Dielectric relaxation of acetonitrile in benzene solution from microwave absorption studies

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The dielectric constant \( \varepsilon' \) and dielectric loss \( \varepsilon'' \) for dilute solutions of acetonitrile (CH\(_3\)CN) in benzene have been measured at 10.04 GHz at different temperatures (25, 30, 35 and 40 °C) by using standard microwave techniques. Following the single frequency concentration variational method suggested by Gopala Krishna, the dielectric relaxation time \( \tau \) and dipole moment \( \mu \) at various temperatures have been calculated. It is found that, dielectric relaxation process can be treated as the rate process, just like the viscous flow. Based upon above studies, monomer structure for CH\(_3\)CN in benzene solution has been inferred. The presence of solute-solvent association in benzene solution has been proposed. Energy parameters for the dielectric relaxation process of CH\(_3\)CN in benzene at different temperatures have been calculated and compared with the corresponding energy parameters for viscous flow.

1 Introduction

Acetonitrile (CH\(_3\)CN) is recognized as the non-aqueous dipolar aprotic solvent\(^1\). It has an intermediate dielectric constant \( \varepsilon=36 \) and high dipole moment\(^2\) \( \mu=3.370 \) D. It has very low basicity, and virtually negligible acidic properties. Because of these properties, it is used in a wide variety of reactions, including nucleophilic substitutions, oxidation, reduction, and organometallic reactions. In the presence of crown ethers, it is used for the generation of naked anions from their salts\(^3\). Acetonitrile serves as a good non-aqueous solvent for chemical reactions and for the studies of physical properties of solutes. The employment of acetonitrile in the recovery of Cu\(^+\), Ag\(^+\) and Au\(^+\) from ores or scrap metals is one of the striking examples of the use of non-aqueous solvents in solvometallurgy\(^4\). Acetonitrile has also been used as the important constituent of binary mixtures of the required characteristics\(^5\). This molecular aspect of CH\(_3\)CN motivated the authors to study the molecular behaviour of CH\(_3\)CN in benzene. Recently, the study of dielectric relaxation of pure and binary mixtures of polar molecules from microwave absorption data has raised great interest to understand solute-solvent and solute-solute type of associations in non-polar medium\(^6\)\(^-\)\(^9\). Dielectric relaxation data obtained from microwave absorption studies is expected to throw light on solute-solvent type of molecular associations present in the solutions as microwave data is sensitive to weaker molecular interactions. The present paper is concerned with the dielectric relaxation studies of CH\(_3\)CN in benzene at different temperatures (25, 30, 35 and 40 °C) for microwave absorption studies at 10.04 GHz. It is found that, CH\(_3\)CN occur in monomer form in the benzene solution. The presence of solute-solvent association is predicted. Dielectric relaxation process of CH\(_3\)CN in benzene can be treated as rate process just like the viscous flow\(^7\).

2 Experimental Details

The reagent of CH\(_3\)CN (Sisco Research Laboratories Ltd, Bombay) was kept at 4Å molecular sieves for about 10-14 hr with occasional shaking. It was then distilled through a long vertical column over phosphorus pentoxide (P.O\(_5\), E. Merck, Bombay). The middle fraction was collected for use. Benzene (A.R. 99.7% pure, from Central Drug House Pvt. Ltd, New Delhi) was dried by refluxing over freshly cut sodium metal for 6-8 hr and distilled through a long, vertical fractionating column. The middle fraction of the distilled benzene was used. The x-band microwave bench (frequency=10.04 GHz) was used to measure wavelengths in the dielectric and voltage standing
wave ratio (VSWR). The experimental techniques of Arawatia used by Sharma & Sharma for microwave measurements were used. A set of dilute solutions of (CH$_3$CN) in benzene was prepared and all the measurements were made at (25, 30, 35 and 40 °C), by circulating thermostated water around the dielectric cell. The temperature control of the thermostat (MLW Bauehie U) was ±0.05 °C. The precision and working of the experiment was tested by measuring dipole moment of purified acetonitrile. The viscosities and densities of the solution were measured by the ubbelohde viscometer and sealel type of pycnometer respectively.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Weight fraction in benzene</th>
<th>ε'</th>
<th>ε''</th>
<th>τ(10$^{-12}$)</th>
<th>µ(D)</th>
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</table>

3 Results and Discussion

Using standing wave techniques, the dielectric constant ε' and dielectric loss ε'' of the dilute solutions of CH$_3$CN in benzene have been calculated and are given in the Table 1. Following equations have been used:

\[
\varepsilon' = \frac{(\lambda_0/\lambda_c)^2 + (\lambda_d/\lambda_d)^2}{1 + \frac{\lambda_0}{\lambda_c}^2 + \frac{\lambda_d}{\lambda_d}^2} \quad \text{(1)}
\]

\[
\varepsilon'' = \frac{2}{\pi} \frac{(\lambda_0/\lambda_c)^2}{\lambda_d} \frac{dp}{dn} \quad \text{(2)}
\]

Here, λ$_0$, λ$_c$, λ$_d$, λ$_a$ are the wavelengths of microwave in free space, the cut-off wavelength, the waveguide wavelength and the wavelength in the waveguide filled with solution, respectively, and p is the inverse of the voltage standing wave ratio. (dp/dn) is the slope of the curve of p versus n. Here, n is the integer (n = 1, 2, 3, ....) such that, λ$_a$/2 represents the length of dielectric filled waveguide. The accuracy in measurements of ε', ε'' values was ±1% and ±3%, respectively. Following the Gopala Krishna’s single frequency concentration variational method, dielectric relaxation time (τ) and dipole (µ) have been calculated by using following equations:

\[
\tau = \frac{1}{\alpha} \left[ \frac{dY}{dx} \right] \quad \text{(3)}
\]

\[
\mu^2 = \frac{9kT}{4\pi n d_e} \left[ 1 + \left( \frac{dY}{dx} \right)^2 \right] \frac{dX}{dW} \quad \text{(4)}
\]

The values of ε', ε'', τ and µ, thus determined are given in Table 1. The linear variation of ε', ε'' ensures the applicability of the Debye theory and hence, that of Gopala Krishna’s method for calculating relaxation time and dipole moment of polar substance CH$_3$CN in non-polar solvents. In this solution, dielectric
relaxation time is found to decrease with increase in the temperature. This behaviour may be explained on the basis of Debye’s theory of dielectric relaxation\(^1\). Both the plots of \(\log (\tau T)\) versus \(10^\delta T\) and \(\log (\eta)\) versus \(10^\delta T\) are found to be linear. This indicates that, the dielectric relaxation process can be treated as the rate process, just like the viscous flow. Energy parameters for dielectric relaxation of CH\(_3\)CN in benzene solutions and corresponding energy parameters for viscous flow of benzene have been calculated, using Eyring rate relations for the process. The following relations were used.

\[
\tau = \frac{\hbar}{kT} \exp \left[ \frac{\Delta F_\tau}{RT} \right] \quad \text{(5)}
\]

\[
\Delta F_\tau = \Delta H_\tau - T\Delta S_\tau \quad \text{(6)}
\]

\[
\eta = (hN/\nu) \exp \left[ \frac{\Delta F_\eta}{RT} \right] \quad \text{(7)}
\]

and \(\Delta F_\eta = \Delta H_\eta - T\Delta S_\eta \quad \text{(8)}\)

Here, \(\nu\) is the molar volume of the solvent and all the other symbols have their usual significance. \(\Delta F_\tau, \Delta H_\tau\) and \(\Delta S_\tau\) are the free energy, enthalpy and entropy of activation for dielectric relaxation process while \(\Delta F_\eta, \Delta H_\eta\) and \(\Delta S_\eta\) are corresponding parameters for viscous flow process. These results are given in Table 2. Dipole moment of CH\(_3\)CN in benzene is found to be very close to literature value of unassociated CH\(_3\)CN molecule \((\mu = 3.37 D)\) (Ref. 2). This shows that, acetonitrile exists in monomer form in benzene solution.

It is interesting to note that, in the benzene solution, the dipole moment of CH\(_3\)CN is found to decrease with the rise in temperature and approaches towards the literature value \((\mu = 3.37 D)\). This small variation in dipole moment value with rise in temperature may be attributed to the possible solute-solvent molecular association\(^1\). It is proposed that, solute-solvent association arises because of the interaction of fractional positive charge at the site of carbon atom of the CH\(_3\)CN molecule and the \(\pi\)-delocalised electron cloud of the benzene ring of the benzene molecule as shown in Fig. 1.

Energy parameters for the dielectric relaxation process of CH\(_3\)CN in benzene present an interesting behaviour. It is found that, free energy of activation for the dielectric relaxation process is less than the free energy of activation for viscous flow of benzene. It may be explained on the basis of the fact that, dielectric relaxation process involves the rotation of participating molecules and the viscous flow involves both the rotational and translational motions of the molecules. Enthalpy of activation \(\Delta H_\tau\) for the dielectric relaxation process is found to be higher than enthalpy of activation for the viscous flow process. Enthalpy of activation depending upon the bonding nature of the molecules and excitation to the activated state involves breaking of the bonds. Difference in the enthalpies of activation for dielectric relaxation process and viscous flow process indicates that, dielectric relaxation process involves different types of bonding and breaking of bonding to the different extents.

Entropy of activation \(\Delta S_\tau\) for the dielectric relaxation process in benzene is found to be positive. This indicates that, in the dielectric relaxation process, the activated state is less ordered than that of the viscous flow process.

**References**