.14
0.3357	12.38	18.18	11.89	17.51	11.24	16.39	10.67	15.45
0.4401	13.15	19.71	12.70	18.81	12.06	17.68	10.96	16.62
0.5411	13.95	21.05	13.26	20.10	12.73	18.90	11.40	17.85
0.6388	14.78	22.36	13.99	21.34	13.23	20.11	12.00	19.20
0.7334	15.79	23.56	15.12	22.91	14.13	21.51	13.06	20.35
0.8251	17.16	25.26	16.61	24.83	15.45	23.22	14.70	22.08
0.9139	19.06	29.28	18.57	28.22	17.21	26.14	16.55	24.62
1	21.12	35.15	20.73	33.64	19.66	31.29	18.80	29.22

ε_s −static dielectric constant, τ -relaxation time, ps- picosecond

Table3: Density and Refractive index of ALB with ACE

Mole fraction of ACE	283.15 K		293.15 K		303.15 K		313.15 K	
	ρ (gm/cm^3)	n_D	ρ (gm/cm^3)	n_D	ρ (gm/cm^3)	n_D	ρ (gm/cm^3)	n_D
0	1.4162	1.473	1.3980	1.467	1.3813	1.460	1.3645	1.455
0.1158	1.3387	1.459	1.3201	1.453	1.3043	1.446	1.2888	1.440
0.2277	1.2565	1.445	1.2399	1.439	1.2237	1.432	1.2093	1.426
0.3357	1.2073	1.432	1.1914	1.426	1.1766	1.420	1.1623	1.414
0.4401	1.1655	1.424	1.1496	1.418	1.1344	1.412	1.1201	1.406
0.5411	1.1291	1.418	1.1143	1.412	1.0994	1.406	1.0853	1.400
0.6388	1.0858	1.411	1.0707	1.405	1.0558	1.399	1.0426	1.393
0.7334	1.0344	1.403	1.0210	1.397	1.0071	1.391	0.9940	1.386
0.8251	0.9843	1.391	0.9716	1.385	0.9581	1.380	0.9453	1.374
0.9139	0.9194	1.378	0.9065	1.372	0.8941	1.367	0.8817	1.361
1	0.8031	1.363	0.7913	1.358	0.7799	1.353	0.7688	1.348

ρ -density, n_D-refractive index

The dipole moments of ALB and ACE in gas phase are 1.90D [22] and 2.88D respectively. Using these values of dipole moments, the values of the Kirkwood factors are 0.78 and 1.12 respectively. It indicates that the dipoles in ALB have tendency to be in antiparallel, whereas dipoles have tendency to remain parallel in pure ACE. As these molecules are not hydrogen bonded liquids, the tendency will be due to dipole-dipole interaction. The excess properties can provide information regarding change in these opposite tendencies in mixtures.

The excess dielectric constant values and excess inverse relaxation time as function of mole fraction of ACE is shown in figure 1 and figure 2 respectively. Figure 1 shows that, the positive dielectric constant in ALB rich region due to the interaction of ACE molecule with ALB is such that the antiparallel tendency of ALB gets reduced. In ACE rich region, the interaction between ACE and ALB is such that the dipoles of ACE have

tendency to be less parallel so excess dielectric constant becomes negative. It is interesting to see the different behavior at both end of the concentrations. From figure 2, the negative excess inverse relaxation in ALB rich region, this indicates that addition of ACE in ALB has created hindered field such that effective dipole rotate slowly. Whereas positive excess inverse relaxation time, it indicates that molecular interaction produce field such that effective dipole rotate faster, i.e. the field cooperates in the rotation of dipoles. Similar results are discussed by V. A Rana et al. [23] for 1-propanol with aniline, 2-Chloroaniline and 3-Chloroaniline.
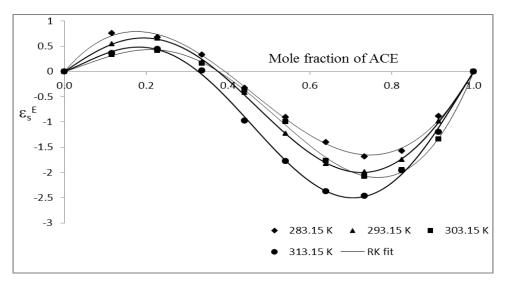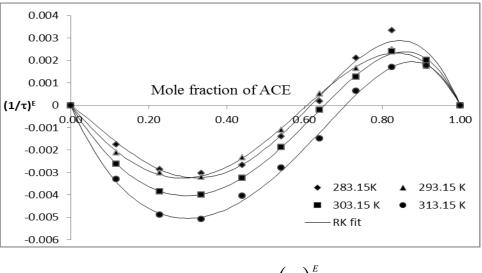

Figure 1: Excess dielectric constant (ε_s^E) of ALB with ACE.
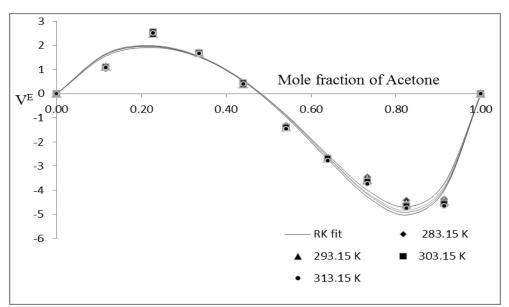

Figure2: Excess inverse relaxation time ($\left(\frac{1}{\tau}\right)^E$ of ALB with ACE

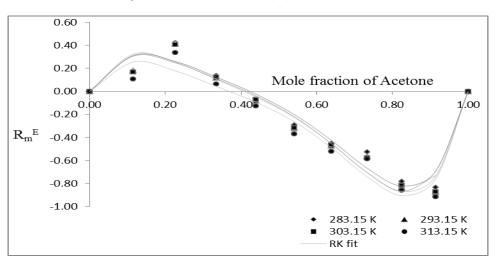**Figure3: Excess molar volume (V^E) of ALB with ACE.**

Figure 4: Excess molar refraction (R$_m^E$) of ALB with ACE.

Molar refraction gives the strength of interaction in mixture and it is a function of wavelength of light used, temperature and concentration [17, 24]. The excess molar volume(V^E)and excess molar refraction (R$_m^E$) are plotted in figure 3 and figure 4 respectively. From figure 3 and 4, it is clear that both result supported to each other, nature of graph is similar. The positive excess molar volume and molar refraction in ALB rich region say that weak intermolecular interaction and negative values in ACE rich region are due to strong intermolecular interaction. The positive V^E indicates that predominant effect of expansion consequent on rupture of dipole–dipole interaction between ACE molecules while negative V^E in ACE rich region are nevertheless indicative of important interaction between unlike molecule. Similar conclusion has drawn by J. Ortega et.al [25] for MBK with n-hexane mixture. The change in excess molar volume and molar refraction with variation of temperature are not appreciable but significant.

Redlich-Kister coefficient (a$_j$) and standard deviation determined from equation 8 and equation 9 respectively and tabulated in table 4. It can be seen from the table that the first two coefficients are dominant indicating formation of dimmers in mixtures.

Table4: a_j coefficients and standard error for excess dielectric *constant, excess inverse* relaxation time, excess molar volume and excess molar refraction.

	a_0	a_1	a_2	a_3	Error(σ)
			283.15 K		
ε_s^E	-2.7566	-12.671	0.63538	0.92599	0.05348
$\left(\frac{1}{\tau}\right)^E$	-0.0077	0.02799	0.02229	-0.0005	0.00029
V^E	-0.9954	-29.13	-20.865	-13.653	0.489
R_m^E	-0.492	-3.5645	-3.0636	-5.7838	0.1204
			293.15 K		
ε_s^E	-3.7298	-15.311	0.09797	6.18625	0.03195
$\left(\frac{1}{\tau}\right)^E$	-0.0064	0.02755	0.01201	-0.0016	0.00011
V^E	-1.1259	-29.641	-21.178	-15.086	0.4752
R_m^E	-0.5921	-3.5675	-3.204	-6.4329	0.1176
			303.15 K		
ε_s^E	-3.1043	-14.115	-5.5311	3.07476	0.03937
$\left(\frac{1}{\tau}\right)^E$	-0.01	0.02814	0.0147	0.00512	5.4E-05
V^E	-1.0467	-29.881	-21.795	-15.949	0.4933
R_m^E	-0.5594	-3.655	-3.3502	-6.0128	0.1163
			313.15 K		
ε_s^E	-5.7249	-17.339	0.90952	9.38161	0.05901
$\left(\frac{1}{\tau}\right)^E$	-0.0141	0.02776	0.01185	0.01034	0.00015
V^E	-1.2531	-30.348	-22.507	-15.694	0.4947
R_m^E	-0.7497	-3.4214	-3.752	-6.2295	0.1265

The values of effective Kirkwood correlation factor are summarized in table 5.The value of g^{eff} is less than one up to 0.8 volume fraction of ACE while greater than one for 0.9 volume fraction of ACE and pure ACE. In pure ALB, the interaction is such that the dipoles have tendency to align in antiparallel direction, whereas the interaction in ACE is such that the dipoles have tendency to align in parallel direction. In mixtures, these two tendencies get mixed, i.e. in ALB rich region, ACE molecules reduces the intensity of the antiparallism tendency resulting increase in values of g^{eff}. Similarly in ACE rich region, ALB molecule reduces the intensity of parallism tendency resulting decrease in values of g^{eff}.

Table 5: Kirkwood correlation factor of ALB with ACE

Volume fraction of ACE	283.15K	293.15K	303.15K	313.15K
0	0.78	0.77	0.74	0.73
0.1	0.95	0.92	0.87	0.87
0.2	0.99	0.99	0.94	0.93
0.3	1	0.99	0.96	0.93
0.4	0.98	0.97	0.95	0.88
0.5	0.96	0.94	0.93	0.85
0.6	0.96	0.93	0.91	0.84
0.7	0.96	0.95	0.91	0.87
0.8	0.99	0.99	0.95	0.93
0.9	1.05	1.06	1.01	1
1	1.12	1.14	1.11	1.1

Bruggeman factor of system is plotted in figure 5. It suggests that volume of complex increases in ALB rich region and decreases in ACE rich region. This result supported to the result of excess molar volume and excess molar refraction.
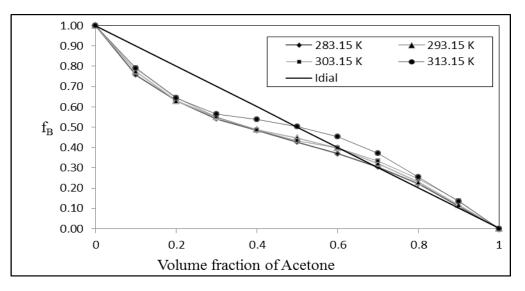

Figure 5: Bruggeman factor of ALB with ACE.

Thermodynamic parameters such as enthalpy, entropy and Gibbs free energy are valuable for extracting changes occurring during complex formation between two different liquids. From table 6, ΔH is positive over entire composition range, it indicates that reaction occurred during complex formation is endothermic reaction that is heat is absorbed by system. Entropy is a macroscopic property of a system; it measures the microscopic disorder within the system. From table 6, entropy of system over entire concentration range is negative and magnitude of entropy increases as concentration of ACE increases in mixture, this shows that disorder of system decreases with increases in concentration of ACE. The negative value of entropy shows that there are fewer configurations possible in dipolar orientation in active state. This may be due to the existence of dipole-dipole interaction; similar conclusion was reported by Sengwa et al. for ethylene glycol and propylene glycol mixture [21].

Table 6: Enthalpy (ΔH) and Entropy(ΔS) of ALB with ACE

Volume fraction of ACE	ΔH(KJ mol^{-1})	ΔS(KJ mol^{-1}K^{-1})
0	2.1495	-0.029
0.1	1.7817	-0.0311
0.2	1.6363	-0.0324
0.3	1.6086	-0.0333
0.4	1.7407	-0.0334
0.5	1.6182	-0.0344
0.6	1.3333	-0.0359
0.7	1.2061	-0.0368
0.8	0.9792	-0.0382
0.9	1.9091	-0.0362
1	2.1282	-0.0369

CONCLUSION

There are two types of tendencies observed in the system. The first type of tendency makes molecular dipoles orientation in antiparallel direction, whereas the second type of tendency makes molecular dipoles orientation in parallel direction. The ALB system is dominated by the type 1 tendency, whereas the ACE system is dominated by type 2 tendencies. The mixtures contain three types of dimmers, i.e. ALB-ALB, ALB-ACE and ACE-ACE.

- Intermolecular interactions in ALB and ACE rich are of different types resulting antiparallel dipoles in first one and parallel dipoles in second one.
- Result of excess dielectric constant, excess molar volume and excess molar refraction are supported to each other.
- The negative excess inverse relaxation time in ALB rich region shows that time required to attain equilibrium position is large while positive excess values in ACE rich region indicate that time required to attain equilibrium position is less.
- Bruggeman factor behaviour shows weak intermolecular interaction due to effective volume expansion in ALB rich region and strong intermolecular interaction in ACE rich region.
- The enthalpy show that reaction formed in complex is endothermic reaction while entropy indicates that disorder of system decreases as concentration of ACE increases.

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