DIELECTRIC RELAXATION STUDIES OF RIGID SPHERICAL POLAR MOLECULES IN BENZENE SOLUTION

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The dielectric constant and dielectric loss of five dilute solutions of two rigid spherical polar molecules — 1,1,2,2-tetrabromoethane and 1,1-dichloro-1-nitroethane — have been determined at 21.96 GHz for different temperatures using benzene as a nonpolar solvent. The dielectric relaxation time is evaluated using the Gopalakrishna method and Fröhlich's equation. The relaxation time evaluated by Fröhlich's equation is found to be greater than that evaluated by Gopalakrishna's method. Relaxation time data at different temperatures are utilized to evaluate the enthalpy of activation for the orientation of dipoles (ΔH). It is observed that ΔH values, evaluated either by using the relaxation time data from Gopalakrishna's method or from Fröhlich's equation, are the same.

1. Introduction

The study of dielectric relaxation parameters is a very useful technique for ascertaining the molecular structure and for understanding the mechanism of relaxation. Dielectric behaviour is usually studied by carrying out measurements either at different frequencies and a fixed temperature [1] or at a fixed frequency and different temperatures [2]. The dielectric relaxation time of a rigid spherical polar molecule in the pure liquid state can, however, be conveniently determined by the single frequency method suggested by Prakash [3]. Measurements carried out in dilute solutions of a polar solute in a nonpolar solvent yield insight into the intrinsic properties of polar molecules because of the absence of dipole-dipole interaction forces. A single frequency method for determining the dielectric relaxation time of a polar solute molecule in a nonpolar solvent has been suggested by Gopalakrishna [4]. It has been shown by Prakash [5] that the Gopalakrishna method is valid only for rigid spherical polar molecules. Further, the dielectric relaxation time of a rigid spherical polar molecule in a nonpolar solvent can also be evaluated from Fröhlich's equation [6]. In cases where multiple relaxation times are involved, the method suggested by Chandra and Prakash [7] can be utilized. To visualize the effect of relaxation time data,

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evaluated from Gopalakrishna's method and Fröhlich's equation, on the thermodynamic parameters, two rigid spherical polar molecules — 1,1,2,2-tetrabromoethane and 1,1--dichloro-1-nitroethane — have been chosen and their dielectric constant and dielectric loss have been determined at 21.96 GHz for different temperatures using benzene as a nonpolar solvent. Relaxation time data evaluated from Gopalakrishna's method (τ_G) and Fröhlich's equation (τ_F) have been utilized to evaluate the value of enthalpy of activation for the orientation of dipoles. It is observed that the enthalpy of activation evaluated using either τ_G or τ_F is the same.

2. Experimental

1,1,2,2-tetrabromoethane (TBE) and 1,1-dichloro-1-nitroethane (DCNE) of purum grade were procured from M/S Fluka AG, Switzerland and AR grade benzene from M/S BDH, India. These chemicals are further fractionally distilled just before use. The experimental arrangements and the methods of measurement are essentially the same as described elsewhere [8, 9]. Dielectric constant (ε') and dielectric loss (ε'') are computed by the method suggested by Heston et al. [10]. ε' and ε'' of five dilute solutions (0.00–0.05 molefraction) of TBE and DCNE have been determined at 21.96 GHz for different temperatures using benzene as a nonpolar solvent. The accuracies of measurement of ε' and ε'' are $\pm 2\%$ and $\pm 5\%$ respectively. Temperature is controlled to within $\pm 0.5°C$ with the help of a constant temperature water bath.

3. Results and discussions

Measured values of ε' and ε'' are found to vary linearly with the concentration. This excludes the possibilities of molecular association and aggregate formation in the concentration range investigated.

It has been reported by Chandra and Prakash [11] that TBE and DCNE behave as rigid spherical polar molecules and they possess a single relaxation time. The values of ε' and ε'', hence, can be utilized in computing the relaxation time (τ_G) following Gopalakrishna's method [4]. According to Gopalakrishna

$$X = P + \frac{1}{\omega \tau_G} Y,$$

where

$$X = \frac{(\varepsilon'_{12} - 1)(\varepsilon'_{12} + 2) + \varepsilon''^2_{12}}{(\varepsilon'_{12} + 2)^2 + \varepsilon''^2_{12}},$$

$$Y = \frac{3\varepsilon''_{12}}{(\varepsilon'_{12} + 2)^2 + \varepsilon''^2_{12}}, \qquad P = \frac{\varepsilon_{\infty 12} - 1}{\varepsilon_{\infty 12} + 2},$$

ω is the angular frequency of measurement, ε_∞ is the optical dielectric constant and subscript 12 represents the measurements recorded in solution. It has been assumed by Gopala-

krishna that P behaves as a constant quantity. This assumption is partially justified since variations in the values of $\varepsilon_{\infty 12}$ with concentration are practically negligible in comparison to the variations in the values of ε'_{12} and ε''_{12}. Thus, X when plotted against Y yields a straight line enabling the evaluation of τ_G. The evaluated values of τ_G of TBE and DCNE at different temperatures are presented in Table I.

<div align="right">TABLE I</div>

Dielectric relaxation time of 1,1,2,2-tetrabromoethane and 1,1-dichloro-1-nitroethane in benzene at different temperatures*

Temperature °C	Relaxation time $\times 10^{12}$s	
	τ_G	τ_F
	1,1,2,2-tetrabromoethane	
19	9.1	12.6
30	8.1	10.4
40	6.5	9.1
50	5.4	7.6
60	4.5	6.7
	1,1-dichloro-1-nitroethane	
21	3.5	5.8
30	3.1	5.0
40	2.6	4.4
50	2.2	3.6
60	1.9	3.3

* Frequency of measurement = 21.96 GHz.

Since TBE and DCNE behave as rigid spherical polar molecules, their relaxation time (τ_F) can also be evaluated from Fröhlich's equation. It has been shown by Prakash [6] that Fröhlich's equation can be rearranged to give

$$\varepsilon'_{12} = \varepsilon_{\infty 12} + \frac{1}{\omega \tau_F} \varepsilon''_{12}.$$

It is apparent that ε'_{12} when plotted against ε''_{12} should give a straight line since the variations in the values of $\varepsilon_{\infty 12}$ with concentration are practically negligible in comparison to the variations in the values of ε'_{12} and ε''_{12}. The slope of the straight line gives the value of τ_F. The evaluated value of τ_F of TBE and DCNE at different temperatures are also presented in Table I.

It is apparent from Table I that the relaxation times τ_G and τ_F decrease with increasing temperature for both TBE and DCNE in accordance with the expected normal behaviour. The magnitude of the relaxation time of TBE is greater than that of DCNE presumably because of its higher molar volume [11]. It can also be seen from Table I, that the value of τ_F is higher than that of τ_G. This is due to the fact that τ_G is evaluated from Gopalakrishna's

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method which is based on the Debye equation dealing with the situations prevailing in gases or very dilute solutions where dipole-dipole interaction forces are absent. Thus, τ_G happens to be the microscopic relaxation time. However, τ_F evaluated from Fröhlich's equation corresponds to the macroscopic relaxation time. It is because of this fact that we obtain a higher value for τ_F than τ_G.

With these differing values of τ_F and τ_G, enthalpy of activation for the orientation of the dipole has been evaluated which intrinsically depends upon the shape, size and neighbourhood of the molecular dipole. It is expected, therefore, that the enthalpy of activation should be independent of τ_G or τ_F. The relaxation time (τ) as a function of temperature can be represented as [1],

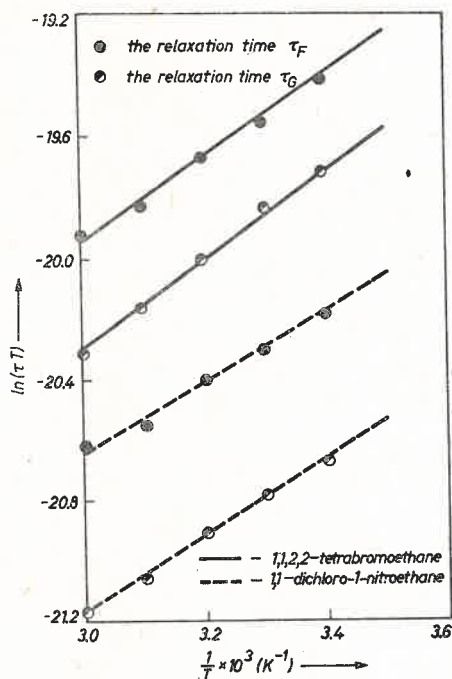$$\tau = \frac{h}{kT} \exp\left(\frac{\Delta F}{RT}\right),$$

Fig. 1. Variation of $\ln(\tau T)$ as a function of $1/T$

where $\Delta F = \Delta H - T\Delta S$ is the free energy of activation for the orientation of the dipole, ΔH is the enthalpy of activation for the orientation of the dipole and ΔS is the entropy of activation for the orientation of the dipole. The above equation can further be rearranged to give [1],

$$\tau = \frac{h}{kT} \exp\left(\frac{\Delta H}{RT}\right) \exp\left(-\frac{\Delta S}{R}\right).$$

This equation suggests that $\ln(\tau T)$ when plotted against $1/T$ should result in a straight line of slope equal to $\Delta H/R$. The slope of the straight line gives the value of ΔH. Variation

of ln (τT) as a function of $1/T$ is shown in Fig. 1 for TBE and DCNE. The evaluated values of ΔH are presented in Table II. Table II also includes the corresponding values for pure liquid state [11] for comparison purposes.

Enthalpy of activation for the orientation of the dipole in benzene

Substance	Enthalpy of activation [K cal/mole]		
	using τ_G	using τ_F	pure liquid [11]
1,1,2,2-tetrabromoethane	2.78	2.68	3.54
1,1-dichloro-1-nitroethane	2.44	2.33	2.61

It is apparent from Table II that the values of ΔH are almost the same whether evaluated using τ_G or τ_F. This is because ΔH depends intrinsically on the shape, size and neighbourhood of the molecular dipole and does not depend upon the method of evaluation of the relaxation time. Since both τ_G and τ_F are determined in a benzene solution, they give the same value for ΔH. The magnitude of ΔH for TBE is greater than that for DCNE, presumably because of its higher molar volume: since more energy is needed to lift the molecular dipole of TBE in crossing over the potential energy barrier. It is also apparent from Table II that the value of ΔH in a benzene solution is less than that required in a pure liquid state. This is due to the fact that in dilute solutions of a polar solute in a nonpolar solvent: (*i*) the viscosity is decreased and (*ii*) the dipole-dipole interaction forces are absent and hence in the benzene solution less energy will be required to lift the dipole over the potential energy barrier in comparison to that required in the pure liquid state. In the case of TBE, the change in the viscosity of the benzene solution in comparison to the pure liquid state is quite marked and hence we observe a reasonably large difference in ΔH values in comparison to DCNE.

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