

# Complex and thermodynamic properties of polar liquids using time domain reflectometry in Microwave frequency

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## ABSTRACT

The complex permittivity spectra and thermodynamic properties of 1,2-dichloroethane (DE) and n,n-dimethylformamide (DMF) polar liquids has been obtained at 15°C temperature in the frequency range of 10 MHz to 30 GHz by using time domain reflectometry technique for 11 different concentrations of the system. Time dependent data is processed to obtained complex reflection coefficient spectra  $\rho^*(\omega)$ . Complex permittivity spectra is obtained from bilinear callibration method and this spectra gives information regarding dielectric dispersion ( $\epsilon'$ ) and dielectric absorption ( $\epsilon''$ ), which indicates the purity of the liquid mixture. The modified Bruggeman model is also a parameter which may be used an indicator of liquid 1 and 2 interactions. In binary mixture of polar liquids, there is a change in the energy of the system. This change in energy can be interpreted with thermodynamic parameters such as free energy of activation ( $\Delta G$ ), molar enthalpy of activation ( $\Delta H$ ) and molar entropy of activation ( $\Delta S$ ).

## 1. Introduction

The dielectric relaxation study of solute-solvent mixture in the microwave frequency range gives information about formation of monomers and multimers as well as interaction between the molecules of the binary liquid mixture [1-3]. The interaction of electromagnetic radiation with the dielectric liquid mixture gives a complex quantity, in which real part indicates the static dielectric constant ( $\epsilon'$ ) and the imaginary part represents the dielectric loss ( $\epsilon''$ ).

1,2-dichloroethane is a polar and aprotic solvent liquid, which is slightly soluble in water. It is a sticky, colorless and heavily non associative liquid. It is an important chemical liquid which is very useful for production of various chemicals such as vinyl chloride, used as a wetting and penetrating agent for dispersant in rubber and plastics, used in chemical industries as in ore flotation, as a grain fumigant, as a metal degreaser, in textile and PVC cleaning.

The n,n-dimethylformamide (DMF) is a polar aprotic solvent. It is a colorless liquid with high boiling point and is miscible with water and majority of organic liquids. It is used as an industrial solvent in chemical industries and also in the production of fibers, films and surface coating.

The effect of chlorine group molecule of DE in C=O functional group of DMF binary mixture, gives very important information. The main object of this paper is to give complex and thermodynamic properties of DE-DMF liquid mixture at 15°C.

**2. Experimental technique**

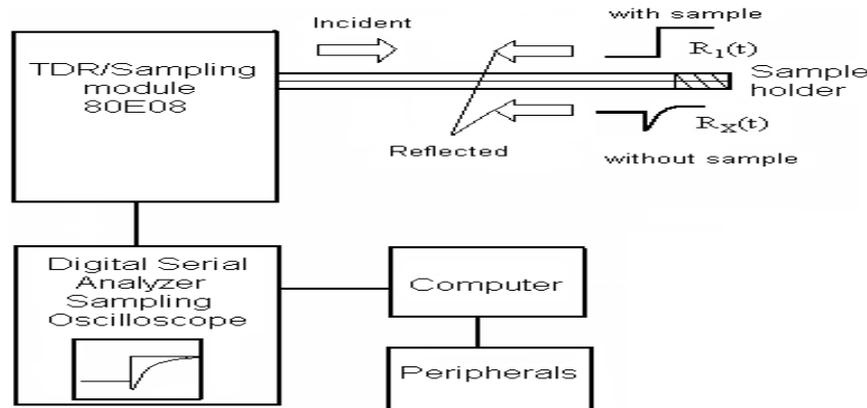
1,2 dichloroethane ( AR Qualigens fine chemicals Pvt. Ltd., Mumbai, India) and n,n-dimethylformamide (Merck Specialties, Pvt. Ltd., Mumbai, India) polar binary liquids are used without further purification. Liquid mixture is prepared at 11 different volume percent by decreasing the liquid 1 (DE) from 100% to 0% and increasing the liquid 2 (DMF) from 0% to 100% just before the measurement. Using these volume percent the mole fraction is calculated as

$$x = \frac{\frac{v_1 \rho_1}{m_1}}{\left[ \frac{v_1 \rho_1}{m_1} + \frac{v_2 \rho_2}{m_2} \right]} \tag{1}$$

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

The time domain reflectometry technique is used to obtain the complex permittivity spectra [4-7]. TDR setup contains the Tektronix model number DSA8200 Digital Serial Analyzer sampling mainframe along with the sampling module 80E08, sample holder connected with coaxial line, computer and peripherals as shown in figure 1. A repetitive fast rising voltage pulse with 18ps incident rise time was fed through coaxial line system of impedance 50 ohm to incident on sample in the sample holder. Figure 2 represents the sampling oscilloscope, which will record the change in the incident pulse after reflection from the sample holder. The reflected pulse without sample  $R_1(t)$  and with sample  $R_x(t)$  were recorded in time window of 5ns and digitized in 2000 points as shown in figure 3. The controller system of water bath is use to maintain constant temperature around the liquid cell and a thermostatically maintained temperature within  $\pm 0.5^\circ\text{C}$ . A heat insulating container through which the constant temperature water was circulated is covered around the sample cell. By using electronic thermometer the temperature of sample cell was measured.

Figure 1 : Block diagram of TDR setup



The nature of the pulses without and with sample is observed. This time dependent data were simplified to obtained reflection coefficient spectra  $\rho^*(\omega)$  over the microwave frequency range using Fourier transformation as [8,9]

$$\rho^*(\omega) = \frac{c}{j\omega\tau} \left[ \frac{p(\omega)}{q(\omega)} \right] \quad (2)$$

where  $p(\omega)$  and  $q(\omega)$  are Fourier transforms of  $[R_1(t) - R_x(t)]$  and  $[R_1(t) + R_x(t)]$  respectively are shown in figures 3 and 4,  $c$  is the velocity of light,  $\omega$  is angular frequency,  $d$  is the effective pin length and  $j = \sqrt{-1}$ .

Figure 2 : Tektronix DSA8200 digital serial analyzer sampling oscilloscope

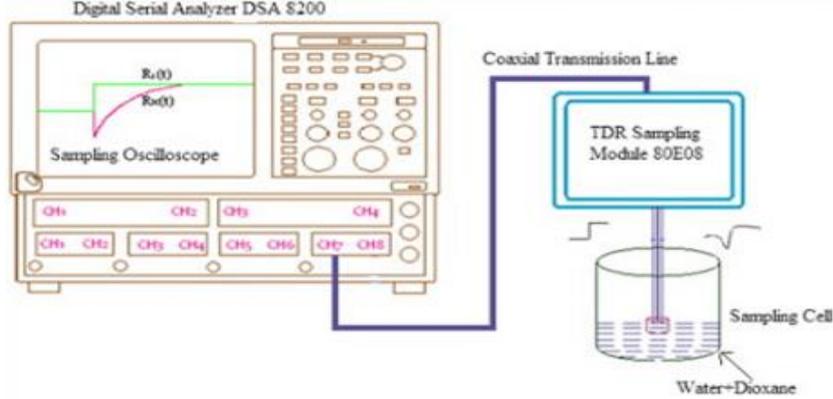
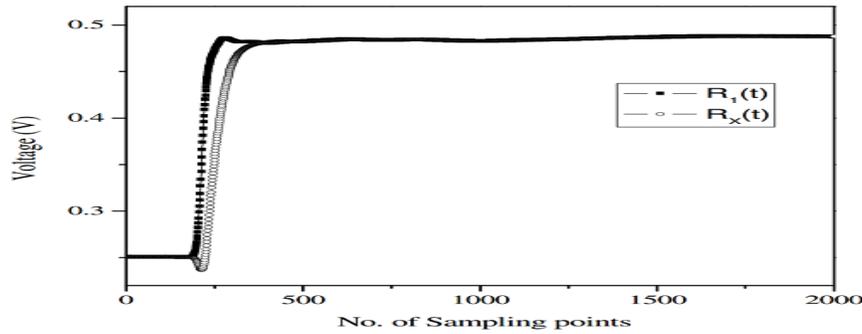


Figure 3 : Tektronix DSA8200 digital serial analyzer sampling oscilloscope



By using bilinear calibration [10] method the complex permittivity spectra  $\varepsilon^*(\omega)$  were obtained from reflection coefficient spectra  $\rho^*(\omega)$ .

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{[1 + (j\omega\tau)^{(1-\alpha)}]^\beta} \quad (3)$$

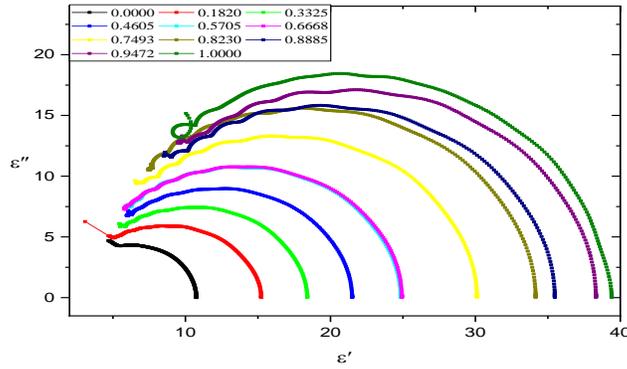
where  $\varepsilon^*(\omega)$  is the complex permittivity at an angular frequency  $\omega$ ,  $\varepsilon_0$  is the static permittivity,  $\varepsilon_\infty$  is the permittivity at high frequency,  $\tau$  is the relaxation time of the system,  $\alpha$  is the shape parameter representing symmetrical distribution of relaxation time and  $\beta$  is the shape parameter of an asymmetric relaxation curve. For Debye model [11] ( $\alpha=0$  &  $\beta=1$ ) shows the single relaxation whereas the Cole-Cole [12] ( $0 \leq \alpha \leq 1$  &  $\beta=1$ ) and Cole-Davidson [13] ( $\alpha=0$  &  $0 \leq \beta \leq 1$ ) models. These models suggest the symmetric and asymmetric distribution of relaxation time.

Since the relaxation behaviour of DE-DMF at 15°C is a semicircle as shown in figure 4, it obeys the Debye's model. So the experimental values of  $\varepsilon^*(\omega)$  were fitted with the Debye equation.

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega\tau} \quad (4)$$

where  $\epsilon_0$ ,  $\epsilon_\infty$  and  $\tau$  are the adjustable parameters. These dielectric parameters were obtained from a nonlinear Least-Square fit method [14].

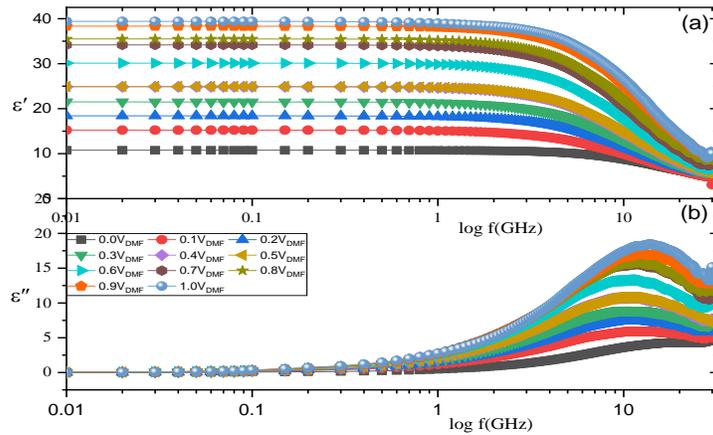
Figure 4 : Complex plane plot of dielectric loss ( $\epsilon''$ ) vs. dielectric constant ( $\epsilon'$ ) for eleven different concentrations of DMF in DE at 15°C temperature



### 3. Results and discussions

The dielectric properties were studied as a function of frequency as shown in figure 5. The static dielectric constant values are high for low frequencies till 3GHz and then decreases as expected. The dielectric loss is less for low frequencies and increases with increase in the applied frequency; it shows that the dielectric loss is mainly a function of applied frequency. Only one relaxation peak is observed for pure DE, DMF and DE-DMF binary mixtures. Further, it seems that in the mixture of these liquids, the individual principle relaxation processes of the components coalesce, and hence the mixture exhibits a single relaxation time. The dielectric loss peaks for these molecules and their mixtures are found in the frequency range 10 to 11 GHz at 15°C. The magnitude of peak of dielectric loss is much higher in DMF rich region as compare to the DE, it's due to higher density and molecular weight of DE over DMF.

Figure 5 : Complex permittivity spectra  $\epsilon^*(\omega)$  of DE-DMF for 11 different concentrations at 15°C



In dielectrics the relaxation process can be considered as the passing of a dipole across a potential barrier which separates the minima of energy is given by the thermodynamic parameters. The thermodynamic parameters like molar enthalpy of activation ( $\Delta H$ ) and molar entropy of activation

( $\Delta S$ ) are may be determined from the Eyring rate equation [15] utilizing least square fit method is given in table 1.

$$\tau = \frac{h}{kT} \exp (\Delta H-T\Delta S) /RT \quad (5)$$

where T is the temperature,  $\tau$  is the relaxation time, h is plank’s constant, k is Boltzmann’s constant. From the table the values of  $\Delta G$  for pure DE less than DMF and increases with the concentration of DMF, it means that the DMF molecule in the liquid dominates over DE molecules. This dominance of FA over DE is primarily due to its large dipole moment values and presence of C=O. The molar enthalpy values for DE-DMF at 15°C temperature are positive for all concentrations except 0.5705 and 0.6658 mole fraction of DMF in DE. The positive values indicate the heat librated during formation of liquid mixture. The values of molar entropy of activation ( $\Delta S$ ) of the system are negative for all concentrations. It represents the environment of the system is cooperative resulting in the activated state, which is more ordered than the normal state.

Table 1 : Molar enthalpy of activation ( $\Delta H$ ), molar entropy of activation ( $\Delta G$ ) and entropy of activation ( $\Delta S$ ) for DE-DMF system

Mole fraction of DMF	$\Delta G$ KJ	$\Delta H$ KJ	$\Delta S$ KJ
0.0000	10.1921	5.4839	-0.0163
0.1812	10.3037	4.9436	-0.0186
0.3325	10.4119	6.7749	-0.0126
0.4606	10.5387	6.0844	-0.0155
0.5705	11.2978	-9.9105	-0.0736
0.6658	12.4741	-1.1684	-0.0474
0.7493	13.3793	7.2601	-0.0212
0.8230	13.4605	6.6465	-0.0237
0.8885	13.2548	5.6574	-0.0264
0.9472	13.3188	7.2307	-0.0211
1.0000	13.8802	22.7513	0.0308

### 5. Conclusion

The frequency dependent complex dielectric properties of DE-DMF mixture are explained by using time domain reflectometry technique. DE-DMF system obeys the Debye model. The static dielectric dispersion ( $\epsilon'$ ) and dielectric loss are observed as a function of frequency. These quantities are mainly depends on the applied frequency. The thermodynamic parameters such as molar entropy and molar enthalpy are also explained.

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