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Structural and dynamics study of polar liquid mixtures by dielectric and FTIR spectroscopic characterizations

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Highlights

•Dielectric constant decreases with increase in temperature and percentage of BENZ.

•Excess properties shows existence of intermolecular association in binary mixture.

•Temperature dependence of relaxation time described by Arrhenius plot for ACN-BENZ.

•Effective Kirkwood correlation factor shows antiparallel alignment of dipoles.

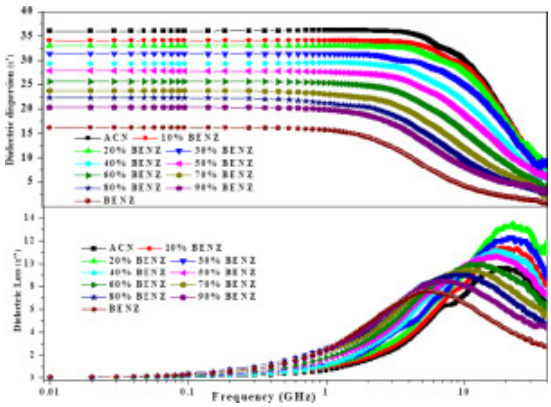
•FTIR spectra shows shifting towards lower wavenumber with increase in BENZ in ACN.

Abstract

Dielectric Permittivity Spectra of the binary mixture of Acetonitrile (ACN) with Benzaldehyde

(BENZ) have been studied at 11 different concentrations in the frequency range of 10MHz–50GHz for four different temperatures (10°C, 15°C, 20°C and 25°C) using TDR technique. The binary system of ACN-BENZ has been selected to understand the effect of nitrile and aldehyde group on the dielectric parameters and intermolecular interaction. Static Dielectric Constant (ε_0), Relaxation Time (τ) are obtained for above mentioned temperatures using nonlinear least squares fit method. Density (ρ) and Refractive Index (n_D) are also obtained for 30°C temperature. These parameters are used to calculate the Excess Static Dielectric Constant (ε_0^E), Excess Inverse Relaxation Time $(1/\tau)^E$ and Excess Molar Volume (V_m^E) and are fitted to Redlich-Kister equation. The departure in the excess parameters expresses the strength of the molecular connectivities and the existence of intermolecular interaction between unlike molecules. Kirkwood correlation factor, Bruggeman factor and thermodynamic parameters are studied to understand the information about the molecular interactions and orientation behaviour of dipoles after intermolecular interaction. The study of Fourier Transform Infrared Spectroscopy has been carried out to support the dielectric characterization and confirms the intermolecular association between ACN-BENZ binary system.

Graphical abstract



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Introduction

Dielectric relaxation spectroscopy is an effective tool to explore the structural and dynamics of the liquids and the nature of intermolecular interactions at microwave frequency [[1], [2], [3]]. This is used to study the polar molecules and its variation with respect to the interaction with the neighbouring polar as well as non-polar molecules. FTIR spectroscopy is used to study the nature and type of intermolecular interactions that are effective in liquid mixtures.

Several binary mixtures are studied extensively to investigate and interpret the medium effects in chemical reactions and molecular interactions [[4], [5], [6], [7], [8], [9], [10], [11], [12], [13]]. The

binary system of ACN-BENZ has been selected to understand the effect of nitrile group with the formyl group of aldehyde.

The acetonitrile (ACN) liquid is non-hydrogen bonded (aprotic) polar liquid with large value of dipole moment. It is simplest organic nitrile which contains one methyl group and cyanide group i.e. carbon atom attached to nitrogen atom by a triple covalent bond. The nitrogen is very electronegative and the electrons in the triple bond are very easily pulled toward the nitrogen end of the bond. The acetonitrile will interact with other liquids through long-range forces like dipole-dipole interactions. The dielectric data [[14], [15], [16], [17], [18], [19]] shows that dipoles of acetonitrile molecules have a tendency to remain antiparallel in liquid state. The importance of the ACN molecule lies in its technological implications and industrial applications as a solvent for the manufacture of pharmaceuticals and photographic film. Aldehydes undergo many different nucleophilic addition reactions. This is because of the positive carbon atom of aldehyde molecules, which always has one bond attached to the small hydrogen atom; and is susceptible to attack by a nucleophilic reagent. Benzaldehyde (BENZ) is a polar aromatic aldehyde bearing a single formyl group i.e. consisting of a carbon atom double-bonded to oxygen atom also bonded to hydrogen atom. The oxygen with non-bounding electron pairs makes aldehydes hydrogen bond acceptor and increases their water solubility relative to hydrogen. It is mostly used in the synthesis of other organic compounds, ranging from pharmaceuticals to plastic additives and it's important in processing of perfumes and flavoring components [26].

A survey of the literature shows that a few workers [11,12,[20], [21], [22], [23], [24], [25], [26]] have tried to investigate some binary systems taking nitriles as one of the constituent components in the binary mixtures. We have also studied the binary mixtures by taking nitrile as one of the component with Chlorobenzene [27] and Bromobenzene [28] at 30°C temperature using pulse width measurement technique. Refractive index, density and their excess properties study of acetonitrile with dimethylformamide, dimethylsulphoxide and 1,4-dioxane have been reported by El-Dossoki at different temperatures [20]. Roy et al. studied the physical properties and excess properties of the nitrile with aldehydes at four different temperatures [23]. Rana et al. [26]. studied the dielectric constant, density and their excess parameters for the binary mixture of Benzaldehyde with Methanol at 293.15K–323.15K. They have also reported the effective Kirkwood correlation factor and Bruggeman factor to understand the dipole orientation under the influence of applied electric field and the existence of intermolecular interaction. The study of FTIR spectra for various molecules has been reported in several articles to understand the molecular structure and molecular interactions [[10], [11], [12], [13]]. Karthick et al. studied the dielectric and FTIR spectroscopic characterizations to understand the molecular association of binary mixture of toluene with butyronitrile [11].

In present work, study of interaction in Acetonitrile (ACN) with Benzaldehyde (BENZ) mixtures over the frequency range of 10MHz–50GHz for 11 concentrations and four different temperatures (10°C, 15°C, 20°C&25°C) have been carried out using Time Domain Reflectometry (TDR) technique. Physiochemical properties such as Density (ρ) and Refractive index (n_D) are estimated at 30°C

temperature. The dielectric parameters such as static dielectric constant (ε_0), relaxation time (τ) of these binary systems were obtained. Using these parameters, Excess parameters, Effective Kirkwood correlation factor (g^{eff}), Bruggeman factor (f_B) thermodynamic parameters viz., enthalpy of activation (ΔH) and entropy of activation (ΔS) have been determined related to molecular interactions. The study of FTIR spectra has been carried out to support the dielectric characterization and confirms the intermolecular association between ACN-BENZ binary system.

Section snippets

Materials and method

Acetonitrile and Benzaldehyde were obtained commercially with 99.0% purity Merck Pvt. Ltd. Mumbai, India and were used without further purification. The solutions were prepared at 11 different volume percentages of Benzaldehyde in Acetonitrile in step of 10% at room temperature. The concentrations were prepared for 5 ml solution using micropipette at room temperature assuming ideal mixing behaviour, within 0.02% error limit.…

TDR setup and data acquisition

The dielectric spectra were obtained by the Time Domain Reflectometry…

Results and discussions

The standard (literature) physical properties of ACN and BENZ are shown in Table 1. The experimental values of Dielectric constant, Relaxation time, asymmetric distribution parameter and effective Kirkwood correlation factor at different temperatures and Density and Refractive index at room temperature of ACN-BENZ mixture are shown in Table 2a, Table 2b(a) and (b).

Measurements of the complex spectra i.e. dielectric dispersion (ε') and dielectric loss (ε'') were carried out over a frequency range …

Conclusions

As from the above results it can be concluded that-

- The dielectric complex spectra of binary mixtures of Acetonitrile with Benzaldehyde confirms that there is large possibility of variations observed in the homo-molecular clusters of ACN-BENZ mixtures, due to molecular interaction between ACN and BENZ molecules.…
- The dielectric parameters (ε_0) and (τ) show the systematic change with the concentration and temperature.…

- The excess static dielectric constant is positive for all concentrations and…

…

Acknowledgements

The financial support from University Grant Commission New Delhi, under the special Assistance Programme (SAP), is thankfully acknowledged (F.530/16/DRS-I/2016 SAP-II Dated 16 April 2016) and we are also thankful to School of Physical Sciences, Swami Ramanand Teerth Marathwada University, Nanded, for providing TDR facility for dielectric characterization. We are also grateful to Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad for providing the FTIR spectroscopy…

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Self and hetero-association in Benzaldehyde/Quinoline – Formamide solutions: Time Domain Reflectometry studies

2024, Journal of Molecular Liquids

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Investigation on interaction of quinoline with primary alcohols: An understanding on dielectric dispersion and relaxation dynamics over a wide frequency regime

2023, Journal of Molecular Liquids

Citation Excerpt :

…The detailed data analysis from the reflection coefficient is well explained in our earlier publications [24–28]. The advanced level of TDR with precise measuring capability of 10 MHz-50 GHz working principle and determination of complex permittivity were explained in detail by various authors [29–31]. Density and viscosity of quinoline complex were measured at ambient conditions (303 K and 0.1 MPa).…

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Dielectric spectroscopy and molecular dynamic simulation study of binary mixtures of benzaldehyde and methanol at 303.15 K

2023, Journal of Molecular Liquids

Citation Excerpt :

…Thus, it will be interesting to study the molecular structures and molecular dynamics of the binary mixtures of BZ and MeOH over the entire concentration range. From the literature survey, it is found that BZ [28–32] and MeOH [33–37] have been studied separately; however, the dielectric and molecular dynamic studies of mixtures of BZ and MeOH with varying concentration have not been reported yet, except our recent studies of dielectric properties and its allied parameters for the binary mixtures of BZ and MeOH [38,39]. These investigations revealed the presence of various molecular interaction, relaxation processes and orientation behavior under the effect of applied electric field, prompting the need for more information to support such reasoning.…

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Heteromolecular H –bond interaction forces and dielectric parameters: Time domain reflectometry studies

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> …DMSO also is a very important solvent being used in chemical reactions and has applications in biochemical and pharmacological technology [16]. Both AN and DMSO have been reported as aprotic molecules [13,15,16] in some of the articles in literature which is not true. Because their proton donating nature has been confirmed [17,18] through the participation of AN/DMSO methyl hydrogens in non-classical H – bond interactions.…

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Molecular interaction in binary mixtures of 3-Bromoanisole and methanol: A microwave dielectric relaxation spectroscopy and molecular dynamic simulation study

2021, Journal of Molecular Liquids

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> …This is due to the transition of parallel aligned molecular aggregates to the antiparallel aggregates in the mixed state, reducing the static permittivity. The static dielectric permittivity of a material is mainly dependent on the dipole moment and the number of molecules per unit volume [66]. It is observed that with rise in temperature there is reduction in the value of static permittivity.…

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