Dielectric Relaxation Study of Ethanol in Benzene from Microwave Absorption Data

Vimal Sharma, Nagesh Thakur, Dhani Ram Sharma, Nainjeet Singh Negi, and Vir Singh Rangra

Department of Physics, H. P. University, Shimla–171005, Himachal Pradesh, India

Reprint requests to N. T.; E-mail: ntb668@yahoo.co.in

Z. Naturforsch. **62a,** 406 – 408 (2007); received March 8, 2007

The dielectric constant (ε') and dielectric loss (ε'') of dilute solutions of ethanol in benzene have been measured at 9.883 GHz at 25, 30, 35 and 40 °C using standard microwave techniques. The dielectric relaxation time (τ) and dipole moment (μ) at 25, 30, 35 and 40 °C have been calculated by using the single frequency concentration variation method suggested by Gopala Krishna. It is found that the dielectric relaxation process can be treated as a rate process like the viscous flow process. A monomer structure of C_2H_5OH in benzene solution has been inferred. Based upon these studies, the presence of solute-solvent associations has been proposed. The energy parameters for the dielectric relaxation process have been calculated and compared with the corresponding energy parameters of viscous flow.

Key words: Dielectric Relaxation; Ethanol; Benzene; Energy Parameters; Microwave Absorption.

1. Introduction

Ethanol (C_2H_5OH) is a non-aqueous protic solvent [1]. It has an intermediate dielectric constant ε' of 25.07 [2] and intermediate dipole moment μ of 1.70 D [2]. Ethanol is a colourless, inflammable liquid having a low boiling point (78 °C) [3]. It is miscible with water in all proportions and is also miscible with most organic solvents [4]. Ethanol is important as an industrial and pharmaceutical solvent, as a reaction medium because of its active chemical and associative molecular nature. This aspect motivated the authors to undertake an extensive study to understand the associative nature of ethanol in non-polar benzene environment. The present work is concerned with the molecular associative nature of C_2H_5OH. For this standard microwave techniques and solution methods have been used.

The study of dielectric relaxation of polar liquids in non-polar solvents by microwave absorption studies gives valuable information about various types of the molecular associations present in the solutions. It is because microwaves can detect weak molecular interactions [5 – 9]. The present investigation deals with the dielectric relaxation of ethanol in benzene solution at different temperatures (25, 30, 35 and 40 °C). Ethanol is found to occur as monomer in the benzene solution. A solute-solvent type of molecular association has been proposed. The present study predicts that the dielectric relaxation process of ethanol in benzene is a rate process like the viscous flow process.

2. Experimental

Ethanol (AR grade) from Merck (Darmstadt, Germany) was distilled through a long vertical fractionating column. The middle fraction was collected for use. Benzene (GR grade) from E. Merck Ltd. (Mumbai, India) was dried by refluxing over freshly cut sodium metal for 6 – 8 h and then distilled through a long vertical fractionating column. The middle fraction of the distilled benzene was used. The X-band microwave bench (frequency 9.883 GHz) was used to measure wavelengths in the dielectric and the voltage standing wave ratio (VSWR). The dielectric constant (ε') and the dielectric loss (ε'') of dilute solutions of C_2H_5OH in benzene at various temperatures (25, 30, 35 and 40 °C) were calculated following the microwave absorption technique of Heston et al. [10]. The temperature of the solution was controlled by thermostated water circulating around the dielectric cell. Following Gopala Krishna's single frequency concentration variation method [11], the dielectric relaxation time (τ) and dipole moment (μ) were calculated.

Table 1. Dielectric constant (ε'), dielectric loss (ε''), dielectric relaxation time (τ) and dipole moment (μ) for ethanol in benzene solution at different temperatures.

Temperature (°C)	Weight fraction of solute in benzene	ε'	ε''	$\tau/10^{-12}$ (s) 4.7%	μ (D) 3.6%
25	0.0096	2.40	0.010		
	0.0124	2.42	0.014	2.48	1.62
	0.0143	2.43	0.015		
	0.0188	2.46	0.020		
30	0.0096	2.37	0.010		
	0.0124	2.39	0.013	2.27	1.64
	0.0143	2.40	0.015		
	0.0188	2.43	0.019		
35	0.0096	2.36	0.009		
	0.0124	2.38	0.011	2.09	1.66
	0.0143	2.39	0.013		
	0.0188	2.42	0.017		
40	0.0096	2.35	0.008		
	0.0124	2.37	0.010	1.92	1.68
	0.0143	2.38	0.012		
	0.0188	2.41	0.016		

The viscosities and densities of the solutions were measured by a Ubbelohde viscometer and sealable type of pycnometer, respectively.

3. Results and Discussion

The dielectric constant (ε') and the dielectric loss (ε'') of dilute solutions of ethanol in benzene are calculated following the microwave absorption technique of Heston et al. [10] and given in Table 1. The accuracy in the measurements of ε' and ε'' is ±1% and ±3%, respectively. The following equations are used:

$$\varepsilon' = \left(\frac{\lambda_0}{\lambda_c}\right)^2 + \left(\frac{\lambda_0}{\lambda_d}\right)^2, \tag{1}$$

$$\varepsilon'' = \frac{2}{\pi}\left(\frac{\lambda_0}{\lambda_d}\right)^2 \frac{\lambda_g}{\lambda_d}\frac{d\rho}{dn}. \tag{2}$$

Here λ_0, λ_c, λ_g and λ_d are the wavelengths of the microwave in free space, the cut off wavelength, the waveguide wavelength and the wavelength in the waveguide filled with solution, respectively, and ρ is the inverse of the voltage standing wave ratio. ($d\rho/dn$) is the slope of the curve of ρ versus n. Here, n is the integer ($n = 1, 2, 3 \ldots$) such that ($n\lambda_d/2$) represents the length of the dielectric filled waveguide. The relaxation time (τ) and dipole moment (μ) of the molecular entities are calculated using the single frequency concentration variation method of Gopala Krishna [11], applying the following equations:

$$\tau = \frac{\lambda_0}{2\pi c}\left(\frac{dY}{dX}\right), \tag{3}$$

$$\mu^2 = \frac{9kTM}{4\pi Nd}\left[1 + \left(\frac{dY}{dX}\right)^2\right]\frac{dX}{dW}. \tag{4}$$

Table 1 represents the values of the dielectric constant (ε'), dielectric loss (ε''), dielectric relaxation time (τ) and dipole moment (μ) for the dilute solution of C_2H_5OH in benzene. The plots of ε' and ε'' versus the weight fraction of ethanol in benzene are found to be linear. This ensures the applicability of the Debye theory and hence, that of Gopala Krishna's method for calculating the relaxation time and dipole moment of C_2H_5OH in non-polar benzene. The relaxation time is found to decrease with increase in temperature. This behaviour may be explained on the basis of Debye's theory of dielectric relaxation [12]. With rise in temperature, thermal energy of the system increases, which in turn causes the relaxation time of the molecular entities to decrease. Plots of $\log(\tau T)$ versus $10^3/T$ and $\log(\eta)$ versus $10^3/T$ are found to be linear, which indicates that the relaxation process can be treated as the rate process, just like the viscous flow process [13].

Using Eyring's rate relations, the energy parameters for dielectric relaxation of C_2H_5OH in benzene solutions and corresponding energy parameters for viscous flow of benzene can been calculated using the following relations:

$$\tau = \frac{h}{kT}\exp\left[\frac{\Delta F_\varepsilon}{RT}\right], \tag{5}$$

$$\Delta F_\varepsilon = \Delta H_\varepsilon - T\Delta S_\varepsilon, \tag{6}$$

$$\eta = \frac{hN}{V}\exp\left[\frac{\Delta F_\eta}{RT}\right], \tag{7}$$

and

$$\Delta F_\eta = \Delta H_\eta - T\Delta S_\eta. \tag{8}$$

Here, V is the molar volume of the solvent, and all the other symbols have their usual meaning. ΔH_ε, ΔF_ε, and ΔS_ε are the enthalpy, free energy and entropy of activation for the dielectric relaxation process, while ΔH_η, ΔF_η and ΔS_η are corresponding parameters for the viscous flow process. Measured dipole moment of C_2H_5OH is found to be very near to the literature value of its unassociated molecules. This shows that

Table 2. Enthalpies of activation (ΔH_ε, ΔH_η in kJ mol^{-1}), free energies of activation (ΔF_ε, ΔF_η in kJ mol^{-1}) and entropies of activation (ΔS_ε, ΔS_η in J mol^{-1} K^{-1}) for ethanol in benzene solution at different temperatures.

Temperature (°C)	ΔH_ε ±0.17	ΔF_ε ±0.14	ΔS_ε ±0.31	ΔH_η	ΔF_η	ΔS_η
25	10.803	6.791	13.47	11.025	12.205	−3.958
30	10.803	6.720	13.47	11.025	12.234	−3.987
35	10.803	6.665	13.43	11.025	12.259	−4.004
40	10.803	6.590	13.47	11.025	12.322	−4.142

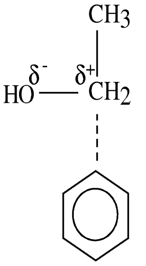

Fig. 1. Solute-solvent association of ethanol in benzene.

C_2H_5OH exists in monomer form in benzene solution. Slight variation in the dipole moment with rise in temperature may be attributed to a possible solute-solvent molecular association [13, 14]. The change in the dipole moment with temperature may be due to the stretching of bond moments and change in bond angles. Again the breaking of solute-solvent associations with temperature may increase μ. It is proposed that solute-solvent association arises because of the interaction of a fractional positive charge at the site of the carbon atom of the C_2H_5OH molecule and the π-delocalized electron cloud of the benzene ring as shown in Figure 1.

Table 2 contains recorded values of the energy parameters for the dielectric relaxation process of C_2H_5OH in benzene solution. These observations show that the enthalpy of activation for the dielectric relaxation process is different from the enthalpy of activation for viscous flow. This difference shows that the dielectric relaxation process involves different types of bonding and breaking of bonding to different extents. The free energy of activation for the dielectric relaxation process is smaller than the free energy of activation for viscous flow of benzene. This may be explained by the fact that the dielectric relaxation process involves rotation of molecular entities, whereas in viscous flow the rotational as well as the translational motion of the molecules are involved [15].

According to Branin and Smyth [16], a negative value of entropy of activation indicates that a comparatively smaller number of configurations is possible in an activated state, which is more ordered in comparison to the normal state. This again indicates the presence of cooperative orientation of the molecules by the steric forces or strong dipole-dipole interactions with the dipoles being more nearly aligned in an activated state. However, the positive entropy of activation indicates that the activated state is more disordered. In the present case it is observed that the change in entropy for the dielectric process is positive, indicating the unstable state, while the negative value of change in entropy for the viscous flow process indicates that the activated state of viscous flow is more stable than the normal state.

[1] G. Mamantov, Characterization of Solutes in Non-Aqueous Solvents, Plenum Press, New York and London 1976, p. 26.

[2] N. E. Hill, W. E. Vaughan, A. H. Price, and M. Davies, Dielectric Properties and Molecular Behaviour, Van Nostrand Reinhold Company, London 1969, p. 2.

[3] B. L. Clapp, The Chemistry of the OH Group, Prentice-Hall, Inc., Englewood Cliffs, New Jersey 1967, p. 19.

[4] G. I. Brown, Introduction to Organic Chemistry, 5th ed., Orient Longmans Private Ltd., Calcutta 1961, p. 110.

[5] V. Sharma, N. Thakur, D. R. Sharma, V. S. Rangra, and N. S. Negi, Z. Phys. Chem. **220**, 325 (2006).

[6] A. D. Vyas and V. A. Rana, Indian J. Pure Appl. Phys. **40**, 69 (2002).

[7] V. S. Rangra and D. R. Sharma, Indian J. Phys. **78B**, 111 (2004).

[8] A. Chaudhari, S. Ahire, and S. C. Mehrotra, J. Mol. Liq. **94**, 17 (2001).

[9] G. D. Rewar and D. Bhatnagar, Indian J. Pure Appl. Phys. **40**, 430 (2002).

[10] W. M. Heston Jr., A. D. Franklin, E. L. Hennely, and C. P. Smyth, J. Am. Chem. Soc. **72**, 3443 (1950).

[11] K. V. Gopala Krishna, Trans. Faraday Soc. **33**, 767 (1957).

[12] A. Sharma and D. R. Sharma, J. Phys. Soc. Jpn. **61**, 1049 (1992).

[13] N. Thakur and D. R. Sharma, Indian J. Pure Appl. Phys. **41**, 808 (2003).

[14] J. S. Dhull and D. R. Sharma, J. Phys. D: Appl. Phys. **15**, 2307 (1982).

[15] N. Srinivasan, S. Kumar, and S. Krishnan, Indian J. Pure Appl. Phys. **41**, 876 (2003).

[16] F. H. Branin and C. P. Smyth, J. Chem. Phys. **42**, 2503 (1965).