JOURNAL OF ULTRA SCIENTIST OF PHYSICAL SCIENCES
An International Open Free Access Peer Reviewed Research Journal of Physical Sciences
website:- www.ultrascientist.org

Estd. 1989

Study of dielectric relaxation mechanism and thermodynamic parameters of binary mixtures of N-methylformamide and dimethylsulphoxide in dilute solution of benzene

AJAY KUMAR SINGH

Department of Physics, Bareilly College, Bareilly, 243005 (India)
Corresponding author Email: aksnmr@gmail.com
http://dx.doi.org/10.22147/jusps-B/290703

Abstract

Present communication reports the experimental values of the dielectric relaxation time (τ) and dipole moment (μ) of binary mixtures of N-methylformamide (NMF) and dimethylsulphoxid (DMSO) in dilute solution of benzene at wavelength 3.13 cm in the microwave region. The measurements have been made at 293, 303,313 and 323 K, in order to calculate the free energy of activation for dipole orientation process (ΔF_ε). The experimental values of t have been correlated with the calculated value of t obtained using different theories of dielectric relaxation time (τ) for mixtures. It is concluded from this comparative study that both the values are comparable to each other. Thermo dynamical parameters like molar free energy of activation (ΔF_ε), molar enthalpy of activation (ΔH_ε) and molar entropy of activation (ΔS_ε) have been evaluated by considering the relaxation as the rate process.

Key words: Dielectric relaxation time, molar free energy of activation, molar enthalpy of activation and molar entropy of activation.

1. Introduction

Study of dielectric behaviour of mixtures of polar molecules, under varying conditions of composition and temperature, helps in formulating adequate models of liquid relaxation and also in gathering information about the relaxation process in mixtures. Several workers[1-5] studied dielectric relaxation behavior of some polar molecules and their mixtures in dilute solutions of non polar solvents and found formation of complexes for mixtures of rigid polar molecules. The investigation of dielectric relaxation phenomenon provides an important tool to explain the structural behavior of complex organic polar molecules in different non polar solvents. As microwaves are capable to detect the weak molecular interactions, these

studies provide valuable information about self association, solute-solute and solute-solvent types of the molecular associations among the polar molecules [6-10].

To understand the structural behavior of molecules it is necessary to determine various dielectric parameters that are related with inter and intramolecular association and internal rotation with temperature variation. The present study is expected to provide better understanding of the nature of molecular orientation process.

2. Experimental Details

All the compounds used were of pure quality obtained from M/S Central Drug House Ltd., New Delhi. The percentage purity of the investigated compounds ranged from 99.8 to 99.9%. The X-band microwave bench was used to measure wavelength in the dielectric medium and voltage standing wave ratio (VSWR) using a short circuiting plunger. The dielectric constant (ε') and dielectric loss (ε'') was calculated by the method of Heston et $al.$[11]. Dielectric relaxation time of molecular entities in benzene solution was calculated using single frequency concentration variation method of Gopala Krishna[12]. All the measurements were carried out at 293, 303 and 313 K by circulating water around the dielectric cell through a thermostat (Mittal Enterprise, New Delhi, India). Densities at different temperatures were measured by using a 10 ml specific gravity bottle and an electronic balance whose accuracy is 0.1 mg.

3. Theory :

The dielectric constant (ε') and dielectric loss (ε'') have been calculated by the method of Heston et $al.$[11] using the following relations:

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

And

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

Where λ_0, λ_c, λ_g, and λ_d are the free space wavelength, the cut-off wavelength, the waveguide

wavelength and the wavelength in the waveguide filled with solution, respectively. ρ is the inverse of voltage standing wave ratio (VSWR) and $(d\rho/dn)$ is the slope of ρ versus n curve, where n = (1, 2, 3…….) such that (n λ_d/2) represents the length of dielectric filled waveguide. The ε' and ε'' values from repeated measurements were reproducible within ±0.05 and 1.67%, respectively.

The dielectric relaxation time (τ) has been calculated by using the Gopala Krishna's single frequency concentration variation method[12]. The dielectric relaxation time (τ) for mixture compositions has been computed by four theoretical methods[13-15] viz :

Simple mixing rule (SM)

$$\tau = \sum_{i=1}^{i=n} x_i \tau_i \tag{3}$$

Reciprocal mixing rule (RM)

$$\frac{1}{\tau_i} = \sum_{i=1}^{i=n} x_i \Big/ \tau_i \tag{4}$$

Yadav and Gandhi method (Y&G)

$$\tau = \left[\sum_{i=1}^{i=n} x_i \tau_i^2 \Big/ \sum_{i=1}^{i=n} x_i\right]^{1/2} \tag{5}$$

Madan method

$$\frac{1}{\tau} = \left[C\mu_1^2 \Big/ \left(C\mu_1^2 + \mu_2^2\right)\tau_1 + \mu_2^2 \Big/ \left(C\mu_1^2 + \mu_2^2\right)\tau_2\right] \tag{6}$$

Where, τ_i is the relaxation time of the ith component of mole fraction x_i in the mixture and C=C_1/C_2. The value of C in dilute solution can be estimated roughly equal to the volume fraction.

The thermodynamical parameters, viz. molar free energy of activation (ΔF_ε), molar enthalpy of activation (ΔH_ε) and molar entropy of activation (ΔS_ε) for dielectric relaxation process for compounds at different temperatures have been calculated by using Eyring's equations[16]

$$\tau = \frac{h}{kT} \exp\left(\frac{\Delta F_\varepsilon}{RT}\right) \qquad (7)$$

$$\Delta F_\varepsilon = \Delta H_\varepsilon - T\Delta S_\varepsilon \qquad (8)$$

Plot of $\ln(T\tau)$ versus $1/T$ should be a straight line in accordance with Eq.(10) if ΔH_ε and ΔS_ε are temperature independent. ΔH_ε has been determined by slope of the Plot of $\ln(T\tau)$ versus $1/T$, while ΔF_ε and ΔS_ε are calculated using Eqs (7) and (8) respectively.

4. Results and Discussion

The experimental values of dielectric relaxation time (τ) and dipole moment (μ) of NMF, DMSO and their binary mixtures in benzene solution of at 293,303, 313 and 323K are reported in Table 1. The experimental values of τ of mixture compositions at four temperatures are compared with computed τ values obtained using given theoretical models are listed in Table 2. Table 3 represents the thermodynamic parameters of the investigated compounds at different temperatures.

4.1 Dielectric relaxation Time :

It is evident from Table 1 that the dielectric relaxation time () of binary mixtures of NMF and DMSO vary anomalously with the increase in concentration in benzene solvent. This variation in comparative observed τ values suggest the existence of heterogeneous cooperative domains(CDs) of polar molecules in dilute solution of benzene and these CDs changes with the change in composition of the constituents of the polar molecules mixture. The τ values of solutes and their mixtures decrease with increase in temperature. This may be due to the fact that the clusters of molecules break slowly with rise in temperature. Table 1 shows that the observed value of τ for the binary mixtures of NMF and DMSO for all compositions at each temperature lie between those for individual molecules. This suggests that there is an overlap of two individual Debye regions. The degree of overlap varies with the concentration ratio of the two components of the mixtures.

The τ value varies non-linearity with the increase in mole-fraction of NMF in the binary mixtures at all temperatures which shows the presence of solute-solute molecular association. The τ values are found to be minimum at 50% mole-fraction of NMF in the binary mixture. In this case, the solute molecules interact in such a manner that the size of resulting associated molecules decreases and there is also a decrease in the relaxation time.

The experimental values of the dielectric relaxation time have been correlated with the calculated values obtained using the SM Rule, RM Rule, Y&G Rule and Madan method. It is evident from Table 2 that, for the mixtures under investigation, the calculated values of τ by different methods are almost in agreement with experimental values. However, small deviations may be attributed to experimental uncertainties. At higher temperature these deviations are quite large and hence solute-solute and solute-solvent interactions among molecules may dominate relaxation process.

4.2 Thermodynamic parameters :

It is evident from Table 3 that free energy of activation (ΔF_ε) is not same for all molecules, which indicates that force of hindrance experienced by molecules for dipolar rotation is a factor dependent on the nature of molecules. In the present study it is found that ΔF_ε values of NMF, Binary solution having 50% mole fraction of NMF and 70% mole fraction of NMF, increase with temperature. Increased temperature decreases viscosity of solvent but increases thermal agitation, so that molecules of the system require more energy to overcome the excited state. The value of molar entropy of activation (ΔS_ε) for dielectric relaxation process of pure NMF and binary mixture having 70% mole fraction of NMF is found to be negative, suggesting that activated state is more ordered than the normal state. In activated state, the dipoles are more aligned than in normal state. But for other binary mixtures ΔS_ε values are positive and almost constant at all temperatures. Positive values of ΔS_ε suggest that cooperative orientation in the single component system becomes non- cooperative in mixture system, resulting in the activated state, which is more disordered in comparison to normal state.

Table1. Dielectric Relaxation Time (τ) (in 10^{-12} sec) and Dipole-moment (μ) at different temperatures for investigated compounds

Temperature(K)	Mole fraction of NMF in mixture	τ(ps)	μ(D)
293	0.00	2.934	3.818$_{DMSO}$
	0.30	4.171	
	0.50	3.743	
	0.70	4.321	
	1.00	5.666	3.463$_{NMF}$
303	0.00	2.534	3.988$_{DMSO}$
	0.30	3.571	
	0.50	3.263	
	0.70	3.921	
	1.00	5.036	3.623$_{NMF}$
313	0.00	186.08	4.158$_{DMSO}$
	0.30	154.75	
	0.50	103.91	
	0.70	51.39	
	1.00	8.23	3.783$_{NMF}$
323	0.00	157.79	4.328$_{DMSO}$
	0.30	139.92	
	0.50	91.31	
	0.70	39.23	
	1.00	5.71	3.943$_{NMF}$

Table 2. Comparison of experimental and computed value of relaxation time using theoretical models for mixtures under investigation at different temperatures

Name of the Sample	Temperature K	Experimental values of τ	Theoretical values of τ calculated by			
			SM Rule	RM Rule	Y&G Rule	Madan Rule
NMF(30%)+DMSO(70%)	293	4.17	3.75	3.43	3.96	3.36
	303	3.57	3.28	2.98	3.48	2.91
	313	2.97	2.82	2.53	3.00	2.45
	323	2.37	2.35	2.07	2.53	1.82
NMF(50%)+DMSO(50%)	293	3.74	4.30	3.87	4.51	3.75
	303	3.26	3.79	3.37	3.99	3.27
	313	2.78	3.27	2.88	3.46	2.85
	323	2.30	2.76	2.38	2.99	2.30
NMF(70%)+DMSO(30%)	293	4.32	4.85	4.43	5.01	4.30
	303	3.92	4.29	3.89	4.44	3.77
	313	3.52	3.72	3.34	3.87	3.23
	323	3.12	3.16	2.79	3.30	2.70

Table 3. Thermodynamic parameters of single components as well as their mixtures in
benzene solution at different temperatures

Name of the sample	Temperature	ΔH_ε	ΔF_ε	ΔS_ε
	K	$(kJ\,mol^{-1})$	$(kJ\,mol^{-1})$	$(kJ\,mol^{-1}K^{-1})$
N-Methylformamide (NMF)	293		8.62	-0.0023
	303	7.94	8.71	-0.0025
	313		8.74	-0.0026
	323		8.70	-0.0024
NMF(30%)+DMSO(70%)	293		7.89	0.0156
	303	12.47	7.86	0.0152
	313		7.70	0.0152
	323		7.44	0.0156
NMF(50%)+DMSO(50%)	293		7.62	0.0092
	303	10.32	7.63	0.0089
	313		7.54	0.0089
	323		7.35	0.0092
NMF(70%)+DMSO(30%)	293		7.96	-0.0063
	303	6.12	8.08	-0.0065
	313		8.14	-0.0065
	323		8.16	-0.0063
Dimethylsulfoxide (DMSO)	293		7.04	0.0148
	303	11.37	6.97	0.0145
	313		6.84	0.0145
	323		6.60	0.0148

Conclusions

The experimental and computed values of dielectric relaxation time of mixture compositions at four different temperatures are comparable to each other. However small deviations may be attributed to experimental uncertainties. At higher temperatures these deviations are quite large and hence solute-solute and solute-solvent interactions among molecules may dominate relaxation process.

Acknowledgement

References

1. R. J. Sengwa, S. Sankhala S. and Abhilasha, "Interaction effect on molecular dynamics of some polar solvents in poly (vinyl pyrrolidone) matrix studied by microwave dielectric relaxation measurements in dilute solutions" *Indian J Phy,* 79(B), 879(2005).

2. N. Kumar, R. Thakur, D. R. Sharma, Vir Singh Rangra and N. Negi , "Dielectric relaxation studies of binary mixtures of N-methylformamide and dimethylsulphoxide in benzene solution using microwave absorption data" *Indian J Phys, 79(12),* 1415 (2005).

3. T. Kalaivini and S. Krishnan, "Dielectric relaxation studies of ternary liquid mixtures of aniline and substituted anilines with acrylonitrile in the microwave region" *Indian J Pure Appl Phys*, *47,* 880 (2009).

4. Raman Kumar, Vinod Sharma and V. S. Rangra, "Dielectric relaxation studies of binary mixtures

of tetrahydrofuran and N-methylacetamide in benzene solutions using microwave absorption data" *Indian J Pure Appl Phys*, *48,* 415 (2010).

5. C. M. Trivedi and V A Rana, "Static permittivity, refractive index, density and related properties of binary mixtures of pyridine and 1-propanol at different temperatures" *Indian J Pure Appl Phys*, *52,* 183 (2014).

6. A. D. Vyas, V. A. Rana, S. P. Bhatnagar and V. M. Vashisth, "Dielectric dispersion and relaxation mixtures of 1-butanol and phenol at lower microwave frequencies" *Indian J Pure Appl Phys*, 49, 47 (2011).

7. P. A. Chalikwar, A. R. Deshmukh and A. C. Kumbharkhane, Dielectric relaxation of Tripropylene glycol–water mixture using time domain reflectometry" *Phys Chem Liq*, *55,* 410 (2017).

8. V. A. Rana, K. R. Chauhan and S. K. Menon, "Dielectric absorption in dilute solutions of dibenzo-18-crown-6 in 1,4-dioxane" *Indian J Pure Appl Phys*, *54,* 177 (2016).

9. S. Sahoo and S. K. Sit, "Dielectric relaxation of amides and tetrahydrofuran polar mixture in C_6H_6 from conductivity measurement under 9.90 GHz electric field" *Pramana*, *88,* 11(2017).

10 A. Mohan, M. Malathi and A. C. Kumbharkhane, "Microwave dielectric relaxation spectroscopy studies on associative polar binary mixtures of nitrobenzene with primary alcohols" *J Mol Liq*, *222,* 640 (2016).

11. W. M. Heston(Jr.), A. D. Franklin, E. L. Hennelly and C. P. Smyth, "Microwave Absorption and Molecular Structure in Liquids. V. Measurement of the Dielectric Constant and Loss of Low-loss Solutions", *J Am Chem Soc*, *72,* 3443 (1950).

12. K. V. Gopala Krishna, "A Method Of Determining the Dipole Moment and Relaxation Time From Microwave Measurements" *Trans Faraday Soc*, *53,* 767 (1957).

13. G. D. Rewar and D. Bhatnagar, "Microwave absorption and relaxation processes of ternary mixtures of non-rigid polar liquids" *Indian J Pure & Appl Phys*, *39,* 707 (2001).

14. J. S. Yadav and J. M. Gandhi, "Simple microwave technique for measuring the dielectric parameters of solids and their powders" *Indian J Pure & Appl Phys*, *30,* 427 (1992).

15. M. P. Madan,"Relaxation processes of quinoline, isoquinoline, and their mixtures" *Can J Phys*, *58,* 20 (1980).

16. S. Glasstone, K J Laider and H. Eyring, *The theory of rate processes*, (McGraw Hill, New York) (1941).