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Bruggeman factor- Tool to indicate the change in volume through intermolecular interaction

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ABSTRACT: Dielectric relaxation measurement of Allyl Chloride with Methanol mixture for different concentration over the frequency range of 10 MHz to 20 GHz have been carried out using picoseconds time Domain Reflectomerty. Static permittivity (ε_0) and relaxation time (τ) were found through dielectric measurements. The Bruggeman factor was determined and discussed to yield information on the molecular interaction and change in volume.

Keywords: Allyl Chloride, Bruggeman factor, dielectric constant, Methanol, Relaxation time.

I. INTRODUCTION

Time Domain Reflectomerty (TDR) is an effective approach to understand the intermolecular interaction within the liquid molecules. Knowledge of frequency dependent dielectric properties of binary liquid mixtures is important both in fundamental studies of solvent structure determination and its dynamics, as well as in the practical application of microwave heating process [1, 2]. At a fundamental level, the frequency dependent dielectric behavior of liquid mixtures provides information on molecular interactions. The dielectric relaxation behavior of mixtures of polar molecules with varying conditions and compositions is very important as it helps in obtaining information about relaxation process in mixtures [3].

The aim of the present investigation is to carry out dielectric relaxation measurements for the investigation of the molecular interaction in Allyl chloride-methanol mixtures in the microwave region (10 MHz to 20 GHz) with varying concentrations (0 % to 100 %) using TDR technique for temperature ranging from 288 K to 318 K. The –OH group in methanol is hydrogen bonded to an electro-negative oxygen atom and methanol molecules are associated with each other through intermolecular hydrogen bonding; whereas double bond and a highly reactive chloride atom (CH_2=CH-CH_2-Cl) are present in the allyl chloride molecules and these molecules are associated with each other through dipole-dipole interaction. Because of presence of different type of association in both molecules, we feel it is interesting to see the nature of intermolecular interaction between Allyl chloride and -methanol molecules. The permittivity, relaxation time, excess permittivity, excess inverse relaxation time is reported. The Bruggeman factor is used for the prediction of intermolecular interaction in the mixtures.

A time domain Reflectomerty technique is proved to be a probe for the measurement of complex permittivity over a wide frequency range from 10 MHz to 20 GHZ [1-4]. The complex permittivity information over wide frequency range is useful for fundamental studies of solvent structure and dynamics and in practical application of microwave heating process [5]. Knowledge of dielectric constant of liquids is important for an understanding of ordering of the molecules in the liquid state and existence of molecular interaction in binary mixture. The Bruggeman factor can be used as an indicator of intermolecular interaction and change in volume. For design and development of microwave heated process (i.e. microwave drying, microwave oven, microwave diathermy, etc.), the availability of quantitative data on dielectric properties of solvent systems or methods for their predication are essential [6-12].

II. EXPERIMENTAL

1.1 CHEMICALS

The chemicals used in the present study are Allyl chloride; methanol,, Dimethyl formamide are of spectroscopic grade and are used without further purification. The solutions were prepared at eleven different volume percentage of Allyl chloride 0% to 100% in steps of 10%. Using these volume percents the mole fraction is calculated.

1.2 APPARATUS

The complex spectra were studied using Time Domain Reflectomerty. The Hewlett-Packard HP 54750 sampling oscilloscope with HP54754. A TDR plug-in module was used. A fast rising step voltage pulse of about 39 ps rise time generator was propagated through a coaxial line system of characteristic impedance of 50 ohm generated by a pulse. The transmission line system under test was placed at the end of the coaxial line in the standard military application (SMA) coaxial cell, coaxial connector with 3.5mm outer diameter and 1.35mm effective pin length.

All measurements were done under open load conditions. The change in the pulse after reflection from the sample placed in the cell was monitored by the sampling oscilloscope. In this experiment, a time window of 5ns was used. The reflection pulse without sampleR1(t) and with sample Rx(t) were digitized in 1024 points in the memory of the oscilloscope and transferred to a PC through a 1.44 MB floppy diskette drive.

A temperature controller system with a water bath and thermostat has been used to maintain the constant temperature within the accuracy limit $\pm 1^0$C. The cell was surrounded by a heat-insulating container through which the water of constant temperature using a temperature controller system was circulated. The temperature at the cell is checked using the electronic thermometer.

III. DATA ANALYSIS

The time dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ over a frequency range 10 MHz to 20 GHz by using Fourier transform [13, 14] as

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

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 velocity of light, ω is the angular frequency, d is effective pin length and $j=\sqrt{-1}$, $R_1(t)$ is reflected pulse without sample and $R_x(t)$ is reflected pulse with sample.

The complex permittivity spectra $\varepsilon^*(\omega)$ is obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying a bilinear calibration method [15].

The experimental values of $\varepsilon^*(\omega)$ are fitted with the Debye equation [16]

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega\tau} \tag{2}$$

where ε_0, ε_∞ and τ are fitting parameters. In equation (2), ε_0 is the static permittivity; ε_∞ is the permittivity at high frequency, ω is the angular frequency and τ is the relaxation time of the system. A non-linear least square fit method [17-24] is used to determine the values of these parameters.

IV. BRUGGEMAN FACTOR

The Bruggeman factor [25] is the parameter, which is used to study intermolecular interaction between two liquids A and B. If we know the static permittivity and dielectric loss (permittivity at high frequency) then Bruggeman factor can be estimated. The Bruggeman factor f_B is given by relation

$$f_B = \left(\frac{\varepsilon 0m - \varepsilon 0B}{\varepsilon 0A - \varepsilon 0B}\right)\left(\frac{\varepsilon 0A}{\varepsilon 0m}\right)^{1/3} = 1\text{-}v$$

Where

ε_{0m} - static permittivity of the mixture
ε_{0A} -static permittivity of the liquid A
ε_{0B} -static permittivity of the liquid B

According to this relation, a linear relationship is expected between Bruggeman factor and volume fraction of mixture.

V. FIGURES AND TABLES

PERMITTIVITY OF AC+M				
Mole fr.of meth	288 K	298 K	308 K	318 K
1	33.61	32.64	31.48	30.53
0.947917	32.85	30.59	30.23	29.67
0.889778	31.48	27.81	27.07	26.52
0.824839	27.84	25.52	25.09	24.47
0.751691	25.67	22.64	22.02	21.52
0.668672	21.73	21.02	20.04	18.52
0.57364	18.54	17.69	17.07	15.04
0.463785	15.4	14.61	14.02	13.06
0.335345	12.51	10.92	10.06	9.65
0.183166	10.35	9.25	8.54	8.04
0	8.26	8	7.8	7.56

PERMITTIVITY OF AC+DMF			**Table 1**	
mole fr. DMF	288 K	298	308 K	318 K
1	42.32	39.44	37.03	35.03
0.9049	38.71	35.85	34.35	32.62
0.8088	35.91	33.8	31.73	30.45
0.7116	32.89	30.71	29.92	28.06
0.6134	29.68	28.17	26.65	24.91
0.5140	26.94	24.99	23.58	22.84
0.4135	24.4	22.16	21.16	20.18
0.3119	21.26	19.21	18.01	17.35
0.2091	17.68	16.27	14.6	14.01
0.1052	13.3	11.81	11.38	10.71
0	8.26	8	7.8	7.56

VI. DISCUSSION

The dotted strait line shows that there is no intermolecular interaction in the liquid mixture. Any deviation from linear relation indicates existence of intermolecular interactions. The plot of Bruggeman factor f_B verses volume fraction Allyl chloride shows deviation from ideal line as shown in figure 1 .This shows that there is intermolecular interaction between liquids A and B.

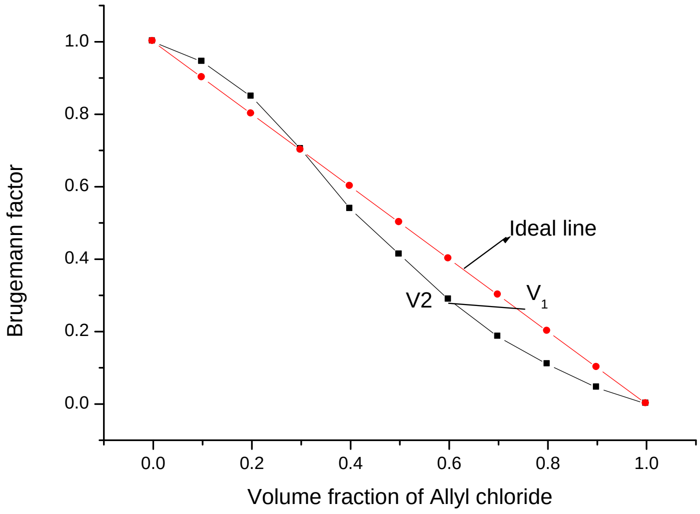

Figure 1 Allyl chloride + Methanol

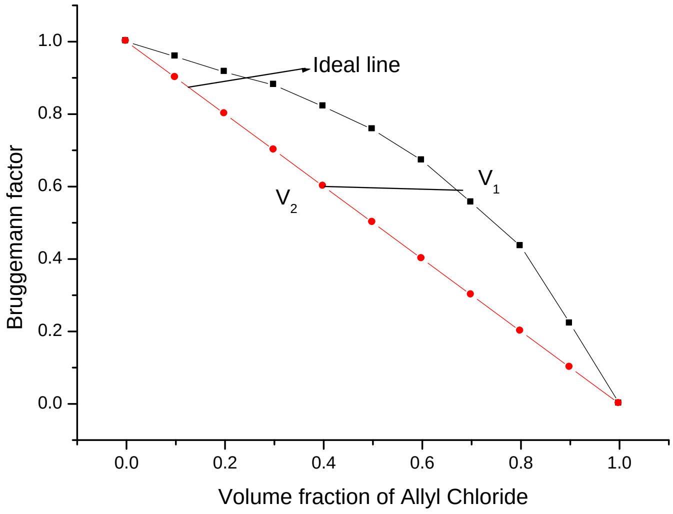

Figure 2 Allyl chloride + DMF

The ideal plot for particular value of f_B in figure 1, the volume at mark A is to be expected but it is found that for the same value of f_B , the volume is found v_2. This volume v_2 is the increase in the volume for the same value of f_B i.e. (v_2-v_1), $v_1/=(v_1/(v_1+v_2))$. In denominator v2 decreases and therefore overall volume increases i.e. In this region there is increase in the volume of the system..

In fig 2, for the particular value of f_B , the volume is expected at A. But it is found that decrease in volume for the same value of f_B. This indicates, there is decrease in volume during the intermolecular interaction of the liquid A and B i.e. (v_2-v_1). In other words $v_1/=(v_1/(v_1+v_2))$ In denominator v2 increases and therefore overall volume decreases i.e. In this region there is decrease in the volume of the system..

VII. CONCLUSION

From above discussion it is conclude that, Bruggeman factor f_B can be used as an indicator to confirm the change in the volume during the intermolecular interaction between liquids A and B. It is observed that when there is deviation below the ideal line, this indicate that there is increase in volume during intermolecular interaction and when there is deviation above the ideal line, this indicate that there is decease in volume during intermolecular interaction

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