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Microwave dielectric spectra and molecular relaxation in formamide–N,N-dimethylformamide binary mixtures

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ABSTRACT

The dielectric dispersion and absorption spectra of formamide (FA), N,N-dimethylformamide (DMF) and their binary mixtures are investigated in the frequency range of 500 MHz to 20 GHz at 30 °C in view of the organic synthesis by microwaves heating using amides solvents. The concentration dependent values of molecular reorientation relaxation times lower than that of the ideal mixing behaviour have been attributed to the cooperative dynamics of H-bonded FA–DMF structures. The molar ratio of stable adduct is 2:1 of FA to the DMF, which is determined from the concentration dependent excess static dielectric constant and the relaxation time plots of these binary mixtures. Electrode polarization effect and ionic conduction in FA and DMF were investigated from their dielectric dispersion spectra in the low frequency region of 20 Hz to 1 MHz.

1. Introduction

The broadband dielectric spectroscopy (BDS) covers nowadays the extraordinary spectral range from 10^{-6} to 10^{12} Hz [1–3], which enables researchers to characterize the complex dielectric function $\varepsilon^*(\omega) = \varepsilon' - j\varepsilon''$ of a variety of dielectric materials in relation to their structural conformation and the molecular dynamics. Dipolar organic solvents and their mixtures show the dielectric dispersion corresponding to molecular reorientation in the microwave frequency region [4–12]. The interactions of the microwaves (electromagnetic radiations) with polar solvents result the microwave dielectric heating, which is rapidly becoming an established procedure in synthesis chemistry [13–15]. The measure of a real part ε' is an indicative of dielectric material energy storing capability in the electric field, whereas the imaginary part ε'' is the absorbed electromagnetic energy by the material that's convert into the thermal energy by Joule heating effect. The ε' and ε'' of a polar solvent depends on the strength of intermolecular hydrogen bonding, and the heteromolecular H-bonded interactions in case of mixed solvents.

For the use of microwaves in organic synthesis, the selection of a suitable polarity (dielectric constant) and physical properties mixed solvent is required. The conformation of H-bonded heterogeneous complex structures of the mixed solvents by dielectric measurements has an importance as a force governing the formation of a variety of structures and their dynamics in the liquid phase [4–19]. Among the organic polar solvents, the amides have high polarity, large liquid range, and strong solvating power due to their H-bond donor and acceptor capability. Besides these properties, the –CO–NH– linkage in amides is an important functional group for their use as solvent in the analytical chemistry, biochemistry, pharmaceutical preparation and material synthesis [20,21].

In view of the facts discussed above, the present paper reports the ε' and ε'' spectra of the binary mixtures of formamide (FA) and N,N-dimethylformamide (DMF) over the microwave frequency range from 500 MHz to 20 GHz at 30 °C in relation to their molecular conformations. The low frequency dielectric spectra of FA and DMF in the frequency range of 20 Hz to 1 MHz are also performed to confirm the effect of electrode polarization and ionic conduction mechanism in their pure liquid state.

2. Experimental details

2.1. Materials

Grade reagent formamide (FA) and N,N-dimethylformamide (DMF) were obtained from Loba Chemie of India. Binary mixtures of these polar liquid were prepared at eight different concentrations over the entire mixing range at room temperature, and by weight

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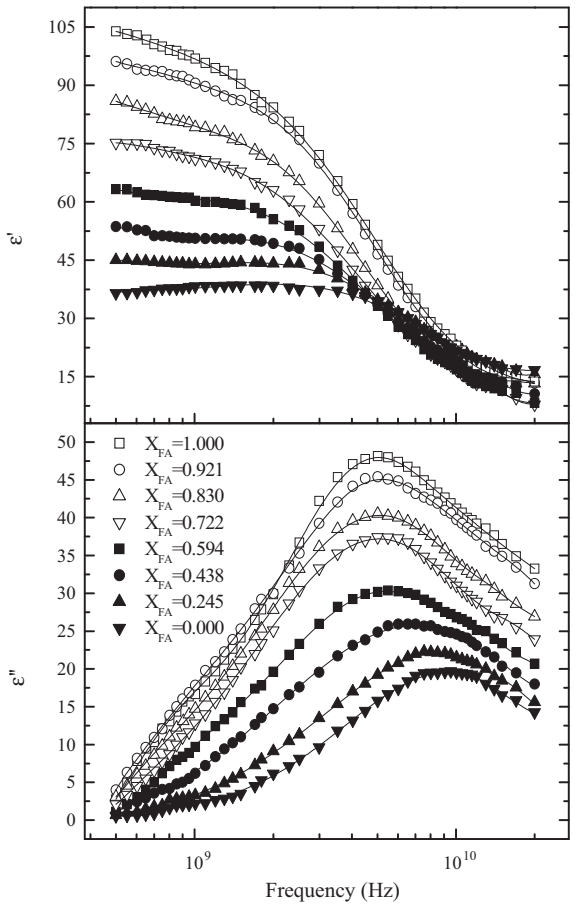

Fig. 1. The microwave dielectric spectra (ε' and ε'') of FA–DMF binary mixtures of varying X_{FA} at 30 °C.

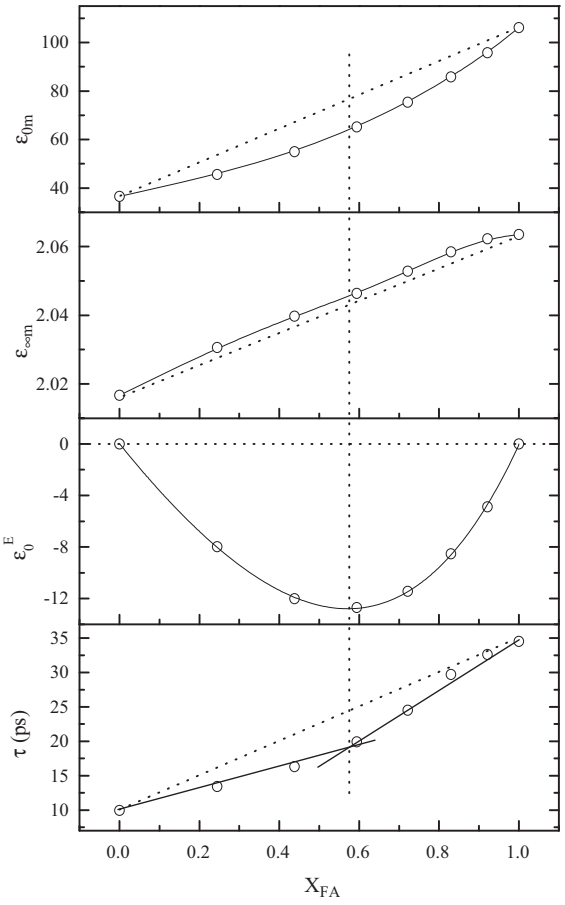

Fig. 2. Plots of various dielectric parameters of FA–DMF binary mixtures against X_{FA} at 30 °C. The dotted lines corresponds to the ideal mixture behaviour were drawn using the dielectric parameter values at X_{FA} = 0 and 1. Vertical dotted line at $X_{FA} \sim 0.6$ corresponds to the maximum deviation in the dielectric parameters from the ideal behaviour.

measurements the mole fractions of the mixture constituents were determined.

2.2. Dielectric measurements

The frequency dependent ε' and ε'' values of FA–DMF binary mixtures in the frequency range of 500 MHz to 20 GHz are measured using HP 8510 C vector network analyzer and the HP 8507B dielectric probe. The measured ε' and ε'' spectra of the FA–DMF mixtures at different mole fraction of FA, X_{FA} are plotted in Fig. 1. Agilent 4284A precision LCR meter along with Agilent 16452A liquid dielectric test fixture is used for the measurement of ε' and ε'' values in the low frequency range from 20 Hz to 1 MHz. The ε' values at 1 MHz are considered as static dielectric constant ε_0 of FA and DMF, and ε_{0m} of the FA–DMF binary mixtures. The ε_{0m} values of FA–DMF mixtures against mole fraction of FA, X_{FA} are plotted in Fig. 2. The measurement accuracy of ε_0 is ±0.3%, which is estimated from the calibration of the dielectric fixture using the standard liquids. The low frequency spectra of ε', loss tangent $\tan\delta = \varepsilon''/\varepsilon'$ and real part of ac conductivity $\sigma' = \omega\varepsilon_0\varepsilon''$ of the FA and DMF are plotted in Fig. 3. The optical frequency limiting values of dielectric constant, ε_∞ of the FA and DMF, and $\varepsilon_{\infty m}$ of the FA–DMF mixtures is taken as square of refractive index n_D, which is measured with an Abbe refractometer at wavelength of sodium-D light. The $\varepsilon_{\infty m}$ values of these mixtures are also plotted in Fig. 2. The maximum measurement error in ε_∞ is ±0.02%. All measurements have been made at 30 °C and the temperature is controlled thermostatically using Thermo-Haake DC10 controller.

3. Results and discussion

The static dielectric constant ε_0 values of FA and DMF are 106.14 and 36.55, respectively, at 30 °C, which confirms the large polarization of FA as compared to that of the DMF molecules. Fig. 1 shows that the ε' values of FA, DMF and their binary mixtures have dielectric dispersion in the microwave frequency region. The large ε'' values are an evidence of the conversion of microwaves electromagnetic energy into the heat energy by these solvents. The ε'' spectra of FA–DMF mixtures have peak in the microwave frequency region (Fig. 1). The frequency f_p corresponds to the ε'' peak represents the molecular reorientation relaxation time $\tau = (2\pi f_p)^{-1}$, which have shift towards high frequency region with the decrease of FA concentration in the mixture. The concentration dependent τ values of FA–DMF mixtures are represented by two straight lines with their intersection at $X_{FA} \sim 0.6$ (Fig. 2). The value of Kirkwood correlation factor g of the FA is 2.22, which is an evidence of its H-bonded linear structures with parallel dipolar alignments, whereas unity g value of DMF infers the absence of H-bond molecular interactions in the pure liquid state [19]. The τ value of FA (34.51 ps) being much higher than that of the DMF (9.95 ps), confirms large hindrance to the molecular reorientation of FA molecules in their H-bonded molecular structures. Although the size of DMF molecule is bigger than that of the FA molecule, yet higher τ value of FA, as compared to the DMF, reveals that the H-bonded molecular interactions in FA structures mask the effect of molecular size in regard to their molecular reorientation dynamics.