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Archives of Applied Science Research, 2012, 4 (4):1665-1669
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0975-508X
CODEN (USA) AASRC9

Study of molecular interaction in binary mixture of dimethylene chloride with dimethylformamide using Bruggeman model

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ABSTRACT

Dielectric relaxation parameters of dimethylene chloride with dimethylformamide in microwave frequency range 10 MHz to 20 GHz has been determined using time domain reflectometry. The HP54750A digitizing oscilloscope with HP54754A TDR module is used for these measurements. The time dependent data is processed to obtain complex reflection coefficient $\rho^*(\omega)$. The complex permittivity spectra $\varepsilon^*(\omega)$ is obtained by applying bilinear calibration method. The Bruggeman Parameters are obtained using static dielectric constant. The paper discusses the weak inter molecular interaction in the binary mixture through Bruggeman parameter model.

INTRODUCTION

The dielectric relaxation measurement at microwave frequencies have provided an effective means of studying mechanism of molecular process and intermolecular interaction between the binary mixtures of the organic compounds[1-5]. The Bruggemen parameters of binary polar liquids provide information regarding solute-solvent intermolecular interaction between the molecules. Dimethylene chloride (DCM) and dimethylformamide (DMF) are both polar nonassociative liquids, one with chloro-group and other with C=O group. It is interesting to see the intermolecular interaction of chloro-group molecule with DMF molecule. The objective of the present paper is to report the fundamental complex permittivity spectra and intermolecular interaction through Bruggeman model for DCM and DMF mixtures.

MATERIALS AND METHODS

DCM and DMF (AR grade, Qualigens fine chemicals Pvt. Ltd., Bombay, India) were used without further purification. The solutions were prepared at 11 different volume percentage of DCM from 0 % to 100 %. Using these volume percents the mole fraction is calculated as

$x_1 = (v_1\rho_1/m_1) /[(v_1\rho_1/m_1) + (v_2\rho_2/m_2)]$

where m_i, v_i, and ρ_i represent the molecular weight, volume percent, and density of the i^{th} (i=1, 2) liquids, respectively.

The complex permittivity spectra were studied using the time domain reflectometry[6] method. The Hewlett Packard HP 54750 sampling oscilloscope with HP 54754A TDR plug in module has been used. A fast rising step voltage pulse of about 39 ps rise time generated by a pulse generator was propagated through a coaxial line system of characteristic impedance 50 Ohm. Transmission line system under test was placed at the end of coaxial line in the standard military applications (SMA) coaxial connector with 3.5 mm outer diameter and 1.35 mm effective pin length. All measurements were carried out 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 the experiment, time window of 5 ns

was used. The reflected pulse without sample $R_l(t)$ and with sample $R_x(t)$ were digitized in 1024 points in the memory of the oscilloscope and transferred to a PC through 1.44 MB floppy diskette drive.

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

DATA ANALYSIS

The time dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ over the frequency range from 10 MHz to 20 GHz using Fourier transformation [7,8] as

$$\rho^*(\omega)=(c/j\omega d)[p(\omega)/q(\omega)] \quad (1)$$

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 angular frequency, d is the effective pin length and $j=\sqrt{-1}$.

The complex permittivity spectra $\varepsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying bilinear calibration method [9].

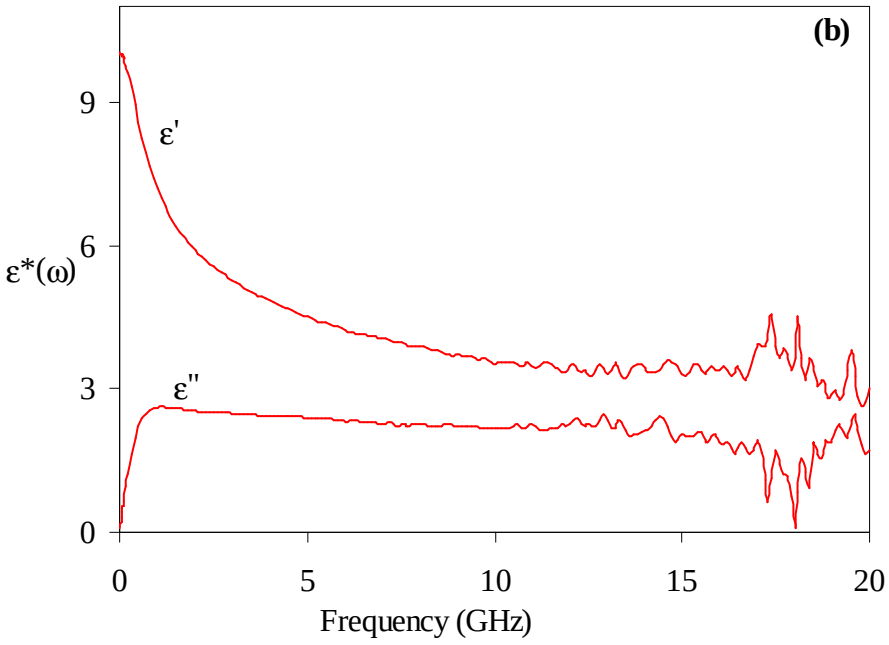
The experimental values of ε^* are fitted with the Debye equation [10]

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

with ε_0, ε_∞, and τ as fitting parameters. A nonlinear least-squares fit method [11] was used to determine the values of dielectric parameters. The value of ε_∞ was taken to be 2 for the system studied since, for the frequency range considered here, ε^* is not sensitive to ε_∞. A sample of complex reflection coefficient $\rho^*(\omega)$ and complex permittivity spectra $\varepsilon^*(\omega)$ for pure DCM at 15^oC are shown in Figure 1 (a) and (b) respectively.

RESULTS AND DISCUSSION

The dielectric relaxation parameters such as dielectric constant and relaxation time of DMF in DCM for 11 different concentration at 15, 25 35 and 45^oC are reported in pawar at al[12]. Bruggeman parameters are obtained by fitting the static dielectric constant at 15, 25 35 and 45^oC.



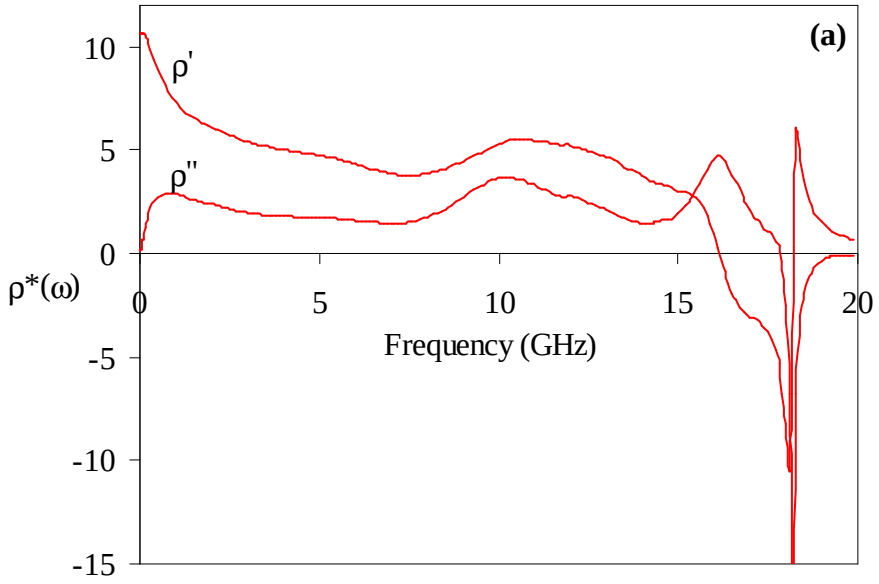


Figure 1. (a) The complex reflection coefficient $\rho^*(\omega)$ and (b) The complex permittivity spectra $\varepsilon^*(\omega)$ for pure DCM at 15°C

The modified Bruggeman equation[13] is a parameter, which may be used an indicator of liquid 1 and 2 interaction. The Bruggeman factor f_B is given by,

$$f_B=\left(\frac{\varepsilon_{0m}-\varepsilon_{02}}{\varepsilon_{01}-\varepsilon_{02}}\right)\left(\frac{\varepsilon_{01}}{\varepsilon_{0m}}\right)^{1/3}=(1-\phi_2) \qquad (3)$$

According to equation (3), a linear relationship is expected which will give a straight line when plotted f_B against ϕ_2. However, here the experimental values of f_B were found to deviate from the linear relationship. The Bruggeman dielectric factor f_B versus volume fraction ϕ_2 of DMF at 15, 25, 35 and 45°C is given in Figure 2.

To fit the experimental data, Eq. (4) has been modified[14]

$$f_B=1-[a-(a-1)\phi_2]\phi_2 \qquad (4)$$

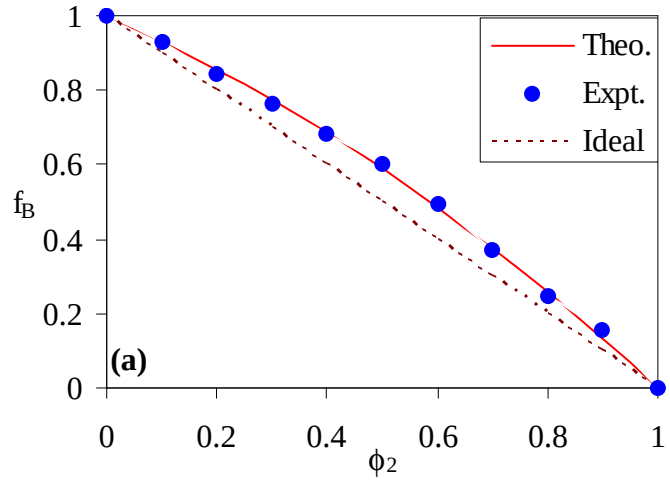
where 'a' is numerical fitting parameter.

The information regarding the intermolecular interaction of liquid 1 and 2 from this Bruggeman parameter is as follows:

(i) a < 1 : The liquid 1 and 2 interaction such as structural breaking which decreases the effective volume of the system.

(ii) a > 1 : The liquid 1 and 2 interaction such as structural formation which increases the effective volume of the system.

The parameters 'a' has been determined by the least squares fit method and it is found to be 0.642, 0.556, 0.408 and 0.214 for temperature 15, 25, 35 and 45°C respectively. The value of 'a' = 1 corresponds to the ideal Bruggeman mixture formula. The deviation from 1 relates to corresponding liquids 1 and 2 interactions. The small deviation of "a" suggest that weak interaction between DCM and DMF binary mixture at four different temperatures as shown in Figure 2.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Ideal
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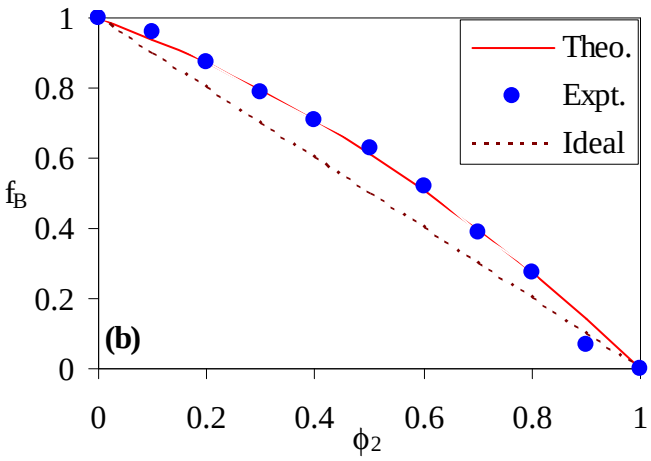
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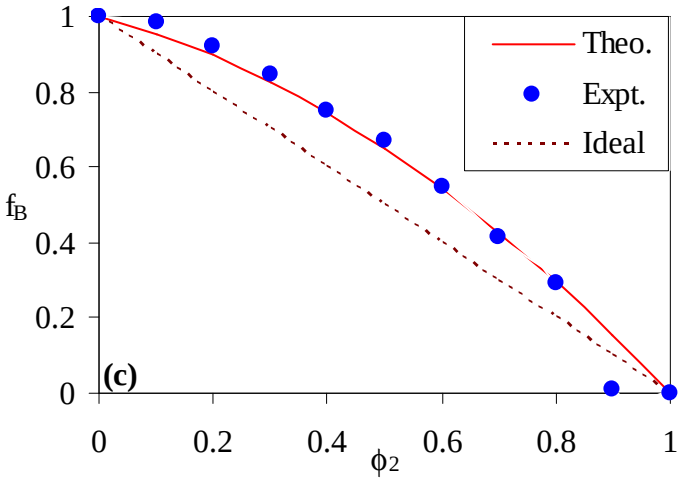
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ϕ_2
(c)
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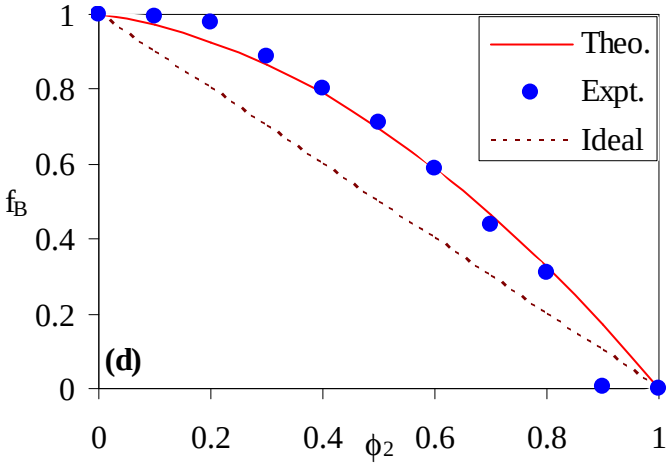

Figure 2. The Bruggeman plot for DMF in DCM mixture at (a) T=15°C, (b) T=25°C, (c) T=35°C and (d) T=45°C. Dashed line denote original model (equation 3). Continuous line is the theoretical curve obtained from equation (4). Experimental points are shown by the symbol •.

CONCLUSION

Bruggeman parameters are reported in this paper for dimethylene chloride-N, N dimethylformamide mixtures at various temperatures. The interaction of the chloro group on the C=O bonded liquids is discussed using Bruggeman model at four different temperatures. This paper indicates weak intermolecular interactions observed in the binary mixture of unlike molecules.

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