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Electrode polarization and ionic conduction relaxation in mixtures of 3-bromoanisole and 1-propanol in the frequency range of 20 Hz to 2 MHz at different temperatures

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ABSTRACT

The complex relative dielectric function $\varepsilon^*(\omega) = \varepsilon' - j\varepsilon''$ of binary mixtures of 3-bromoanisole (3-BA) with 1-propanol (1-PrOH) of varying concentration have been measured using precision LCR meter in the frequency range 20 Hz to 2 MHz at different temperatures (303.15 K, 313.15 K, 323.15 K and 333.15 K). The electric/dielectric properties of the liquid samples are represented in terms of complex relative dielectric function $\varepsilon^*(\omega)$, complex electric modulus $M^*(\omega)$, complex electrical conductivity $\sigma^*(\omega)$ and complex impedance $Z^*(\omega)$. All of these presentations are used to explore various processes contributed in the electrical/dielectric properties of the mixtures of 3-BA and 1-PrOH. Effects of concentration variation of constituents of the binary liquid system and also of temperature on the various relaxation processes are discussed.

1. Introduction

One of the most powerful techniques for examining the underlying physics of liquid mixture systems and for exploring the molecular dynamics of liquids, characterized by inter and intra molecular structures that vary rapidly with time, is dielectric spectroscopy. In dielectric spectroscopic study complex permittivity spectra of the material under study is obtained over a range of frequencies of electrical signal at a fixed temperature or over a range of temperatures.

In recent past dielectric spectroscopy studies of dipolar liquids in the static permittivity region (frequency region of few Hertz to few MHz), where dielectric relaxation due to dipolar rotation of molecules is absent, has drawn attention of many researchers [1–13]. In this frequency region the polar liquids exhibits dielectric dispersion due to electrode polarization and ionic conduction relaxation processes due to the presence of volatile ionic impurities (natural impurities) or due to the added ions. In the highly polar liquids presence of ionic impurities, even in their pure form is confirmed by many researchers [1,3,7,12–14]. These ions strongly contribute to the dielectric behaviour of polar liquids in the low frequency region (static permittivity frequency region). Electrode polarization often is an undesirable effect in dielectric relaxation spectroscopy which makes it difficult to understand the slow dipolar relaxation processes in moderately to highly conducting materials [15–17]. However, if low frequency region complex permittivity data, which are influenced by electrode polarization effect, are appropriately modeled it can be used to determine the thickness (Debye length) of the ion built up at the electrode surface. This knowledge can be exploited to determine the concentration of the ions in the medium. Importance of study of dielectric properties of polar liquids in low frequency region from the chemical, industrial and technological point of view is well emphasized in references [4,5,13].

3-Bromoanisole is one of the derivatives of anisole, which is the simplest aromatic compound to which ether group is linked. Anisole has wide applications in perfumery, chemical synthesis, agrochemicals etc. [18,19]. 3-BA is used as intermediate in pharmaceutical field to produce drugs like Tramadol [18]. 1-Propanol has exceptional importance in chemical reaction, cosmetic, plastics industry, bio-fuel as well as in pharmaceutical industries [20]. Wide range of chemical and pharmaceutical applications has prompted us to select 3-BA and 1-PrOH for this study. Recently, we reported experimental data of static permittivity measured at 2 MHz and permittivity at optical frequency, which was taken as square of refractive index measured at optical frequency, of the binary mixtures of 3-BA and 1-PrOH over a wide range of concentrations at four different temperatures [21]. This study provided information about the modification of molecular structures and dipolar orientation due to mixing of 3-BA and 1-PrOH. Numerous studies on the dielectric and physical properties of the binary mixture of aromatic ether with different polar/nonpolar solvents have been reported [8,19] but no attempt is made, so far to study dielectric properties of binary mixtures of 3-BA and 1-PrOH in the low frequency regime (20 Hz to 2 MHz) where electrode polarization effect and ionic conductivity

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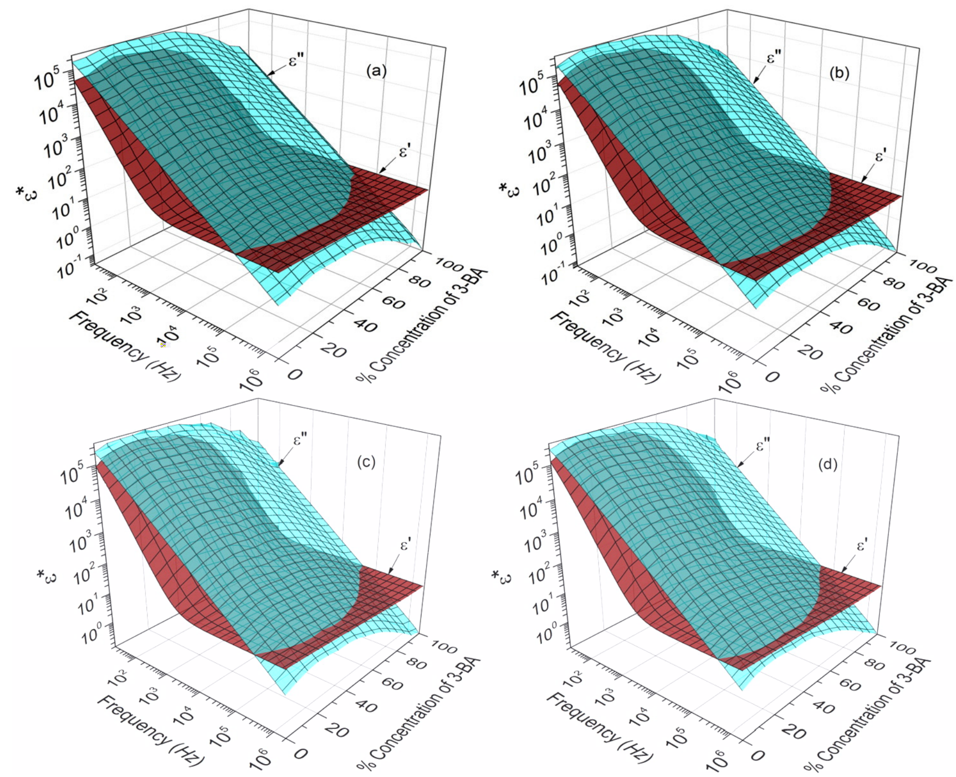

Fig. 1. Frequency dependence of the real and imaginary part of relative dielectric function ε^* for 3-BA, 1-PrOH and mixtures of 3-BA + 1-PrOH at (a) T = 303.15 K, (b) T = 313.15 K, (c) T = 323.15 K, (d) T = 333.15 K.

relaxation effects are dominant. Objective of the present investigation is to study the dielectric behaviour in the presence of natural ionic impurities in 3-BA and 1-PrOH in their pure form as well as on their binary mixtures of varying concentrations, through dielectric spectroscopy in the static frequency regime (20 Hz to 2 MHz) over a limited temperature range (T = 303.15 to 333.15 K). In the present paper complex permittivity spectra of 3-BA and 1-PrOH over complete concentration range at four different temperatures are presented. From the measured complex permittivity several other functions such as complex dielectric modulus, complex impedance and complex ac conductivity are derived. Although these functions are derived from the same experimental data, they represent different aspects of electrical properties of studied system.

2. Experimental section

2.1. Materials and sample preparation

3-Bromoanisole with 99% purity (minimum assay (GC)) was supplied by Spectrochem Pvt. Ltd. (India) and 1-propanol with 99.5% purity (minimum assay (GC)) was supplied by High Purity Laboratory Chemical Pvt. Ltd. (India). Both compounds were used without any further purification. The solutions of 3-BA with 1-PrOH were prepared at 16 different concentrations by volume.

2.2. Measurements

An Agilent E 4980A precision LCR meter with a four terminal liquid dielectric test fixture (Agilent 16452A) was used for the capacitance and resistance measurement in the frequency range 20 Hz to 2 MHz with a standard uncertainty of 0.04 [22]. The temperature was maintained using a thermostat (MIC Fourtech; India) with standard uncertainty of 0.1 K.

3. Evaluation of different parameters

The complex dielectric constant $\varepsilon^*(\omega)$ of the material is determined using the equation [22].

$$\varepsilon^*(\omega) = \varepsilon' - j\,\varepsilon'' = \alpha\left(\frac{C_p}{C_0} - j\frac{1}{\omega C_0 R_p}\right) \tag{1}$$

where $\omega = 2\pi f$ is the angular frequency, C_0 is the capacitance of empty measuring cell, C_p and R_p are the parallel capacitance and resistance of the measuring cell with sample and α is the corrective co-efficient of the cell. It eliminates the effect of stray capacitance during the evaluation of the value of complex dielectric function [22].

The general relation between the real (ε') and imaginary (ε'') parts of the dielectric permittivity and those of the electric modulus, the

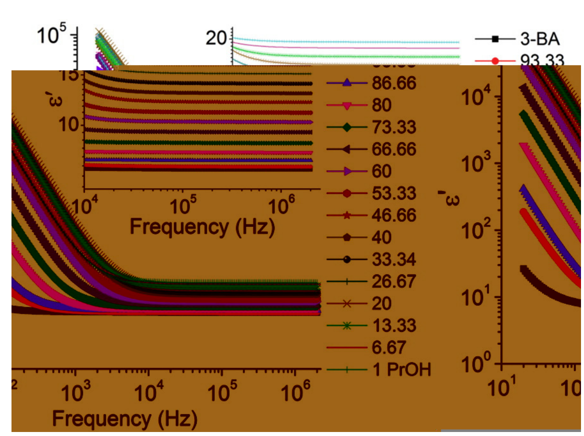

Fig. 2. Plots of ε′ versus frequency for different concentration of 3-BA in 1-PrOH at 303.15 K.