

Dielectric studies of some binary liquid mixtures using microwave cavity techniques

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MS received 15 February 1993; revised 22 April 1993

Abstract. The excess parameter studies in the microwave frequency region (X-band) on complex dielectric permittivity for the binary mixtures are reported. The methods employed are fixed cavity perturbation technique and adjustable plunger cavity technique. Also Gopalakrishna method is used to calculate the relaxation time of the polar solute in a non-polar solvent. The samples under study are acetonitrile, chlorobenzene, dimethyl formamide, carbon tetrachloride and benzene.

Keywords. Cavity techniques; excess dielectric parameter; acetonitrile; dimethyl formamide and chlorobenzene binary mixtures; relaxation time.

PACS Nos 77·20; 77·40

1. Introduction

When a binary mixture is formed, the expected properties such as thermodynamic parameters, volume measurement, dielectric parameters and refractive index do not vary linearly [1]. The deviation of these parameters from the linear behaviour (termed as *excess parameters*) is considered to be very important and helps to find the nature of bonding between the two liquids. The polar–non-polar binary mixtures are studied with acetonitrile (AN), chlorobenzene (CBZ) and dimethyl formamide (DMF) in carbon tetrachloride (CTC) and benzene (BZ). The binary mixture of polar–polar combination is also studied with AN in CBZ. Gopalakrishna's method [2] is used to study the variation of relaxation time of polar liquid, AN, highly diluted mixture in non-polar solvents, CTC and BZ. Adjustable plunger cavity method described elsewhere [3] is used for most of the dilute solution studies.

2. Experimental techniques

2.1 Fixed cavity perturbation technique

The expression to find the complex dielectric permittivity of a solid sample (cylindrical or rectangular shaped) inserted in an electric field maximum position in a rectangular cavity (TE_{10p} mode; p can be any integer denoting the number of half wavelengths inside the cavity in the propagation direction) given by Murthy and Raman [4] is modified for liquid samples to get

$$\epsilon' = 1 + \frac{V_c \cdot (1/f_2^2 - 1/f_1^2) \cdot f_0^2}{4V_s} \quad (1)$$

and

$$\epsilon'' = \frac{V_c * f_0^2 * (1/(f_2^2 Q_2) - 1/(f_1^2 Q_1))}{4 * V_s} - \frac{(\epsilon' - 1)}{Q_0} \quad (2)$$

where

f_0, f_1 and f_2 = Resonant frequencies of the empty, with holder and with sample loaded cavity respectively.

and

Q_0, Q_1 and Q_2 = Quality factors of the empty, with holder and with sample loaded cavity respectively

V_c and V_s = Volume of the cavity and sample respectively.

The derivations are based on the lumped resonance circuit approximation. The resonance frequency of the cavity changes because of the change in the lumped capacitance due to the insertion of the sample. The sample is kept at the electric field maximum in the cavity.

2.2 Adjustable plunger cavity technique

A plunger waveguide is converted into a cavity by introducing a coupling hole in the entrance and shorting the other end with the calibrated plunger. The sample occupies the entire volume of the cavity. The frequency is kept constant and the length of the plunger cavity is changed. Hence several nodes appear as one increases the length of the cavity plunger. Whenever the length of the cavity equals the half integral multiples of the guide wavelength inside the medium, the plunger waveguide resonates. The distance through which the plunger is moved between two successive cavity nodes gives half of the wavelength (λ_d) of the microwave inside the medium. The measurement of reflected power at resonance gives the attenuation coefficient of the sample [3].

$$P_1 = 1 - \frac{1}{2\lambda_d} \left[\frac{\beta^2(1 - \exp(-2\alpha\lambda_d))}{2\alpha(\alpha^2 + \beta^2)} + \lambda_d \exp(-\alpha\lambda_d) \right] \quad (3)$$

where α is the attenuation constant to be calculated, λ_d the wavelength inside the medium measured, β the propagation constant, $2 * \pi / \lambda_d$ and ρ_1 the normalized reflected power at TE₁₀₁ mode.

2.3 Relaxation time measurement

Sobhanadri [5] and Gopalakrishna [2] have suggested two different techniques of measuring the relaxation time of binary mixture. Both the methods use single frequency concept. Sobhanadri's method requires the measurement of refractive index of the mixture as well as the complex dielectric permittivity. This method gives the dipole moment of the particular mixture directly and from that, the relaxation time can be calculated.

Gopalakrishna's method uses the concentration variation at single frequency. The derivations are based on the Debye's equation [6] for the complex dielectric permittivity as a function of frequency for a dilute solution of a polar compound in

a non-polar solvent and is given by

$$\frac{\epsilon^* - 1}{\epsilon^* + 2} = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} + \frac{4\pi n\mu^2}{9KT} \frac{1}{1 + i\omega\tau} \quad (4)$$

where n is the concentration of dipole molecules and ϵ^* is the complex dielectric permittivity, ω is the angular frequency of the microwave, τ is the relaxation time of the mixture, K is the Boltzman's constant and T is the temperature. Splitting ϵ^* into real and imaginary parts

$$\frac{\epsilon'^2 + \epsilon' + \epsilon''^2 - 2}{(\epsilon' + 2)^2 + \epsilon''^2} = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} + \frac{4\pi n\mu^2}{9KT} \frac{1}{1 + \omega^2\tau^2},$$

$$= x(\text{say}), \quad (5)$$

$$\frac{3\epsilon''}{(\epsilon' + 2)^2 + \epsilon''^2} = \frac{4\pi n\mu^2}{9KT} \frac{\omega\tau}{1 + \omega^2\tau^2},$$

$$= y(\text{say}). \quad (6)$$

Writing $(\epsilon_\infty - 1)/(\epsilon_\infty + 2)$ as P ,

$$x = P + y/\omega\tau. \quad (7)$$

For various low dilution mixtures, the values of x and y are calculated by measuring ϵ' and ϵ'' . The slope of the graph, x against y , gives the relaxation time. The slope observed is not a constant as expected, but varies with concentration. Hence, a graph between the relaxation time and concentration can be plotted.

3. Experimental procedure

The samples used here are all analytical grade samples and twice distilled before use. All the measurements are carried out at room temperature (27°C) and at 9.1 GHz frequency.

3.1 Fixed cavity perturbation

The experiments are carried out using a microwave bench consisting of an X-band Klystron (Varian X-13). The cavity used here is a reflection type TE₁₀₅ mode rectangular cavity with resonance frequency 9.15674 GHz. A specially designed sample holder is used to keep the sample at the electric field maximum in the cavity. To avoid the error in measuring the volume of the sample, a standardization procedure is adopted. The shift in resonance frequency with holder and with sample of known dielectric permittivity is measured. By this the constant $(V_c * f_0^2 / (4 * V_s))$ is calculated. The cavity resonance is plotted and the resonance frequency and the quality factor are noted for cavity with holder and with sample. Using these, the complex dielectric permittivity can be calculated.

3.2 Adjustable plunger cavity

A standard non-lossy sample, benzene or carbontetrachloride fills the entire cavity volume. The reflected power at a cavity resonance is noted. This serves as the reference

(zero) level for all the future power measurements. The maximum power flow into the cavity (P_0) is also noted. Now the sample liquid fills the cavity and the reflected power is monitored for various thicknesses of the sample. All the power measurements are normalized with respect to P_0 . The cavity resonances for the first two nodes are obtained. The distance moved between two successive nodes gives half the wavelength of the microwave (λ_d) inside the sample. The reflected power at resonance for the first node is noted as P_1 . Using (3), the attenuation coefficient can be calculated. The complex dielectric permittivity can be calculated from α and β .

4. Results and discussion

The binary mixtures of AN in BZ, CTC and CBZ are studied. The excess dielectric parameters in each case is plotted in figures 1, 2 and 5 respectively. Figures 3 and 4 describe the variation of dielectric parameters for the binary mixtures of DMF in BZ and CTC. The variation of dielectric parameters for the binary mixtures of CBZ in CTC is described in figure 6.

All the samples chosen are aprotic in nature. The excess parameters are calculated by the formula defined by Payne and Theodorou [7].

$$\Delta\epsilon_m^* = \epsilon_m^* - (X_1 \epsilon_1^* + X_2 \epsilon_2^*) \quad (8)$$

where ϵ_m^* is the dielectric parameter for the mixture, ϵ_1^* and ϵ_2^* are the values for pure components, and X_1 and X_2 are their respective mole fractions. For the ideal mixture, the excess parameter is zero, but real mixtures have finite values. The excess may be positive or negative depending on the complex formation.

For the aprotic binary systems, primary interactions will be dipole-dipole and dipole-induced dipole interactions. This is controlled by the molecular structure of the added component in the case of AN.

It is well-known from the conventional thermodynamic studies [1, 8] that AN-BZ and AN-CTC binary mixtures show positive excess heats, free energy and small negative excess volume. The excess functions are observed to be small for BZ mixtures than CTC mixtures. The excess heat is a measure of the number of hydrogen bonds or other electrostatic interactions broken as a result of formation of the binary mixture. The excess entropy is negative if some orientational ordering exists as a result of hydrogen bond formation or due to self association as in the case of AN. At higher concentration of AN, the excess entropy is negative. But on dilution, it becomes less negative. At around 0.3 to 0.4 mole fraction, the excess heat is positive and its value is maximum.

Kolling [9] had fit the non-linear variation of dielectric parameter with mole fraction at radio frequency (5 MHz) to get the correlation functions and dipolarities. Work on excess dielectric parameter at radio frequency is reported by Kolling [10] on AN. The excess functions clearly show a maximum in the mole fraction range 0.5-0.55.

The excess dielectric permittivity is associated with the polarization and loss is related to the molecular motions which are governed by complex forces of inter-molecular interactions. Thus the excess loss can be regarded as a parameter which reflects the entropy change in a binary system. Hence the observed excess dielectric parameters for AN-BZ and AN-CTC binary mixtures in the microwave region coincide well with the excess entropy data and RF data. A similar trend is also observed for DMF-BZ and DMF-CTC mixtures.

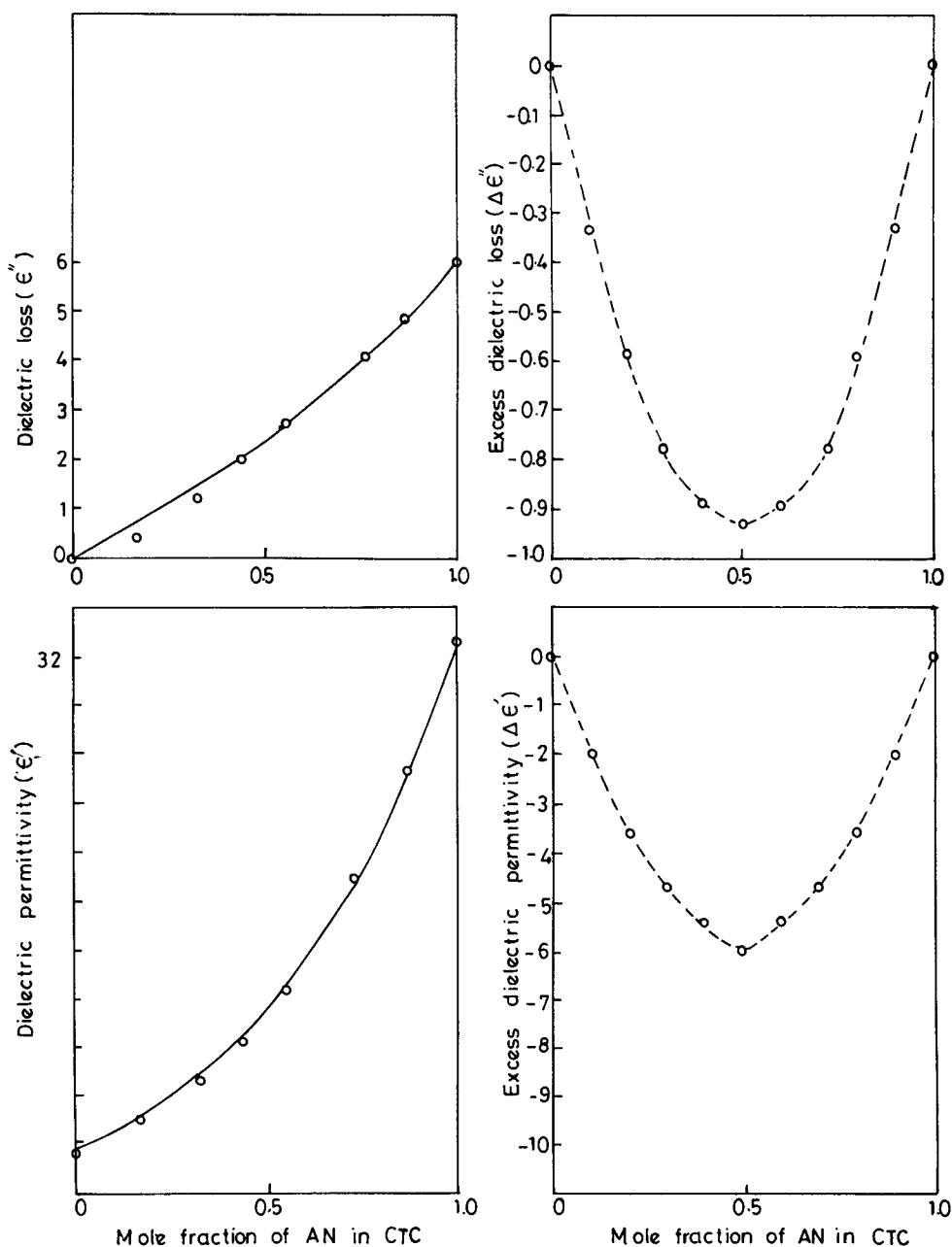


Figure 1. Dielectric permittivity, loss, excess dielectric permittivity and excess dielectric loss for AN-CTC system.

The excess permittivity for AN-CBZ system is negative whereas the excess loss is positive. But around 33 GHz, the excess loss is observed as negative [11]. It appears to be that the excess dielectric loss is zero for a microwave frequency between X band and Q band for all the binary mixture combination. It may be explained from the fact that the dielectric loss is observed as maximum around 21 GHz for pure CBZ whereas AN has the maximum loss around 33 GHz. For CBZ-CTC system, the

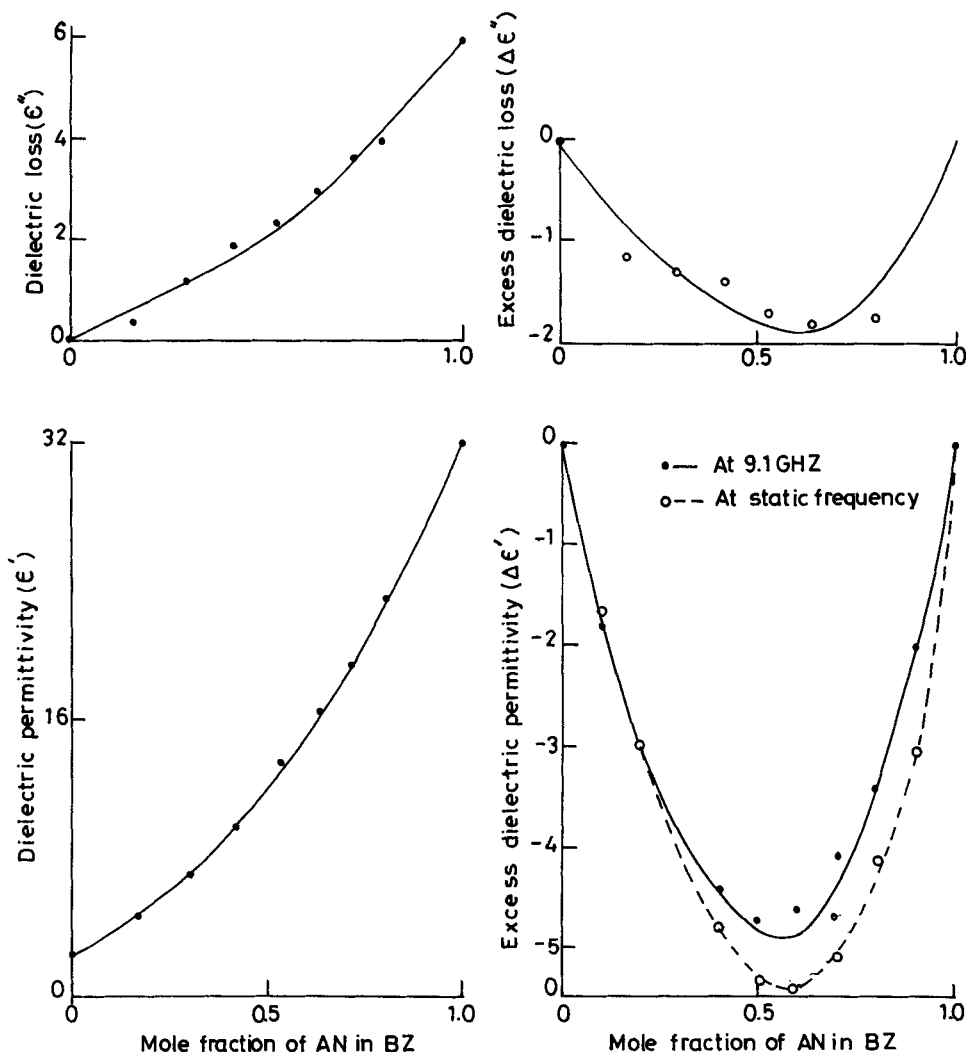


Figure 2. Dielectric permittivity, loss, excess dielectric permittivity and excess dielectric loss for AN-BZ system.

excess dielectric parameter is positive at 9.1 GHz reflecting the trend of AN-CBZ system.

One of the aprotic samples, AN is highly diluted in CTC and BZ and the relaxation time is measured using Gopalakrishna's method. This is shown graphically in figure 7. It is observed that the relaxation time tends to increase around 0.15 mole fraction in both cases. To verify this trend, the relaxation time is measured using conventional plunger technique by plotting Cole-Cole plots.

Though the cosolvents CTC and BZ are non-polar, these affect the relaxation time of the aprotic polar molecules. Even in the very dilute condition, the influence of CTC and BZ is not negligible. The hindrance of these non-polar solvents is at the maximum around 0.15-0.2 mole fraction and the magnitude is higher for CTC than BZ. The peak of the relaxation time may be attributed to the formation of stable complex mixture.

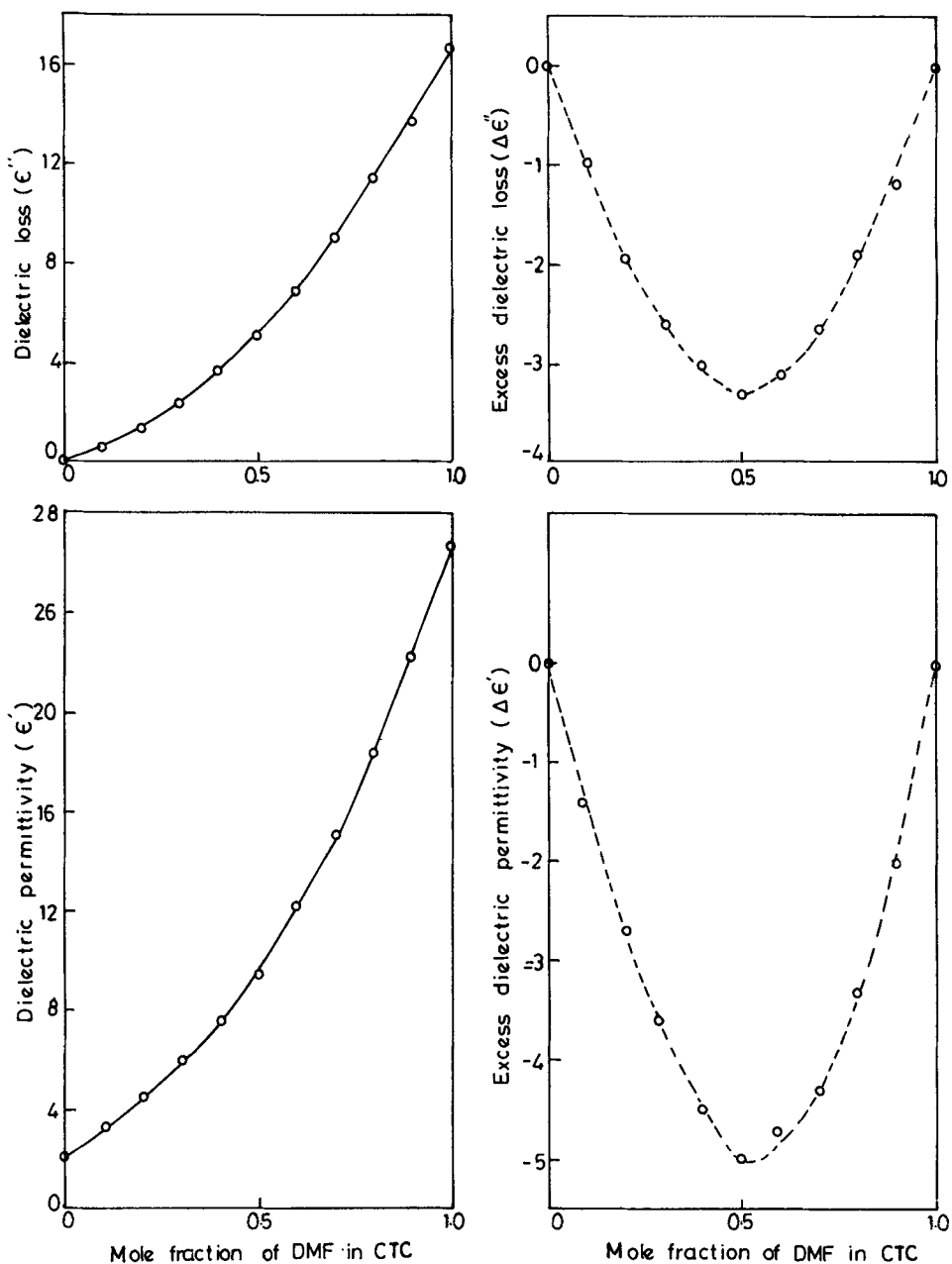


Figure 3. Dielectric permittivity, loss, excess dielectric permittivity and excess dielectric loss for DMF-CTC system.

It is generally accepted that correlation times from infrared, Raman and NMR relaxations are single particle in origin corresponding to auto-correlation functions. On the other hand, dielectric relaxation is a many molecule property and involves complex cross-correlation functions also. Tiffon *et al* [12] have shown from NMR studies of AN in CTC that the self association between AN molecules continue down to 0.2 mole fraction and below that the single particle (auto-correlation) times decrease

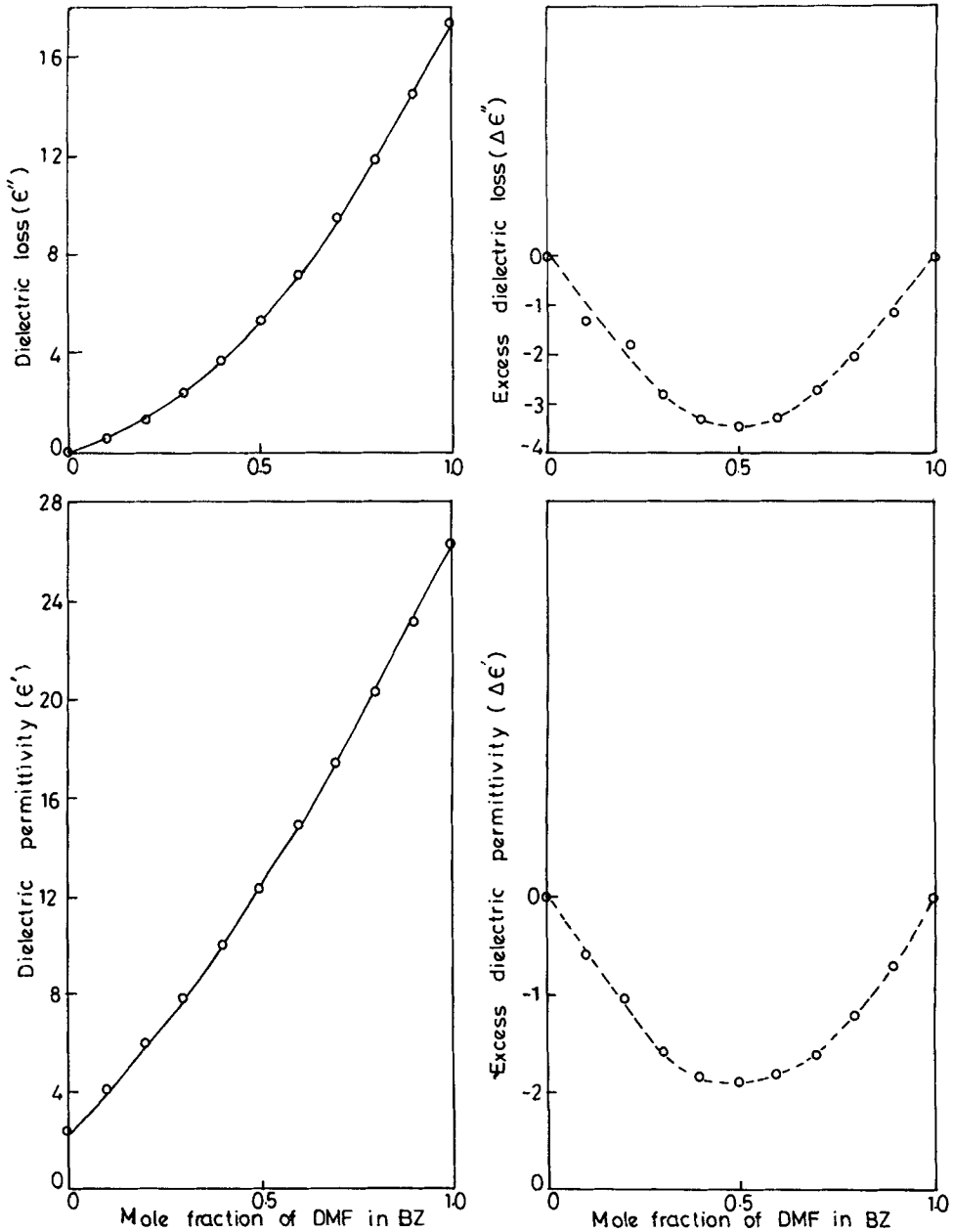


Figure 4. Dielectric permittivity, loss, excess dielectric permittivity and excess dielectric loss for DMF-BZ system.

drastically. This is consistent with the far infrared results of Knoesinger *et al* [13] who found that AN clusters remain in CTC down to 0.2 mole fraction. Evans [14] summarized these results and compared the molecular dynamics of AN from different techniques with the computer simulation calculations.

The higher sensitivity of the cavity perturbation technique enabled evaluation of the relaxation time even in the very dilute region as evident from figure 7 where the relaxation time is maximum around 0.15–0.2 mole fraction. From this it can be

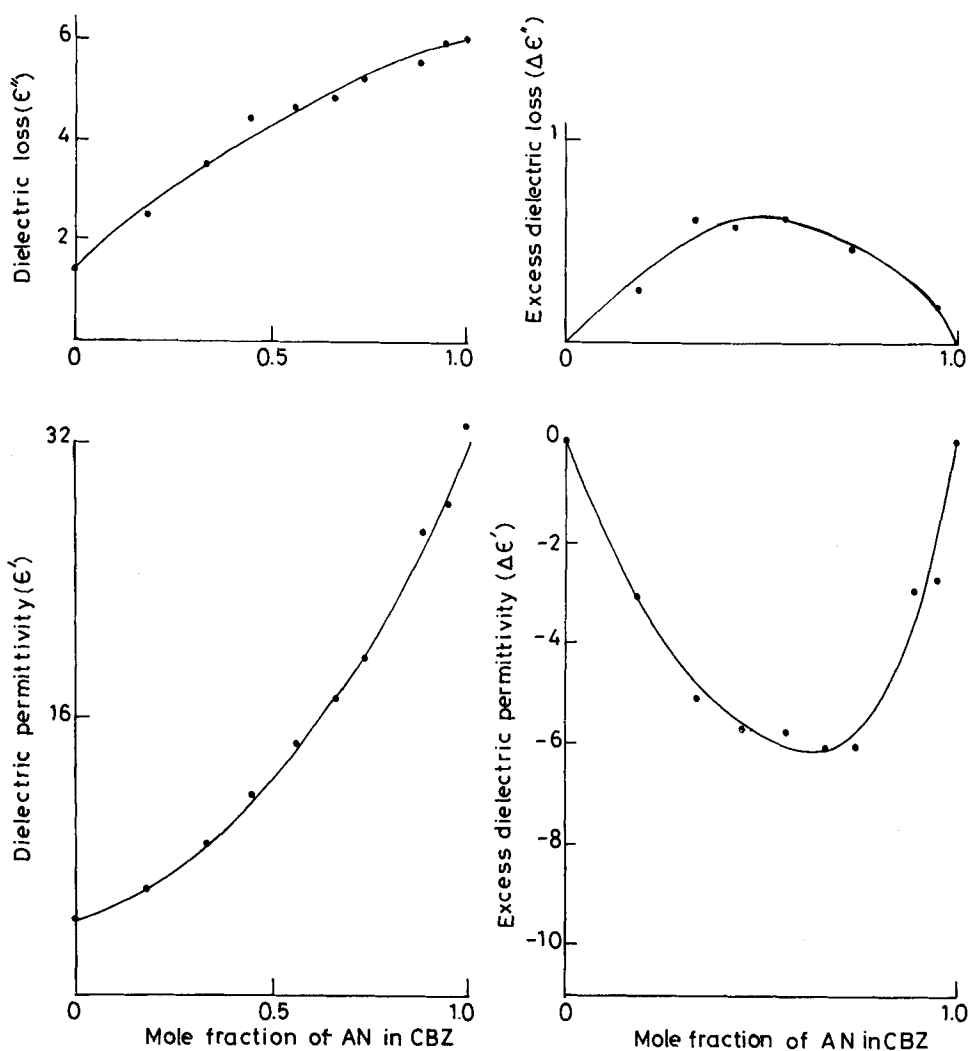


Figure 5. Dielectric permittivity, loss, excess dielectric permittivity and excess dielectric loss for AN-CBZ system.

inferred that self association and AN clusters remain in non-polar solvent down to 0.2 mole fraction.

5. Conclusion

The excess dielectric parameters at 9.1 GHz for the binary mixtures AN-CTC, AN-BZ, AN-CBZ, DMF-CTC, DMF-BZ and CBZ-CTC are studied using cavity perturbation and adjustable plunger cavity techniques. The excess dielectric loss reflects the excess entropy of the system. The observed excess parameters coincide well with the RF data for AN binary systems. The relaxation time measured for the highly diluted AN in CTC and BZ systems are studied using Gopalakrishna's method. The relaxation time is maximum around 0.15-0.2 mole fraction. The trend is verified using conventional plunger and Cole-Cole plot technique. The maximum in the

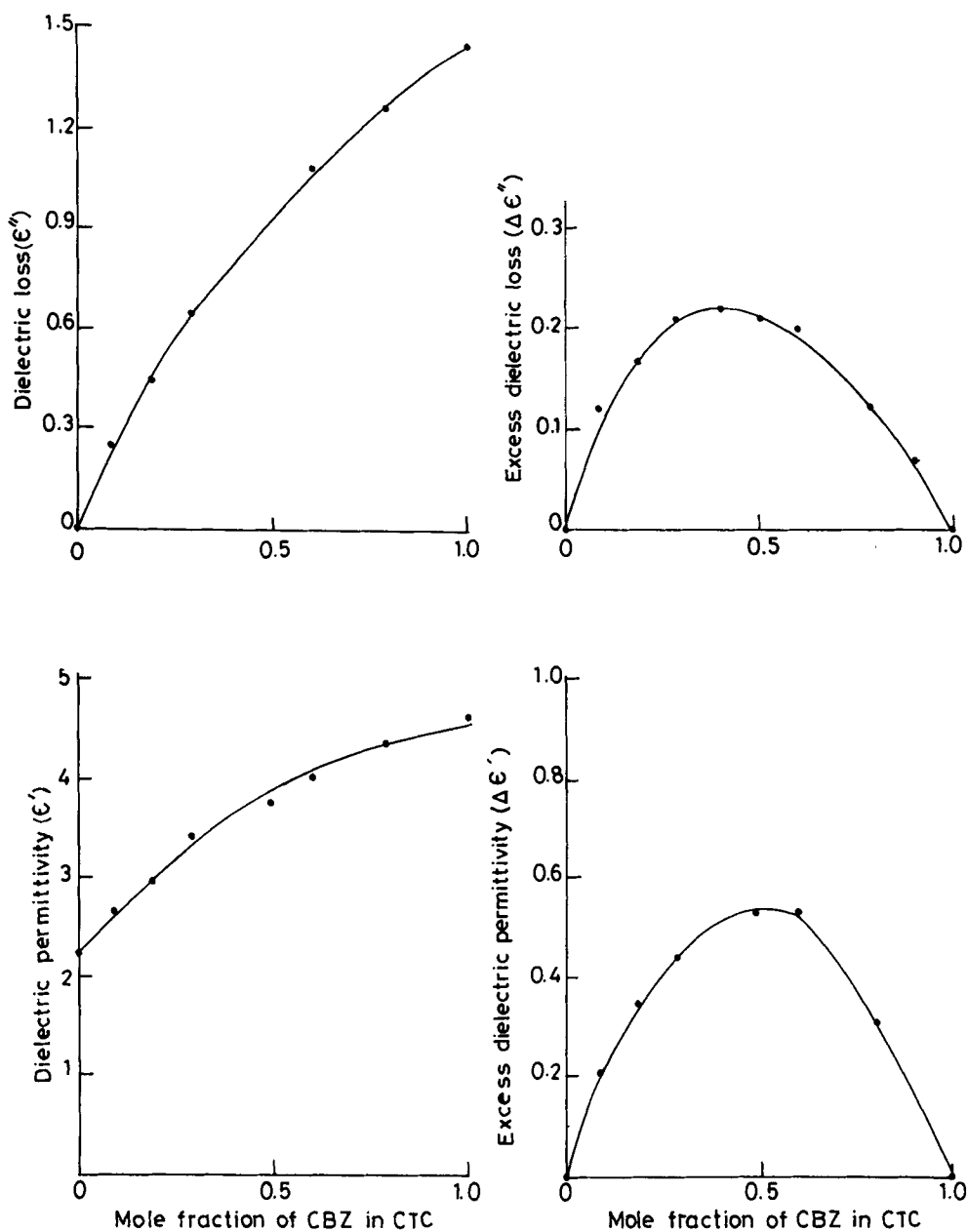


Figure 6. Dielectric permittivity, loss, excess dielectric permittivity and excess dielectric loss for CBZ-CTC system.

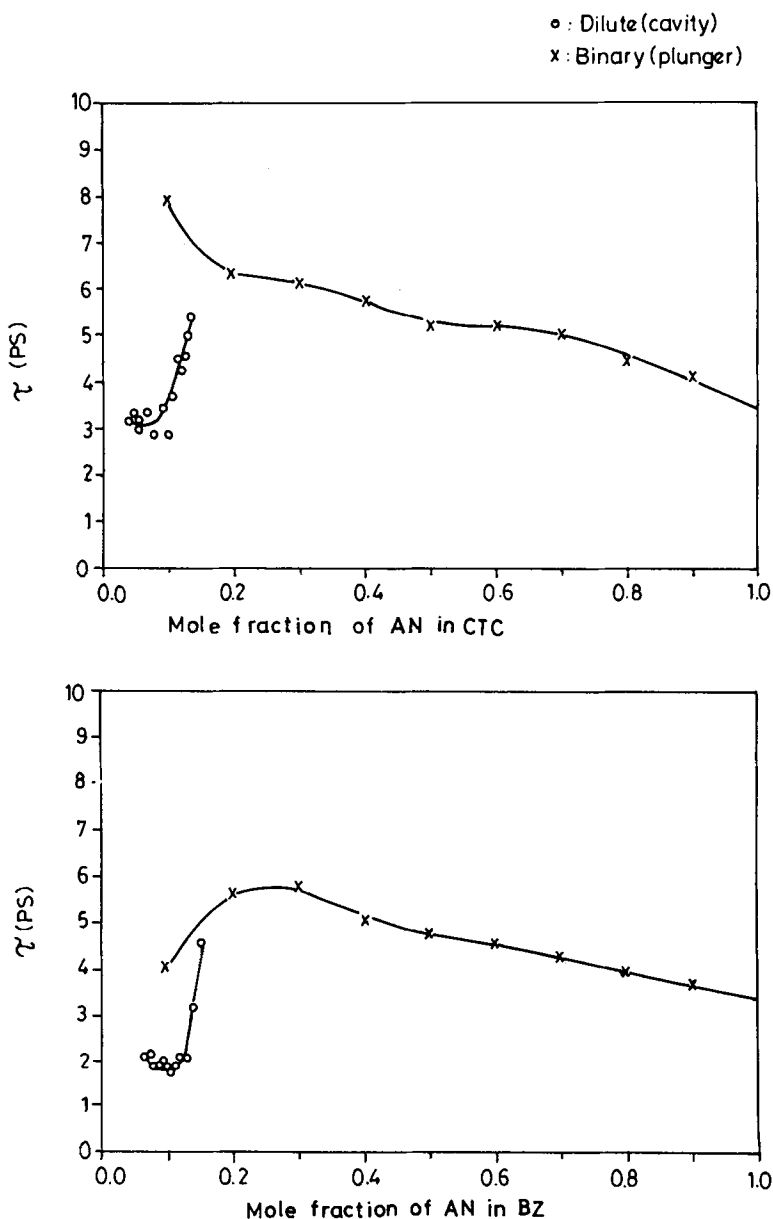


Figure 7. The relaxation time behaviour of diluted AN-CTC and AN-BZ systems.

relaxation time behaviour may be attributed to the formation of stable complex mixture even though the solvent is a non-polar sample. This variation of relaxation time also ensures the self association of AN down to 0.2 mole fraction in non-polar solvent.

Acknowledgments

One of the authors, VS, wishes to acknowledge CSIR, India for financial support in the form of a Senior Research Fellowship (NET). BS wishes to acknowledge UGC,

India for its support under the Quality Improvement Programme. The authors are thankful for the financial support in the form of an INDO-US project for procuring some of the experimental facilities.

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