Dielectric Relaxation Studies of the System Copper(II) Soap– Non-polar Solvent at Microwave Frequencies

V.P. MEHTA*, R.K. KHANNA, P.R. TALESARA and RASHMI SHARMA
Research Laboratories
S.D. Government College, Beawar-305 901, India

There has been a renaissance of interest to understand micellar characterization of surfactant solutions using dielectric relaxation studies. Measurements of the complex dielectric constant of the system: Copper(II) soap (C_6 and C_8)–Non-polar solvent (benzene and carbon tetrachloride) have been carried out at 8.82 GHz and 8.86 GHz frequencies at 30°C. The results have been analysed in terms of dielectric relaxation time (τ) evaluated using the single frequency concentration variation method enunciated by Gopal Krishna.

INTRODUCTION

The study of dielectric absorption at microwave frequencies has provided evidence for the existence of inter- and intramolecular orientation in several organic molecules[1–3]. The dielectric constant (ε') and loss factor (ε'') of liquids are some of the macroscopic properties which could be utilised to develop its various models. Dielectric behaviour of liquids not only depends on the molecular structure but also on its surroundings *i.e.* inter and intramolecular interactions[4–7]. The study of dielectric properties of some liquids at radio and microwave frequencies has recently shown evidences of providing some conclusive results for determining structural configurations[8–11]. The present work is the result of our fascination to understanding micellar characterization of the system: copper(II) soap (C_6 and C_8)–non-polar solvent (*i.e.* C_6H_6 and CCl_4) in terms of relaxation time (τ). Further the work has been elaborated to enumerate qualitatively the effect of the nature of the solvent on the micellar aggregate and to gain insight of the chainlength compatibility in the midst of lucid micellar profile prevailing in such systems.

EXPERIMENTAL

Merck or B.D.H. reagent grade organic solvents were used after purification and drying. Copper soaps were prepared by direct metathesis at 50–55°C from the corresponding potassium soaps as given in the previous communication[12].

Measurements of the complex dielectric constant of the system: Copper(II) soap (C_6 and C_8)–non-polar solvent (C_6H_6 and CCl_4) have been carried out at 8.82 GHz and 8.86 GHz frequencies at 30°C. Plunger type cell has been used and hence short- circuited termination method is adopted for convenience. The calculation of dielectric constant (ε') and loss factor (ε'') have been made following the method of Heston *et al.*[13]

RESULTS AND DISCUSSION

Gopal Krishna method[15-17] is used for determining the dielectric relaxation time (τ) for the measurment of complex dielectric constant at single frequency of a dipolar substance as a function of its concentration in non-polar solvent. Debye equation for such a sample can be written as,

$$\frac{\varepsilon^* - 1}{\varepsilon^* + 2} = \frac{4\pi N}{3}\left(\alpha_0 + \frac{\mu_0}{3kT} \cdot \frac{1}{1 + jw\tau}\right)$$

where N = Avogadro's number, ε^* = Complex dielectric constant = $\varepsilon' + j\varepsilon''$, k = Boltzmann constant, T = Temperature, μ = Dipole moment and τ = Relaxation time.

This equation can be separated into real and imaginary parts into two equations such as:

$$\frac{\varepsilon'^2 + \varepsilon' + \varepsilon''^2 - 2}{(\varepsilon' + 2)^2 + \varepsilon''^2} = X = \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} + \frac{4\pi N\mu^2}{9kT} \cdot \frac{1}{1 + w^2\tau^2}$$

and

$$\frac{3\varepsilon''}{(\varepsilon' + 2)^2 + \varepsilon''^2} = Y = \frac{4\pi N\mu^2}{9kT} \cdot \frac{w\tau}{1 + w^2\tau^2}$$

If $P = \dfrac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}$, then we get

$$X = P + \frac{1}{w\tau}Y$$

Gopal Krishna's usual procedure[15-17] to obtain relaxation time involves measurements of ε' and ε'' as a function of soap concentration in its solutions of benzene and carbon tetrachloride respectively. The relaxation time has been obtained from the slope of the X versus Y plots, which are characterized by two straight lines corresponding to solutions below and above critical micelle concentration (CMC). The values of CMC range for C_6 and C_8 soaps are (0.04–0.05 M)[12]. Enumerated values of τ have been summarised in Table-1.

TABLE-1

VALUES OF RELAXATION TIME ($\tau \times 10^{12}$ sec) FOR THE COPPER SOAPS IN NON-POLAR SOLVENTS

Name of Soap	Benzene		Carbon tetrachloride	
	Below CMC	Above CMC	Below CMC	Above CMC
Copper Caprylate (C_6)	11.9	29.8	3.9	22.5
Copper Caprate (C_8)	28.6	259.0	5.4	58.6

The variation of τ with respect to chain length of the soap anion for the copper(II) soap solutions both in benzene and carbon tetrachloride follows the order (Table 1): $C_8 > C_6$.

The results are in conformity with the fact that agglomeration of the soap molecules in the form of micelles is more pronounced as the number of carbon atoms in the hydrophobic chain increases[14]. Obviously, with the increase in the chain length of the soap anion, there is some hindrance in the free rotation of the lucid micellar aggregate prevalent in the system: soap–non-polar solvent.

This enunciation is based on the studies of relaxation time of organic molecules in benzene by Khanna *et al.*[1]

The enhanced values of τ at higher soap concentration for the referred system have been attributed to the gain in the size of soap aggregated due to sufficient intake of the solvent molecules in the palisade layers of the micelles.

With regard to solvent the values of τ both for copper caprylate and caprate follow the order (Table 1): benzene > carbon tetrachloride. This may be ascribed to the appreciable soap-benzene interaction as compared to soap-carbon tetrachloride and the soap exhibits different degrees of aggregation in such systems.

ACKNOWLEDGEMENTS

REFERENCES

1. E. Fischer and F.C. Frank, *Phys. Z.*, **40**, 345 (1939).
2. K. Higasi and C.P. Smyth, *J. Am. Chem. Soc.*, **82**, 4759 (1960).
3. W.E. Vaughan and C.P. Smyth, *J. Phys. Chem.*, **65**, 98 (1961).
4. C.P. Smyth, Dielectric behaviour and structure, McGraw-Hill, New York (1955).
5. M. Davies, Some Electrical and Optical Aspects of Molecular Behaviour, Pergamon, London (1965).
6. N. Hill, W.E. Vaughan, A.H. Price and M. Davies., Dielectric Properties and Molecular Behaviour, London (1969).
7. K. Higasi, Dielectric Rel. and Mol. Structure, Monograph No. 9, Res. Inst. of Appl. Ele., Hokkaido Univ., Sappora, Japan (1981).
8. V.I. Gaiduk and Y.P. Kalmykov, *J. Mov, Liqs.*, **34**, 1 (1987).
9. P. Preundlich, E. Jakuser, H.A. Kolodziet, A. Koll and S. Sorriso, *J. Phys. Chem.*, **87**, 1034 (1983).
10. M.W. Evans, G.J. Evans and A.R. Davies, *Adv. Chem. Phys.*, **44**, 252 (1980).
11. R.K. Khanna and Abha Bhatnagar, *Recl. Trav. Chem. Pays-Bas, J. Royal Neth. Chem. Soc.*, **108**, 227 (1989).
12. K.N. Mehrotra, V.P. Mehta and T.N. Nagar, *J. Prakt. Chem.*, **3B**, 607 (1971).
13. W.M. Heston (Jr.), A.D. Franklin, E.J. Hennely and C.P. Smyth, *J. Am. Chem. Soc.*, **72**, 3443 (1950).
14. V.P. Mehta, M. Hasan and L.C. Heda, *Affinidad*, **39**, 385 (1982).
15. K.V. Gopal Krishna, S.L. Srivastava and Dinanath, *J. Chem. Phys.*, **52**, 940 (1970).
16. K.V. Gopal Krishna, *Trans Faraday Soc.*, **53**, 767 (1957).
17. Krishnaji, S.L. Srivastava and D. Nath, *Bull. Chem. Soc. Japan*, **43**, 2805 (1970).