

Temperature dependent dielectric relaxation study of 2-butanol-water mixtures from 10 MHz to 30 GHz

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A study has been made to investigate the hydrogen bond interaction between binary mixtures of 2-butanol and water using time domain reflectometry technique (TDR). Various volume concentrations of 2-butanol-water have been used in the frequency range of 10 MHz to 30 GHz at 0 to 20 °C. Complex permittivity spectra for 2-butanol-water mixtures determined which shows a Debye type of behavior. Dielectric parameters, i.e., dielectric constant (ϵ_0) and relaxation time (τ) have been obtained using least square fit method. Using the fundamental properties Kirkwood correlation factor, Bruggeman factor, excess dielectric properties and thermodynamic properties have also been determined to study the interaction between regular dipole interaction of hydrogen-Bonded (H-bonded) liquids the mixtures.

Keywords: Complex permittivity, Hydrogen bond, TDR, Kirkwood correlation factor, Bruggeman factor

1 Introduction

Key importance to investigate dielectric relaxation properties of H-bonded liquids is because such liquids generally show anomalous dielectric behavior, which is not observed in non H-bonded liquid. This is due the regular alignment of dipolar molecule in the H-bonded cluster. To study the molecular dynamics dielectric relaxation and interactions in these H-bonded liquids TDR has confirmed to be a dominant tool. In the GHz region, molecular dynamics is related to the hydrogen-bonding phenomena that differentiates H-bonded liquids from simple liquids. Therefore, the observation serves as a solution to explain complicated physical properties in hydrogen-bonded liquids.

In recent years numerous works have been done in the field of dielectric relaxation. Vishwam *et al.*¹ studied the dielectric relaxation of acetonitrile and propylene glycol in 20 MHz - 20 GHz range. Excess dielectric and thermodynamic properties of isobutanol and ethyl benzoate systems² were also been studied by scientists. Further various researchers³⁻⁵ have shown their interests to use dielectric relaxation spectroscopy as a study of inter- and intra-molecular interactions between several binary systems up to GHz frequency ranges.

Alcohols contain hydroxyl (-OH) group which is attached to saturated hydrogen atom as their general

formula becomes R-OH. There are different classes of alcohols as monohydric, dihydric, trihydric and polyhydric alcohols depending upon the number of hydroxyl groups. 2-butanol (secondary butyl alcohol) monohydric alcohol with formula of C_4H_9OH . 2-butanol is a flammable, color less liquid which is very soluble in water. It is produced on a large scale, primarily as a precursor to the industrial solvents.

The aim of the present work is to study the complex permittivity spectra of 2-butanol- water mixture at various temperatures, to find temperature dependent dielectric constant, relaxation time, excess permittivity and thermodynamic properties of 2-butanol-water mixtures in the frequency range 10 MHz to 30 GHz. Further we have special interest to study the interaction of two hydrogen bonded liquids using Bruggeman factor and Kirkwood correlation factor, as both 2-butanol and water contains strong hydrogen bond.

2 Materials and Methods

2.1 Materials

2-butanol was purchased from Merck India Limited and used without further purification. Solutions were prepared at different volume fraction of 2-butanol. The HPLC grade double distilled water was used in preparation of 2-butanol mixtures.

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2.2 Measurements

The complex permittivity spectra were studied using time domain reflectometry (TDR) method^{6, 7}. The basic TDR setup consists of broadband sampling oscilloscope, TDR module and coaxial transmission line. The Tektronix DSA8200 sampling oscilloscope with 30 GHz bandwidth and TDR module 80E08 with step generator unit was used. A 250 mV step pulse with 18 ps incident pulse was fed through coaxial line system of 50 Ω impedance. Sampling oscilloscope monitors changes in step pulse after reflection from sample. Reflected pulse without sample $R_1(t)$ and with sample $R_X(t)$ were recorded in time window of 5 ns and digitized in 2000 points. Temperature of the sample was controlled electronically within accuracy of ± 0.1 °C.

3 Data Analysis

The step pulses recorded without sample $R_1(t)$ and with sample $R_X(t)$ and are subtracted and added to get:

$$p(t) = [R_1(t) - R_X(t)] \quad \dots (1)$$

$$q(t) = [R_1(t) + R_X(t)] \quad \dots (2)$$

The complex reflection coefficient $\rho^*(\omega)$ over a frequency range of 10 MHz to 30 GHz were determined as follows:

$$\rho^*(\omega) = \frac{c}{j\omega d} \frac{p(\omega)}{q(\omega)} \quad \dots (3)$$

Where $p(\omega)$ and $q(\omega)$ are Fourier transforms of $p(t)$ and $q(t)$ obtained using summation and Samulon methods⁸, respectively, c is the velocity of light, ω is angular frequency and d is effective pin length (0.161 mm). The complex permittivity spectra $\epsilon^*(\omega)$ was obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying the bilinear calibration method suggested by Cole^{6, 7}.

The complex permittivity spectra for aqueous 2-butanol at 20 °C are shown in Fig. 1. The complex permittivity spectra of aqueous 2-butanol fitted to Havriliak-Negami (HN)⁹ model given as in Eq. (4):

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{[1 + (j\omega\tau)^{1-\alpha}]^\beta} \quad \dots (4)$$

The static dielectric constant (ϵ_0), relaxation time (τ) and dielectric constant at high frequency (ϵ_∞) (distribution parameters β kept 1 α kept to zero) for entire concentrations at 0-20 °C were determined by using least square fit method. The parameters show a systematic change with the concentration.

4 Results and Discussion

4.1 Dielectric constant and relaxation time

For the aqueous solution of 2-butanol, the static dielectric decreases and relaxation time increases with increases in volume fraction of 2-butanol in water and are reported in Table 1, this may be due to the smaller value of the dipole moment of 2-butanol molecules. A significant change in relaxation time at all three temperatures can be seen for pure 2-butanol to its aqueous solutions. As Debye's diffusive theory of relaxation¹⁰ predicts linear relationship between relaxation time and viscosity, these smaller values of relaxation time in aqueous solutions can be correlated to minute viscosity of water (0.890 cP) compared to 2-butanol (3.10 cP); suggests dominance of water in mixtures.

4.2 Kirkwood correlation factor

The static dielectric constant for the mixture can be explained using the Kirkwood-Frohlich equation as follows^{11, 12}:

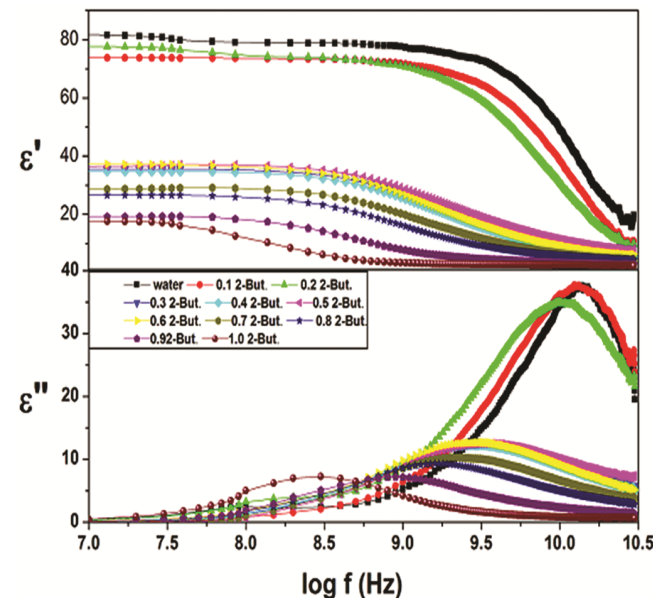


Fig. 1 – Frequency dependent complex permittivity spectra ϵ' and ϵ'' for 2-Butanol-water at 20 °C.

Table 1 – Dielectric Relaxation Parameters for aqueous solution of 2-butanol at different temperatures.

2-Butanol	ϵ_∞	ϵ_0	τ (ps)
20 °C			
0.0	6.62(18)	80.57(18)	10.12(11)
0.1	1.02(3)	73.18(9)	12.91(2)
0.2	1.09(5)	72.71(13)	16.13(5)
0.3	4.57(5)	32.40(21)	36.84(1)
0.4	4.47(5)	31.17(21)	39.57(1)
0.5	5.76(7)	33.31(25)	30.93(1)
0.6	5.22(5)	33.67(21)	40.32(1)
0.7	4.02(4)	26.76(17)	47.89(1)
0.8	3.92(4)	24.53(17)	62.89(1)
0.9	2.67(2)	18.35(13)	127.49(2)
1.0	2.20(1)	17.62(10)	463.22(7)
15 °C			
0.0	6.76(10)	82.11(10)	10.58(6)
0.1	3.89(3) 74.31(8)	13.53(2)	
0.2	0.28(5)	74.69(16)	17.98(6)
0.3	4.91(6)	33.17(23)	40.56(1)
0.4	4.90(5)	42.39(1)	
	33.70(23)		
0.5	5.91(9)	27.20(1)	
	37.78(30)		
0.6	5.40(6)	45.79(1)	
	33.87(25)		
0.7	4.41(4)	27.84(20)	54.05(1)
0.8	4.01(4)	24.34(18)	67.48(1)
0.9	3.13(3)	18.96(15)	145.99(2)
1.0	2.62(1)	18.65(11)	572.07(9)
10 °C			
0.0	4.86(6)	85.41(32)	12.08(7)
0.1	9.58(6)	77.52(15)	14.61(4)
0.2	1.38(7)	73.31(21)	20.37(9)
0.3	5.40(7)	36.42(28)	45.91(1)
0.4	5.61(7)	36.12(28)	42.15(1)
0.5	6.36(9)	38.87(34)	30.47(1)
0.6	3.25(2)	40.82(13)	74.35(1)
0.7	5.29(5)	30.36(24)	62.71(1)
0.8	4.92(4)	25.60(21)	74.87(1)
0.9	4.01(3)	21.02(17)	212.10(4)
1.0	3.35(2)	19.83(13)	674.45(12)
5 °C			
0.0	3.17(10)	86.21(32)	12.69(35)
0.1	11.79(11)	81.95(34)	18.03(10)
0.2	3.29(7)	74.99(24)	22.61(10)
0.3	6.17(8)	39.45(34)	52.83(1)
0.4	6.29(8)	41.30(37)	49.77(1)
0.5	8.08(10)	45.40(1)	49.90(1)
0.6	6.65(7)	37.15(33)	70.40(1)
0.7	6.27(6)	32.59(29)	83.20(1)
0.8	5.66(4)	27.52(24)	100(2)
0.9	5.04(3)	21.84(20)	244.55(6)
1.0	4.34(2)	20.42(16)	801.79(18)

0 °C

0.0	13.31(60)	90.02(50)	14.27(47)
0.1	10.41(13)	84.47(46)	24.04(17)
0.2	1.83(10)	76.83(36)	27.91(19)
0.3	6.68(11)	49.62(51)	52.55(1)
0.4	6.12(12)	53.17(56)	45.91(1)
0.5	8.40(11)	40.81(51)	54.07(1)
0.6	7.49(7)	38.00(37)	87.39(2)
0.7	10.31(8)	37.97(40)	93.10(2)
0.8	8.94(7)	36.35(37)	114.36(3)
0.9	8.04(4)	26.26(27)	216.72(6)
1.0	7.22(3)	22.54(21)	719.06(22)

Note: Numbers given in parentheses denote uncertainties in the least significant digits obtained by the least square fit method, e.g. for 719.06 (22) means 719.06 ± 0.22

$$\frac{4\pi N\rho}{9kTM} g\mu^2 = \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} \dots (5)$$

Where μ , ρ and M correspond to the dipole moment in gas phase, density and molecular weight, respectively, k is the Boltzmann constant, T is the temperature and N is the Avogadro's number.

The Kirkwood correlation factor “ g ” determined from the dielectric constant gives information on the collective orientation correlation between molecules. The deviation of the Kirkwood correlation factor from unity is a measure of the extent of inter-molecular hydrogen bonding. For the mixture of two polar liquids a and b, Eq. (5) is modified as described in the literature¹², with the assumption that g for the binary mixture is expressed by an effective averaged correlation factor g^{eff} such that the Kirkwood equation for the mixture can be expressed by:

$$\frac{4\pi N}{9kT} \left[\frac{\mu_w^2 \rho_w}{M_w} V_w + \frac{\mu_A^2 \rho_A}{M_A} (1 - V_w) \right] g^{\text{eff}} = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \dots (6)$$

With V_w and $1 - V_w$ as volume fractions of liquids a and b, respectively.

The values of effective Kirkwood factor are reported in Table 2. As water is added in 2-butanol solutions, the value of g^{eff} increases. The g^{eff} values for entire range of concentrations are greater than unity; this indicates parallel orientation of electric dipoles in molecules^{13, 14}. g^{eff} for pure water is found to be 2.86 which indicate parallel orientations between water molecules and for pure 2-butanol it is

found to be 0.48 at 20 °C. As the 2-butanol amount increases in water g^{eff} value start to decrease which shows reduction in parallel orientation in water molecules due to 2-butanol molecules.

4.3 Bruggeman factor

The Bruggeman equation¹⁵ is another parameter which may be used as an indicator of solute solvent interaction. The Bruggeman factor (f_B) is given by:

$$f_B = \left[\frac{(\epsilon_{0m} - \epsilon_{02})}{(\epsilon_{01} - \epsilon_{02})} \right] \left(\frac{\epsilon_{01}}{\epsilon_{0m}} \right)^3 = 1 - V \quad \dots (7)$$

Where ϵ_{0m} , ϵ_{01} and ϵ_{02} are the static dielectric constant corresponding to mixture, solute and solvent, respectively; V is the volume fraction of solvent (water). From above equation, the linear relation is expected from a plot f_B Versus volume fraction of water. But in binary liquids, there is non-linear relationship. To explain non-linear relationship of the plot, above equation has been modified as¹⁶:

$$f_B = \left[\frac{(\epsilon_{0m} - \epsilon_{02})}{(\epsilon_{01} - \epsilon_{02})} \right] \left(\frac{\epsilon_{01}}{\epsilon_{0m}} \right)^3 = 1 - [a - (a-1)V]V \quad \dots (8)$$

In this equation, volume fraction (V) is changed by a factor ' $a - (a-1)V$ ' of the mixture.

The value of ' a ', equal to 1 corresponds to ideal mixture with no additional interaction between two liquids and reduces to Bruggeman equation. ' a ' has been determined by least square fit method. The experimental values of ' a ' are found to be 0.562, 0.565, 0.638, 0.782 and 0.921 at 20 °C, 15 °C, 10 °C, 05 °C and 0 °C, respectively. As the

Table 2 – Effective Kirkwood correlation factor (g^{eff}) for aqueous solutions of 2-butanol.

Vol. Fract. Of 2-Butanol	g^{eff}				
	20 °C	15 °C	10 °C	05 °C	00 °C
0.0	2.86	2.86	2.93	2.90	2.98
0.1	2.20	2.18	2.46	2.79	1.76
0.2	1.93	1.92	2.19	2.60	1.14
0.3	0.75	0.74	1.03	1.39	0.55
0.4	0.68	0.70	1.00	1.52	0.49
0.5	0.69	0.75	1.08	1.79	0.31
0.6	0.68	0.66	1.17	1.58	0.26
0.7	0.54	0.54	0.91	1.54	0.24
0.8	0.52	0.49	0.83	1.49	0.23
0.9	0.40	0.40	0.77	1.43	0.15
1.0	0.48	0.49	0.94	1.80	0.13

volume concentration of water increases and temperature decreases, the ideality of the mixture deviates. According to Eq. (8) a linear relationship is expected between f_B and volume fraction as shown in Fig. 2, which shows the nonlinear relation between f_B and volume fraction of water. The Bruggeman factor f_B shows a negative deviation above 80% volume fraction of water and big positive deviation around 40-80% volume fraction of water, for rest volume fraction f_B shows small positive deviation from the ideal line. This indicates that inter-molecular interaction is taking place in the mixture.

4.4 Excess permittivity

The information related to liquids 1(water) and 2(2-butanol) interaction may be obtained by excess properties¹⁷ related to the permittivity and relaxation times in the mixture. The excess permittivity ϵ^E is defined as:

$$(\epsilon_0)^E = (\epsilon_0)_m - [(\epsilon_0)_W X_W + (\epsilon_0)_A (1 - X_W)] \quad \dots (9)$$

Where X_W is the volume fraction of water, subscripts m , W and A represent the mixture, water and 2-butanol, respectively. The excess permittivity may provide qualitative information about multimer formation in the mixture as follows:

- $\epsilon^E = 0$ indicates that the liquids W and A do not interact at all.
- $\epsilon^E < 0$ indicates that the liquids W and A interact in such a way that the total effective dipoles get reduced. The liquids W and A may form multimers leading the less effective dipoles.

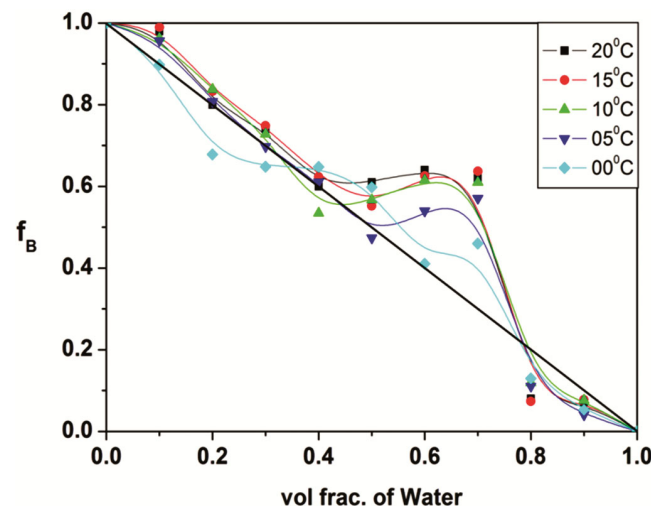


Fig. 2 – Variation of Bruggmann factor (f_B) for 2-Butanol-water mixture as a function of volume fraction

(iii) $\epsilon^E > 0$ indicates that the liquids W and A interact in such a way that the total effective dipole moment increases. There is a tendency to form multimers, dipole aligned in parallel direction.

Excess permittivity values for all aqueous 2-Butanol studied here exhibit a pronounced minimum and remain negative for whole concentration range as shown in Fig. 3. These negative values suggest solute-solvent interaction such that the number of effective dipole contributed in dielectric polarization gets reduced.

4.5 Thermodynamics properties

Using the Eyring equation, thermodynamic properties like enthalpy of activation and entropy of activation have been obtained¹⁸:

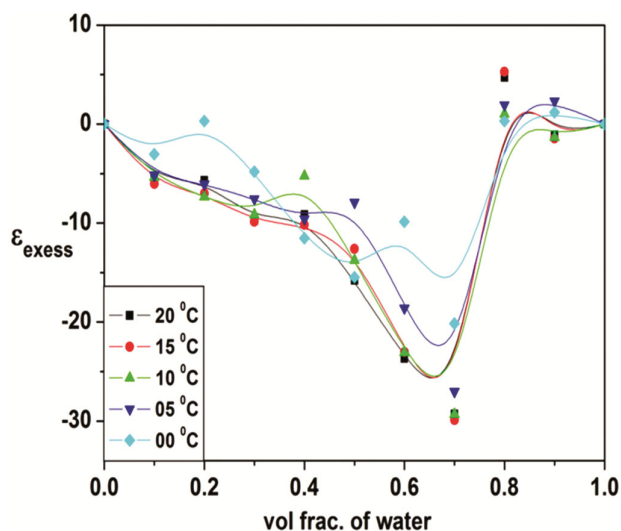


Fig. 3 – Excess permittivity of 2-Butanol-water mixture as a function of volume fraction.

Table 3 – Enthalpy and entropy of activation for aqueous solution of 2-Butanol.

Volume Fraction of	Enthalpy of activation ΔH (kJ mol ⁻¹)	Entropy of activation ΔS (J mole ⁻¹ K ⁻¹)
0.0	9.22(9)	0.22(0)
0.1	18.14(38)	0.25(1)
0.2	15.32(12)	0.24(0)
0.3	10.56(19)	0.22(0)
0.4	3.7(25)	0.19(0)
0.5	20.75(75)	0.25(2)
0.6	23.85(56)	0.26(2)
0.7	21.09(19)	0.25(0)
0.8	18.85(27)	0.24(2)
0.9	18.44(64)	0.23(2)
1.0	13.68(47)	0.21(2)

Numbers given in parentheses denote uncertainties in the least significant digits, e.g. 18.14 (38) means 18.14 ± 3.8 and 0.25(1) means 0.25 ± 0.01 .

$$\tau = \frac{h}{kT} \exp(\Delta H - T\Delta S\tau) / RT \quad \dots (10)$$

Where ΔH is the enthalpy of activation in kJ/mol, ΔS is the entropy of activation in J mole⁻¹ K⁻¹. h is Plank's constant, T is temperature in °K, τ is the relaxation time in ps, k is the Boltzmann constant and R is the gas constant. The values of thermodynamic properties are reported in Table 3. The endothermic reaction occurred in entire concentrations, causing the ΔH values to become positive. The sudden decrease at 40% 2-butanol in the ΔH value may be due to no hydrogen bonding between water and 2-butanol molecules.

5 Conclusions

A sharp increase is observed in relaxation time from aqueous 2-butanol to pure 2-butanol due to high viscosity of 2-butanol. Kirkwood correlation factor found to be greater than 1 in water rich region suggests parallel orientation of dipoles. Bruggmann factor shows a strong influence of water molecules so as to deviate the ideality of mixture. All values of activation energies are found to be positive and has sudden decrease at 40% of 2-butanol which may be due to no hydrogen bond between water and 2-butanol molecules. Excess permittivity is negative which suggests reduction in effective dipoles.

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References

- Vishwam T, Sharma N K S P S, Murthy V R K & Sreechary S S, *Indian J Pure Appl Phys*, 55 (2017) 403.
- Vishwam T, Parvateesam K & Shaikh B, *Indian J Pure Appl Phys*, 54 (2016) 597.
- Pathan AW & Kumbharkhane A C, *Phys Chem Liq*, 55 (2017) 179.
- Rawat A, Mahavar H K, Tanwar A & Singh P J, *Indian J Pure Appl Phys*, 52 (2014) 632.
- Chalikwar P A, Deshmukh A R & Kumbharkhane A C, *Phys Chem Liq*, 55 (2017) 410.
- Cole R H, Berbarian J G, Mashimo S, Chrysikos G, Burns A & Tombari E, *J Appl Phys*, 66 (1989) 793.
- Kumbharkhane A C, Puranik S M & Mehrotra S C, *J Chem Soc*, 87 (1991) 1569.
- Hager N E, *The Rev Sci Instrum*, 65 (1994) 887.
- Havriliak S & Negami S, *J Polym Sci*, 8 (1967) 161.
- Hill N E, *Theoretical Treatment of Permittivity and Loss* (Van Nostrand Reinhold Co), London, (1969) 1.

- 11 Frolich H, *Theory of Dielectrics*, (Oxford University Press: London), 1949.
- 12 Fattepur R H, Hosamani M T, Deshpande D K & Mehrotra S C, *J Chem Phys*, 101 (1994) 9956.
- 13 Kumbharkhane A C, Puranik S M & Mehrotra S C, *J Mol Liq*, 51 (1992) 261.
- 14 Kumbharkhane A C, Puranik S M & Mehrotra S C, *J Sol Chem*, 22 (1993) 219.
- 15 Bruggeman D A G, *Ann Phys (Leipzig)*, 5 (1935) 636.
- 16 Mashlkar G V, Chalikwar P A & Kumbharkhane A C, *Phys Chem Liq*, 53.3 (2015) 307.
- 17 Kumbharkhane A C, Puranik S M & Mehrotra S C, *J Sol Chem*, 22 (1992) 12.
- 18 Hill N E, Vaughan W E & Price A H, *Dielectric Properties and Molecular Behavior*, (London: Van Nostrand Reinhold Co), 1969.