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Research Article

COMPARATIVE STUDY OF BRUGGEMAN FACTORS AS A DIELECTRIC PARAMETERS OF ETHANOL, METHANOL AND PROPANOL WITH DIAZEPAM USING TIME DOMAIN REFLECTOMETRY

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ABSTRACT

Objective: The dielectric relaxation study of binary mixture at different concentration and different temperature has been carried out using time domain reflectometry technique in the frequency range of 10MHz to 50MHz.

Materials and Methods: Ethanol, Methanol and Propanol with Diazepam used as a binary mixture for the dielectric relaxation study.

Results: The dielectric parameters have been determined. The Bruggeman model has been fitted to the dielectric data of mixture.

Conclusion: It is concluded that f_B shows a small deviation to upper side from the ideal Bruggeman behavior in Ethanol and Propanol and lower side in Methanol with Diazepam binary mixture.

Keywords: Ethanol, Methanol, Propanol, Diazepam, Bruggeman factor.

INTRODUCTION

Many researchers have reported dielectric relaxation studies of binary mixtures to understand hydrogen bonding and intermolecular interaction in the mixture. Psychopharmaceutical medicine Diazepam is mainly used to treat anxiety, insomnia, panic attacks and symptoms of acute alcohol withdrawal [1].

In this work we report the dielectric study, Bruggeman factor of Ethanol, Methanol and Propanol with Diazepam binary mixture at 20% of volume fraction concentration and 283, 288, 293 and 298K temperature. The static permittivity of two component mixture must lie somewhere between two extremes corresponding to static permittivity of two liquids. In order to understand the dipole interaction in the mixture of two liquids, a various mixture formulae have been proposed [2, 3]. Bruggeman mixture formulae [3-5] can be used as first evidence of molecular interactions in binary mixture. This formula states that static permittivity of binary mixture (εsm), solute A (εsA) and solvent B (εsB) can be related to volume fraction of solvent (V) in mixture as

$f_B = 1 - V$

$$f_B = \left(\frac{\varepsilon_{sm}-\varepsilon_{sB}}{\varepsilon_{sA}-\varepsilon_{sB}}\right)\left(\frac{\varepsilon_{sA}}{\varepsilon_{sm}}\right)^{1/3} = 1 - V$$

According to above equation linear relationship is expected in Bruggeman factor f_B and (V). Any deviation from this linear relation indicates molecular interactions. Experimentally, it was found that the Bruggeman factor deviates from the linear behavior. It was proposed to modify the model as follows [6]

$$f_B = \left(\frac{\varepsilon_{sm}-\varepsilon_{sB}}{\varepsilon_{sA}-\varepsilon_{sB}}\right)\left(\frac{\varepsilon_{sA}}{\varepsilon_{sm}}\right)^{1/3} = \quad 1 - [a - (a-1)V]V$$

Table 1: Physical constant of pure liquids.

Name of Compound	Mol. Formula	Literature Value of ε_s	Mol. Wt. g/mol	Density in g/cm³	Dipole Moment μ D
Diazepam	$C_{16}H_{13}ClN_2O$	N.A.	284.743	1.26	N.A.
Ethanol	C_2H_5OH	24.3	46.03	0.789	1.69
Methanol	CH_3OH	32.7	32.04	0.792	1.69
Propanol	C_3H_8O	20.1	60.09	0.803	1.68

In this model, it is assumed that the volume fraction V is modified by a factor a-(a-1)V in the mixture due to solute – solvent interaction. The value of a=1 corresponds to the Bruggeman's equations. The value of a can be determined by statistical technique of least square fit method [7].

EXPERIMENTAL

Chemical and sample preparation

The chemical used in the present work are Diazepam, Ethanol, Methanol and Propanol are of spectroscopic grade, obtained commercially with 99% purity and used without further purification. The solutions were prepared at six different compositions in steps of 20 % by volume. These volume fractions are converted to mole fractions for further calculations. Using this volume percentage the weight fraction is calculate [8] as

$$X_A = \frac{V_A\rho_A}{[(V_A\rho_A)+(V_B\rho_B)]}$$

where, V_A and V_B are the volume and ρ_A and ρ_B is the density of liquid A(Atarax) and B (other chemical) respectively.

B. T.D.R. specification, Time domain reflectometry set up and data acquisition.

The Tektronix DSA8300 sampling oscilloscope sampling main frame with the dual channel sampling module 80E10B has been used for time domain reflectometry. The sampling module provides 12ps incident and 15ps reflected rise time pulse. The coaxial cable used to feed pulse has 50 Ohm impedance, inner diameter of 0.28mm and outer diameter of 1.19mm. Sampling oscilloscope monitors changes in pulse after reflection from end of line. 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. To minimize the signal to noise ratio the signal reflected is obtained from 512 samples after an optimum average of 100 times for each record. The subtraction [p(t) = $R_1(t) - R_x(t)$] and addition [q(t) = $R_1(t) + R_x(t)$] of these pulses are done in oscilloscope memory. These subtracted and added pulses are transferred to PC through compact disc for further analysis. [9]

C. Data analysis

The time dependent data were processedto obtain complex reflection coefficient spectra, ρ*(ω) over the frequency range from 10 MHz to 50 GHz using Fourier transformation [10,11] as

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

Where, ρ(ω) and q(ω) are Fourier transforms of [R_1 (t) - R_x (t)] and [R_1 (t) + R_x (t)], respectively. C is the velocity of light, ω is angular frequency and d is the effective pin length and j = root (-1). The complex permittivity spectra [12] ε^* (ω) were obtained from reflection coefficient spectra ρ^* (ω) by applying a bilinear calibration method. The experimental values of ε^* (ω) are fitted by Debye equation [13].

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega\tau}$$

where, ε_0, ε_∞ and τ as fitting parameters. The value of ε_∞ was kept to be constant as the fitting parameters are not sensitive to ε_∞. A non-linear least squares fit method [14] used to determine the values of dielectric parameters.

THEORY

The Bruggeman factor

The Bruggemen factor which is the ratio of theoretical value of static dielectric constant computed from Bruggemen mixture formulae and practically obtained values, has been obtained [15]. A linear relationship has been expected from the Bruggemen factor values, which gives a straight line when f_B plotted against volume fraction. However the experimental values of f_B were found to deviate from the linear relationship. The nonlinear relationship of Diazepam with Ethanol, Methanol and Propanol system suggest an intermolecular interaction takes place in the mixed components. It is assume that volume fraction in the mixture is modified by a factor [a-(a-1)φ]. This modification may be due to the structural rearrangement of solute molecules in the mixture. The value of 'a' contain information regarding the change in orientation of solute molecules in the mixture. The value of 'a' determined from the least square fit method, for all the studied system. The value of 'a' = 1 corresponds to ideal Bruggemen mixture formulae. The deviation from unity relates to corresponding mixture interaction [16]. The parameter 'a' in the modified Bruggemen model also provide information regarding nature of molecular interaction as [17]

- The straight line from (0,1) to (1,0) represents noninteraction between solute – solvent system. In such case, the value of parameter 'a' will be 1.
- The deviation to the upper part of the straight line indicates that effective volume of the solvents gets enhanced in presence of solute. The value of 'a' becomes less than one in such case.
- The deviation to the lower part of the straight line indicates reduction of effective volume and value of the parameter 'a' gets larger than one.

RESULT AND DISCUSSION

Table 2: Temperature dependent dielectric parameters for binary mixture of Ethanol + Diazepam.

Mole Fraction of Diazepam	283K		288K		293K		298K	
	ε_s	τ (ps)	ε_s	τ (ps)	ε_s	τ (ps)	ε_s	τ (ps)
0	25.71	175.2	24.39	157	23.74	142.7	23.8	142.5
0.0606	29.33	157.1	28.77	130.3	27.74	119.6	26.25	104.2
0.1468	33.14	131.3	31.76	97.93	30.9	91.92	30.74	86.77
0.2791	39.04	130.5	36.97	97.5	35.88	92.33	35.43	85.93
0.508	46.4	123.5	44.39	91.25	43.35	85.99	42.88	82.46
1	57.28	106.1	55.27	74.53	54.74	68.09	53.97	64.81

Table 3: Temperature dependent dielectric parameters for binary mixture of Methanol + Diazepam.

Mole Fraction of Diazepam	283K		288K		293K		298K	
	ε_s	τ (ps)	ε_s	τ (ps)	ε_s	τ (ps)	ε_s	τ (ps)
0	21.57	57.63	23.09	54.9	23.09	47.48	26.7	45.72
0.0428	42.16	63.81	41.99	60.61	41.99	59.58	40.62	58.32
0.1066	49.12	91.75	44.04	64.58	44.04	61.49	42.78	61.17
0.2117	51.02	92.08	44.79	70.14	44.79	64.24	43.22	62.93
0.4173	52.5	103.6	44.86	99.39	44.86	79.23	44.51	66.25
1	57.28	110.1	55.27	104.5	55.27	98.09	47.97	86.81

Table 4: Temperature dependent dielectric parameters for binary mixture of Diazepam + Propanol.

Mole Fraction of Diazepam	283K		288K		293K		298K	
	ε_s	τ (ps)	ε_s	τ (ps)	ε_s	τ (ps)	ε_s	τ (ps)
0	20.65	315.9	21.61	315.9	20.79	316.2	20.1	263.4
0.0765	19.85	200.3	19.52	199.4	19.52	199.4	19.06	159.7
0.1808	23.28	175	23.08	159.3	23.14	144.7	22.82	144.8
0.3319	29.51	131.3	28.59	96.98	28.33	86.23	28.19	81.85
0.5698	36.02	99.72	37.66	92.79	36.87	87.28	35.96	82.57
1	57.28	80.1	55.27	75.5	54.74	68.09	47.97	64.81

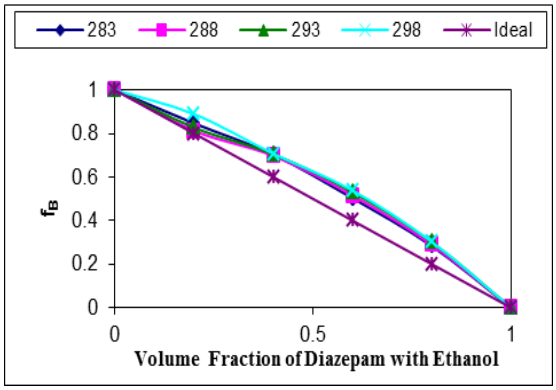

Fig. 1: The Bruggeman plot for Ethanol + Diazepam.

It can be seen from figure 1 f_B shows a small deviation to upper side from the ideal Bruggeman behavior [15]. Indicate reduction of effective volume value of Bruggeman parameter get smaller than one. This confirms the strong intermolecular interaction in the mixture. Furthermore values of (f_B) increase with increase in temperature and decrease in volume fraction of Diazepam, which shows temperature dependent nature of molecular interactions [18].

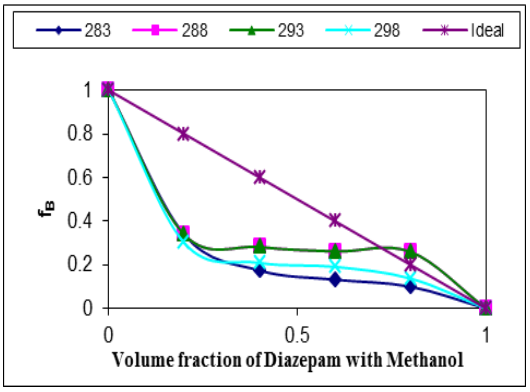

Fig. 2: The Bruggeman plot for Methanol +Diazepam.

It can be seen from figure 2 f_B shows a small deviation to lower side from the ideal Bruggeman behavior [15]. Indicate reduction of effective volume value of Bruggeman parameter get larger than one. This confirms the weak intermolecular interaction in the mixture. Furthermore values of (f_B) increase with increase in temperature and decrease in volume fraction, which shows temperature dependent nature of molecular interactions [18].

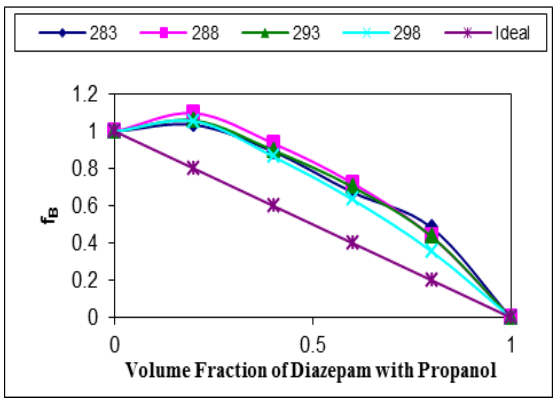

Fig. 3: The Bruggeman plot for Propanol + Diazepam.

It can be seen from figure 3 f_B shows a small deviation to upper side from the ideal Bruggeman behavior [15]. Indicate effective volume of solvent gets enhanced in the presence of solute. The effective volume value of Bruggeman parameter get less than one. This confirms the strong intermolecular interaction in the mixture. Furthermore values of (f_B) decrease with increase in temperature, which shows temperature dependent nature of molecular interactions [18].

CONCLUSION

It can be concluded that f_B shows a small deviation to upper side from the ideal Bruggeman behavior in Ethanol and Propanol with Diazepam binary mixture. The effective volume of the solvents gets enhanced in presence of solute and there is strong intermolecular interaction in the mixture. The value of 'a' becomes less than one in such case.

In Methanol mixture there is reduction of effective volume, value of Bruggemen parameter gets larger than one. Values of (f_B) increase with increase in temperature and decrease in volume fraction of Diazepam, which shows temperature dependent nature of molecular interactions.

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