April 2009 Volume 5 Issue 2

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 5(2), 2009 [153-160]

Dielectric relaxation studies of aqueous sodium dodecyl sulphate with some additives as co-solvents in time domain reflectometry technique

T.Kalaivani[1]*, Prabhakar Undre[2], R.Sabesan[3], S.Krishnan[4]

[1]Department of Physics, SRM University, Kattankulathur-603203, Tamilnadu, (INDIA)

[2]Department of Physics, Dr. B.A.M. University, Aurangabad-431004, (INDIA)

[3]Department of Physics, Annamalai University, Annamalainagar-608002, Tamilnadu, (INDIA)

Tel : 94862 57028

E-mail : tkv_p@yahoo.co.in

Received: 4th February, 2009 ; Accepted: 9th February, 2009

ABSTRACT

Dielectric relaxation studies of aqueous sodium dodecyl sulphate with formamide and acetamide, have been carried out for different concentrations at 303k. Dielectric Relaxation Spectroscopy (DRS) is a versatile tool to monitor the dynamic process of micellar systems. The time domain dielectric data were obtained in the reflection mode in the frequency range of 10MHz to 20GHz using a HP54750A sampling oscilloscope and HP54754A TDR plug-in-module. The sample was held at 303k in a SMA cell with an effective pin length of 1.35mm. We have determined the relaxation time (τ) using the Cole-Cole method. The relative viscosity η_r of the micellar solutions was also determined. We find that η_r increases with increasing concentrations of SDS and there is a non-linear increase in η_r beyond 80mM SDS. The observed relaxation time is explained by considering the superposition of two relaxation times. One is due to the rotation of the hydrated water molecule around the micelle ions and the other due to the hydrated water squeezed in the hydrophobic interior of the micelle. Our results are explained on this basis. The results on adding amides are similar to that of adding alcohols but the interaction of the amines with the head group of the micelle is not as effective as hydroxy group of alcohols.

KEYWORDS

Dielectric relaxation spectroscopy;
Time domain reflectometry;
Surfactants;
SDS.

1. INTRODUCTION

The permanent interest in sodium alkyl sulphates results from their wide ranging potential of scientific and technological applications[1-10].

Surface-active molecules self-assemble or form micelles or vesicles in dilute solutions so as to minimize the contact between their hydrophobic tails and water molecule. As a result, the interior of micelles and the spherical shells of vesicles are highly non-polar capable of accommodating other non-polar molecules[11-18].

However the micelle formation in an aqueous solution is known to be affected by organic additives. Recently increasing attention is being devoted to the study of the incorporation or solubilization of neutral molecules into micelle in aqueous solution. Some of the most studied solubilizates are alcohols, because of the important role they have in the preparation of microemulsions.

Many studies reported about various aspects of solubilization, for example the capacity of micelles for solubilization of different additives, the different equilibrium of an additive between the micelles and solvent, the distribution of an additive between the micelles, the specificity of solubilization of additives in micelles, the location of an additive in the micelles, the thermodynamics of solubilization, and the dynamics and mechanism of solubilization.

Mats Almgren et al.[19-22] studied the effect of organic polar solvents on the micelle formation of SDS in water using fluorescence quenching method. Studies of the effect of non-electrolytes additions on ionic micelle formation were mostly on the effect of alcohol. There are also reports of the organic molecules used as co-solvents[23,24].

The dielectric relaxation studies of surfactants + additives micellar solutions are rare and are mostly confined to microemulsions. For example, the structural characteristics of systems containing sodium stearate, with varying amounts of water in the presence of n-pentanol, n-hexanol and n-heptanol were investigated by Bansal et al.[25]. The results were interpreted in terms of ionization of the carbonyl group and the concomitant formation of the electrical double layer.

Sjoblom and Gestblom[26] studied the dielectric spectra between 50MHz and 11GHz in the system sodium octanoate-decanol water. Several dielectric dispersion regions were observed and the results are discussed in relation to models consisting of rather well defined aggregates. Most of the dielectric studies of micellar solutions were restricted to a frequency range up to 10MHz only.

Time domain dielectric relaxation spectroscopy can monitor relaxation in the region of τ=15-25ps which are attributed to water molecules within the micelles and the vicinity of the hydrophobic tail of surfactant ions. Hence the application of dielectric time domain spectroscopic method to complex equilibria of additives + micellar aqueous systems would offer a great deal of insight into 'bound water' dispersion phenomenon.

The present study investigates the relaxation time of Organic polar solutes such as acetamide and formamide on micellar solutions of anionic sodium dodecyl sulphate. SDS offers a preferential solvation of the hydroxy group by the counterions.

2. MATERIALS AND METHODS

The surfactants SDS is the product of BDH 99% pure and is used 'as such' without further purification. The co-solvents acetamide and formamide were purified using standard procedures. All solutions were prepared in doubly distilled conductivity water of specific conductance 1-2 μscm^{-1} at 303K.

The dielectric measurements were made using Time Domain Reflectometry in the frequency range of 10MHz to 20 GHz using HP54750A sampling oscilloscope and HP54754A TDR plug-in-module. A fast rising step voltage pulse of 200mv with 39ps time is generated by a tunnel diode and propagated through a coaxial cable system. The sample was placed at the end of the coaxial line in a standard Military Application (SMA) coaxial cell of 3.5mm outer diameter and 1.35mm effective pin length. All measurements were made under open load conditions.

The sampling oscilloscope monitored the change in the pulse shape after detecting reflection from the sample placed in the cell. A time window of 5ns was used. The reflection pulse with Rx(t) and without sample $R_1(t)$ were digitized in 1024 points and transferred to computer through GPIB. A water circulated thermostat bath was used to maintain constant temperature within $\pm 1^0$C. The sample cell is surrounded by a heat-insulated container in which the water from the bath is circulated.

The Fourier transform for $\{R_1(t) - R_X(t)\}$ and $\{R_1(t) + R_X(t)\}$ namely $p(\omega)$ and $q(\omega)$ respectively was obtained. Spectra $\rho^*(\omega)$ over the frequency range of 10MHz to 20GHz are obtained as,

$$\rho^*(\omega) = \frac{c / j\omega d}{p(\omega)q(\omega)}$$

where 'ω' is the angular frequency, 'c' is the velocity of light and 'd' is the effective pin length. The complex permittivity spectra $\varepsilon^*(\omega)$ were obtained from reflection coefficient $\rho^*(\omega)$ by applying bilinear calibration method[27]. The experimental values ε^* are fitted with Debye equation with ε_0 and τ as fitting parameters. A non- linear least square fit method was used[28]. The $\varepsilon\infty$ is taken as an adjustable parameter but ε^* is not sensitive to small changes in $\varepsilon\infty$ in the similar class of liquid systems.

3. RESULTS AND DISCUSSION

The complex dielectric permittivities of different (2.0mM to 100mM) solutions of SDS in the presence of various additives were recorded at room temperature. ε′ and ε″ were obtained on resolving the spectra. The values of density, static dielectric constant and relative viscosity of the SDS solution is given in TABLE 1.

The determined relaxation time (τ) is calculated from Debye method. It is the overall relaxation time consisting of different overlap relaxation. The calculated values of the $\tau/\eta r$, the volume fraction of the hydrated micelles, the molar volume of the hydrated micelles and the activation energies for the dielectric and viscous relations are given in TABLE 2.

In the present study all the organic additives are aprotic polar molecules. It is generally conceived that the polar substances dissolve with the polar groups at the hydrocarbon/water interface of the micelle surface and thereby promote the formation of micellar growth. The additives chosen in the present investigation do not disturb the dielectric properties of water except for a slight decrease in static permittivity. Our studies show that for anionic surfactant solutions increase in the concentration of the additives systematically decrease the overall relaxation time.

The relative viscosity increases with the increase in mole fraction of the additives, i.e., the mobility of the micelle decreases. We have calculated the molar volume of the hydrated micelles using the Guveli equa-

TABLE 1: Density, static dielectric constant, relative viscosity data for SDS micellar solutions

Acetamide	Conc. mM	Density Kgm^{-3}	ε_0	η_ρ	τ ps	Formamide	Conc mM	Density Kgm^{-3}	ε_0	η_ρ	τ ps
0.05	2	994.3	77.14	1.001	14.09	0.05	2	998.2	77.26	1.002	14.02
	4	996.1	78.02	1.002	15.36		4	1002.5	78.32	1.004	15.14
	6	998.7	79.36	1.003	16.48		6	1010.6	79.45	1.008	16.32
	10	999.6	80.58	1.004	18.03		10	1013.2	80.62	1.018	17.86
	30	1000.2	82.41	1.01	19.78		30	1015.2	82.53	1.068	18.84
	50	1008.2	83.31	1.026	20.32		50	1017.4	83.44	1.092	19.99
	80	1014.3	87.43	1.043	23.02		80	1019.2	87.51	1.108	22.84
	100	1016.9	88.14	1.083	24.16		100	1022.2	88.26	1.13	23.86
0.10	2	996.7	76.89	1.001	13.58	0.10	2	998.6	76.92	1.002	13.52
	4	998.3	77.6	1.001	14.81		4	1002.5	77.69	1.003	14.64
	6	998.5	78.31	1.004	15.04		6	1012.4	78.4	1.008	15.01
	10	100.3	79.82	1.009	17.29		10	1013.9	79.91	1.018	17.2
	30	1008.3	81.89	1.016	19.48		30	1015.8	81.92	1.068	19.32
	50	1010.2	83.33	1.029	19.81		50	1017.5	83.45	1.092	19.71
	80	1015.1	87.41	1.056	21.71		80	1020.1	87.51	1.107	21.64
	100	1017.8	88.12	1.074	22.22		100	1023.6	88.23	1.132	22.03
0.15	2	997.3	76.51	1.002	13.41	0.15	2	999.2	76.54	1.001	13.21
	4	999.2	76.68	1.004	14.59		4	1002.5	76.71	1.002	14.04
	6	1002.4	76.79	1.004	14.62		6	1012.8	76.83	1.007	14.39
	10	1003.6	78.48	1.009	16.74		10	1014.5	78.52	1.018	16.71
	30	1009.2	80.13	1.013	18.46		30	1016.2	80.16	1.067	18.21
	50	1011.1	81.29	1.021	18.52		50	1018.4	81.31	1.071	18.33
	80	1016.3	84.06	1.058	20.73		80	1021.2	84.11	1.106	20.42
	100	1018.2	84.52	1.098	21.6		100	1023.4	84.61	1.131	21.49
0.20	2	998.2	75.81	1.002	12.69	0.20	2	999.7	75.86	1.001	12.52
	4	999.8	75.87	1.003	14.02		4	1003.2	75.91	1.002	13.86
	6	1002.9	76.46	1.007	14.24		6	1013.4	76.5	1.006	14.11
	10	1004.1	77.83	1.018	15.86		10	1015.6	77.86	1.017	15.72
	30	1009.8	79.63	1.027	17.73		30	1017.2	79.67	1.067	17.51
	50	1012.3	80.72	1.048	17.92		50	1019.5	80.78	1.091	17.63
	80	1017.3	82.85	1.067	19.21		80	1022.2	82.91	1.106	18.94
	100	1018.8	83.32	1.078	20.29		100	1024.6	83.41	1.132	20.03

tion[29].

$$\eta_r = 1 + 2.5\phi_m + 14.1\phi_m^2$$

where ϕ_m is the volume fraction of the hydrated micelles. The molar volume of the hydrated micelle (Vm) is ϕ/CM where CM is the concentration of the hydrated micelles, CM= C_{total}-C_{CMC}. The volume of the hydrated micelle is V_h=Vm/N, where N refers to Avogadro number.

3.1. Micellar SDS solutions

In the case of SDS solutions, the range of our study is 2mM to 100mM. Generally solubilization is known to occur at different sites in the micelles. (i) at the water-micelle surface (ii) between the hydrophilic head groups (iii) in the palaside layer of the micelle, i.e., between the hydrophilic groups and the first few carbon atoms of the hydrophobic group and (iv) in the inner hydrophobic core of the micelles. We analysed our dielectric data on the basis of the interactions of these additives with the surfactant in aqueous solutions.

According to Cole[30], if a solution behaves as a single relaxation system, ε' of the complex dielectric constant and ε'', the imaginary part must be linked by the following relationship.

$$\varepsilon' = -\tau\omega\varepsilon'' + \varepsilon_0$$

Hence a plot of ε' *Vs* $\omega\varepsilon''$ must be a straight line. We have found that no such straight line is obtained for any concentration of SDS and hence obviously more than one relaxation mechanism operate. It is a common knowledge that amide + water system shows a dielectric dispersion which can be explained by a two state model at least in water rich concentrations. The relaxation time can be fitted with two relaxation times that correspond to two types of water in solution (i) the bulk water and (ii) the hydration water. The exchange between these two types is the rate process that determines the relaxation time of water + alcohol mixtures[31]. But it has been found that both the relaxation times increase with increasing amide concentrations in the water rich region.

In our studies of acetamide + water + SDS, we found that increase of acetamide concentration decreases the average relaxation time, which implies that the two state models cannot be extended to aqueous SDS solution in the presence of acetamide There is a clear interference of acetamide molecules on the micelles of SDS. The bulk solution dielectric constant decreases with increase of acetamide concentration as is expected in a binary n- acetamide + water system, but the relaxation mechanism seems to be different. For aqueous SDS, Buchner et al.[32] have identified four relaxation times. One of them at 120ps (≈2GHz) is attributed to the slow water hydrating the micelles. The hydration of SDS micelles is classified as 'hydrophilic' since the water hydrates the O-SO $-_3$ groups of SDS ion through hydrogen bonding and the hydration shell extends beyond micelle volume.

This strong hydration gets interfered by the presence of amides. The acetamide molecules cannot go into the interior of the micelles interfering with the hydrophobic interactions of the micelle, but certainly decreases the ion-ion interactions of the head groups. Hence the dynamic equilibrium of the hydrated water is disturbed. The overall relaxation time consequently gets decreased. The shift of this peak is distinctly visible at higher concentration of SDS it around 3GHz.

$$\frac{1}{\tau_{obs}} = \frac{1}{\tau_1} + \frac{1}{\tau_2}$$

where τ_1 and τ_2 are that of the rotation of the hydration water around the micelle ions and τ_2 is that of hydrated water squeezed in the hydrophobic interior of the micelle. The other relaxations of 0.5ns and 5ns do not contribute at this region.

What is the role of other organic additives on the aqueous SDS micellar solutions? In case of addition of amine, the variations of molar conductivity of SDS solutions showed that the CMC of SDS is systematically lowered on addition of aniline[33]. It was suggested that the addition of amine perturbs the interface of surfactant micelles by intercalation of the acetamide into the head group region. This behaviour of acetamide is similar to normal alcohols[34]. Perhaps it is not as effective as primary alcohols.

The addition of amines does not yield any perceptible change in the relaxation time. It appears, the changes in τ noticed can, at best, be attributed to the changes in the dielectric medium due to the dissolution of these organic additives and their effect on the micelles seems to be minimal.

We have drawn $\varepsilon''/\varepsilon'$ *Vs* frequency curve for all systems investigated (**Figures** 1-4) highlights the region 2GHz to 8GHz. This region is characterized by two distinct peaks one around 4.5GHz and another

TABLE 2 : Fractional volume, volume of the hydrated micelles, activation energies for dielectric and viscous flow for SDS micellar solutions at 303 K

Acet M/l	Conc mM	τ/η_ρ ps	ϕ_μ	V_h(ml) $\times 10^{-20}$	ΔF_τ KJ/m	ΔF_η KJ/m
0.05	2	14.08	0.002	-	11.31	15.33
	4	15.33	0.004	-	11.52	15.82
	6	16.43	0.005	-	11.71	15.96
	10	17.96	0.006	0.13	11.92	16.31
	30	19.58	0.017	0.08	12.16	16.87
	50	19.81	0.028	0.06	12.23	16.99
	80	22.07	0.041	0.02	12.54	17.1
	100	22.31	0.052	0.02	12.67	17.32
0.10	2	13.57	0.003	-	11.21	15.31
	4	14.79	0.005	-	11.43	15.81
	6	14.98	0.006	-	11.47	15.92
	10	17.13	0.008	0.12	11.82	15.29
	30	19.17	0.018	0.06	12.12	16.86
	50	19.25	0.029	0.04	12.16	16.98
	80	20.56	0.043	0.03	12.41	17.08
	100	20.69	0.055	0.02	12.45	17.31
0.15	2	13.38	0.004	-	11.18	15.31
	4	14.53	0.006	-	11.39	15.77
	6	14.56	0.007	-	11.41	16.01
	10	16.59	0.009	0.11	11.74	16.76
	30	18.22	0.021	0.04	11.99	16.97
	50	18.13	0.032	0.03	12.01	17.02
	80	19.59	0.046	0.02	12.28	17.21
	100	19.67	0.059	0.02	12.38	17.29
0.20	2	12.66	0.004	-	11.04	15.31
	4	13.97	0.007	-	11.29	15.74
	6	14.14	0.008	-	11.33	15.99
	10	15.57	0.012	0.1	11.61	16.71
	30	17.26	0.023	0.05	11.89	16.89
	50	17.09	0.034	0.03	11.92	16.98
	80	18.01	0.048	0.03	12.09	17.13
	100	18.82	0.061	0.02	12.23	17.21

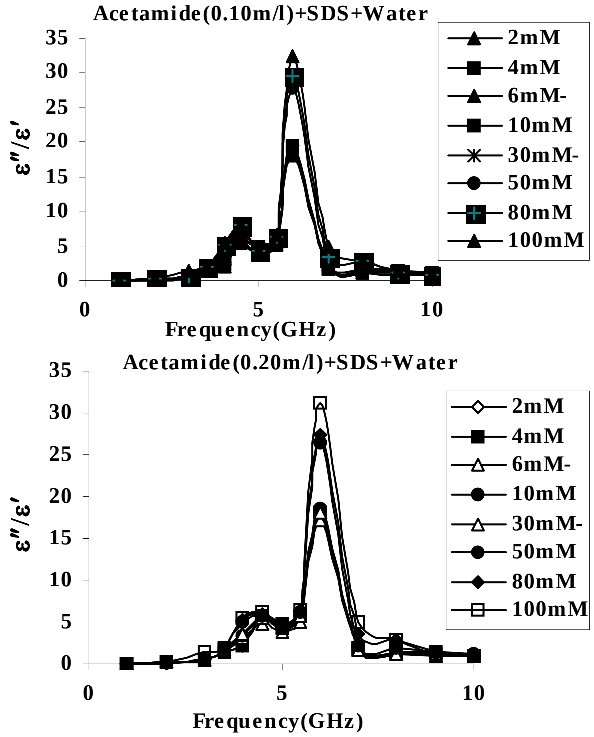
For M/l	Conc mM	τ/η_ρ ps	ϕ_μ	V_h(ml) $\times 10^{-20}$	ΔF_τ KJ/m	ΔF_η KJ/m
0.05	2	13.99	0.002	-	11.41	15.42
	4	15.07	0.004	-	11.61	15.88
	6	16.19	0.005	-	11.76	15.99
	10	17.54	0.007	0.36	12.02	16.38
	30	17.64	0.027	0.15	12.15	16.97
	50	18.31	0.036	0.14	12.31	17.06
	80	20.61	0.043	0.09	12.64	17.14
	100	21.11	0.053	0.07	12.75	17.34
0.10	2	13.49	0.003	-	11.32	15.41
	4	14.59	0.005	-	11.52	15.82
	6	14.89	0.007	-	11.58	15.97
	10	16.89	0.009	0.61	11.93	16.31
	30	18.08	0.028	0.2	12.21	16.92
	50	18.04	0.039	0.14	12.26	17.02
	80	19.54	0.045	0.09	12.51	17.11
	100	19.46	0.056	0.09	12.55	17.31
0.15	2	13.19	0.004	-	11.26	15.37
	4	14.01	0.006	-	11.41	15.78
	6	14.28	0.008	-	11.48	15.91
	10	16.41	0.011	0.58	11.85	16.25
	30	17.06	0.031	0.2	12.07	16.84
	50	17.11	0.042	0.14	12.09	16.89
	80	18.46	0.047	0.09	12.35	17.11
	100	19.01	0.059	0.09	12.49	17.29
0.20	2	12.51	0.005	-	11.12	15.38
	4	13.83	0.008	-	11.38	15.78
	6	14.02	0.009	-	11.43	15.92
	10	15.45	0.013	0.6	11.71	16.28
	30	16.41	0.034	0.2	11.97	16.87
	50	16.15	0.046	0.14	11.99	16.99
	80	17.12	0.049	0.09	12.17	17.11
	100	17.69	0.062	0.08	12.31	17.31

Countinue right column

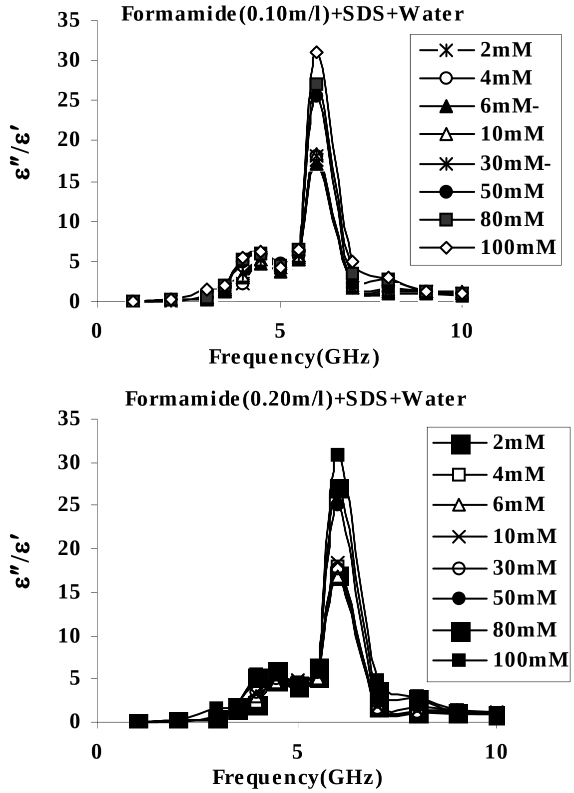
around 6.2GHz ($\tau \approx 35$ps and $\tau \approx 28$ps). The SDS concentration dependence of the relaxation amplitudes in this region is smooth and increases with increasing concentration of SDS, showing that there are more hydration water around SDS micelles. Above CMC the increase is proportional to the concentration of the micelle i.e., (C_{SDS}-CMC). The relaxation amplitude at 35ps is much smaller than of 28ps. The increase in amplitude with concentration at 28ps is also larger compared to that of 35ps. The CMC is lowered in the presence of these additives, and the lowering depends on the solubilization of different additives in the aqueous solution. Hence below CMC the relaxation times increases rather slowly with concentration of SDS.

The changes in the viscosity of the solution are directly related to the hydrodynamic volume of the micelle and their rigidity against rotational and translational motion. The ratio τ/η_r are hence related to the micellar radius.

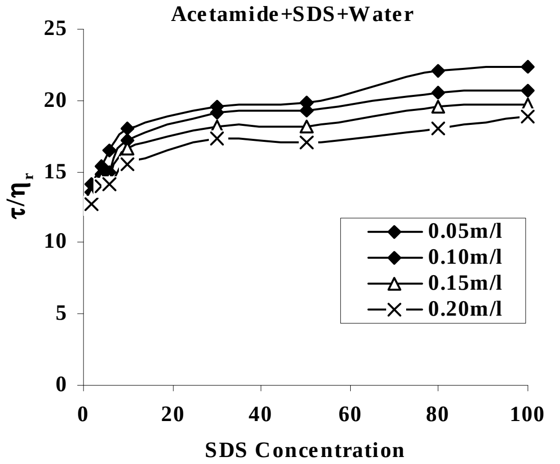
In SDS solution, we found that the relaxation time τ is decreased by the addition of these polar molecules. The calculated values of η and τ are shown in TABLE 2. A plot between concentration against τ/η_r is shown in figures (5-8). It is almost constant at all concentration of SDS. This indicates that the kinetic equilibrium is not disturbed at higher concentrations.



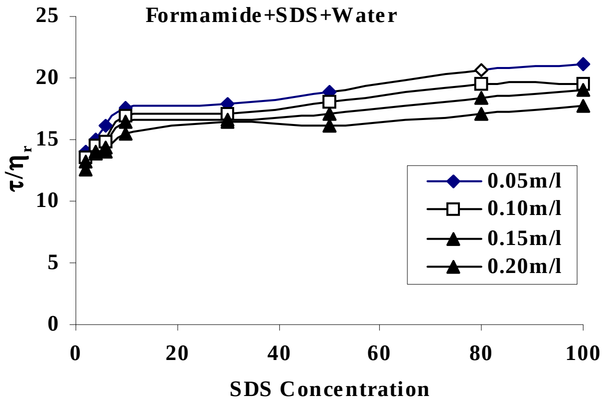
Plot between ε″/ε′ Vs frequency for Acetamide+SDS +Water



Plot between ε″/ε′ Vs frequency for Formamide+ SDS +Water



Plot between τ/η_r Vs frequency for acetamide + SDS+ water



Plot between τ/η_r Vs frequency for formamide + SDS+ water

On the other hand the volume fraction of the hydrated micelle decreases rapidly with the increasing concentration of SDS as well as that of the additives. i.e., the hydrodynamic volume of the micelle decreases with increase of concentration. The hydrated water is squeezed out from the interior with increasing SDS concentration. It is found that the hydrated volume increases in the order of acetamide<formamide. It is known that the hydration extend beyond the Grosse radius in SDS, but the number of hydrated water molecules are not proportionally increased with the increase in concentration.

The molar activation of free energy for viscous flow ΔFη is greater than ΔFτ, the free energy of activation of dielectric relaxation. The process of viscous flow involves greater interference by neighbouring molecules than does dielectric relaxation, as the later takes place by rotation only, whereas the viscous flow involves both the rotational and translational forms of motion. However it is found that $\Delta F>0.5\,\Delta F\eta$, which suggests that there is an inhibition of rotational motion also and this increases with the increase in additive concentration.

4. CONCLUSION

Dielectric dispersion of aqueous solutions of biological materials is well studied. In micellar solutions, the polydispersive character makes the permittivity Vs frequency curve more complex. The water of hydration (i.e.,) bound water in the immediate environment of the surfactant micelle is known to produce in δ-dispersion. The strong forces between the bound water and its polar neighbours make the relaxation time longer than that of free water. The outer core of the micelle 'the stern layer' consists of the hydrated head groups and the bound counterions outside this layer is the unbound counterions. The delicate balance between these layers is disturbed by organic additives like alcohols, which not only influence the micellization through a modification of the water structure but also incorporate it into the micelles. The studies of the effect of other polar molecules as cosolvents are rare. Our studies indicate the presence of atleast two large dispersions in the region 2GHz to 10GHz. This dispersion is caused by the relaxation of the water molecules in the immediate environment of the micelle and that of the hydrated water around the counterions. Using Debye model we have determined the average relaxation time of the micellar solution in this region, which reflects the average dynamics of bound water molecules. The significant changes in the values of $\varepsilon''/\varepsilon'$ with changes in the concentrations of the surfactants were noticed.

5. ACKNOWLEDGMENTS

The authors thank the AICTE, New Delhi, for the financial support under R&D Project. The authors are thankful to Prof. Dr. S.C.Mehrotra, Department of Computer Science and Information Technology and to the Head of the Department of Physics, Dr B.A.M. University, Aurangabad for providing necessary laboratory facilities. One of the authors, Prof. Dr. R.Sabesan, is thankful to the Authorities of Annamalai University for having provided the Visiting Professorship. Prof Dr. S.Krishnan is thankful to the AICTE, New Delhi for having provided the Emeritus Fellowship.

6. REFERENCES

[1] D.Vollhardt, G.Czichocki, R.Rudert; Eng.Asp., **76**, 217 **(1993)**.

[2] T.Nakagawa, M.J.Schick, ' Nonionic Surfactants', Marcel Dekker, New York, **(1967)**.

[3] P.H.Elworthy, A.T.Florence, C.B.McFarlane; Solubilization by surface-active agents and its application in chemistry and the biological sciences, Chapman and Hall, London, **(1968)**.

[4] K.Shinoda; 'Solvent Properties of Surfactant Solutions', Marcel Dekker, New York, **(1967)**.

[5] Sjoblom, Bo Gestblom; J.Colloid Interface Sci., **115**, 535 **(1987)**.

[6] J.H.Fendler, E.Fendler; Academic Press, New York, **(1975)**.

[7] K.L.Mittal, P.Mukherjee; 'Micellization, Solubilization and Microemulsions', Plenum press, New York, **(1977)**.

[8] V.K.Bansal, K.Chinnaswamy, C.Ramachandran, D.O.Shah; J.Colloid Interface Sci., **72(3)**, 537 **(1979)**.

[9] Y.Nozaki, J.A.Reynold, C.Tanford; J.Biol.Chem., **249**, 14 **(1974)**.

[10] T.Ganesh, D.Balamurugan, R.Sabesan, S.Krishnan; J.Mol.Liq., **123**, 80 **(2006)**.

[11] D.Balamurugan, S.Kumar, S.Krishnan; J.Mol.Liq., **122**, 11 **(2005)**.

[12] T.Ganesh, R.Sabesan, S.Krishnan; J.Mol.Liq., **137**, 31 **(2008)**.

[13] C.Tanford; Adv.Protein Chem., **23**,121 **(1968)**.

[14] S.Uren; J.Biochem., **302**, 69 **(1994)**.

[15] D.Ajloo, A.A.Moosavi Morahedi, G.H.Hakimelahi, A.A.Sobowy, H.Gharibi; Colloids Surf, B. Biointerfaces., **26**, 185 **(2002)**.

[16] H.Gharibi, S.Jaradian, M.Hashemianzadeh, H.Gharibi, S.Jaradian, M.Hashemianzadeh; Colloids Surf, A.Physicochem, Eng.Asp., **232**, 77 **(2004)**.

[17] G.Parthipan, T.Thenappan; J.Mol.Liq., **133**, 1 **(2007)**.

[18] I.G.Shere, V.P.Pawar, S.C.Mehrotra; J.Mol.Liq., **133**, 116 **(2007)**.

[19] Mats Almgren, Shanti Swarup; J.Phys.Chem., **86**, 4212 **(1982)**.

[20] Mats Almgren, Shanti Swarup; J.Colloid Interface Sci., **91**, 256 **(1983)**.

[21] Mats Almgren, Shanti Swarup; J.Phys.Chem., **87**, 876 **(1983)**.

[22] Mats Almgren, Shanti Swarup; J.E.Loefroth, J.Phys.Chem., **89**, 4621 **(1985)**.

[23] S.Miyagishi; Bull.Chem.Soc.Jpn., **48**, 2349 **(1975)**.

[24] S.Miyagishi; Bull.Chem.Soc.Jpn., **49**, 34 **(1976)**.

[25] V.K.Bansal, K.Chinnaswamy, C.Ramachandran, D.O.Shah; J.Colloid Interface Sci., **72**, 524 **(1979)**.

[26] J.Sjoblom,, J.Bo Gestblom; Colloid interface Sci., **115**, 535 **(1987)**.

[27] R.H.Cole, J.G.Berbariani, S.Mashimo, G.Chryssiko, A.Burns, E.Tomari; J.Appl.Phys., **66**, 792 **(1989)**.

[28] P.R.Bevington; 'Data Reduction and Error Analysis for the Physical Sciences', McGraw Hill, New York, **(1969)**.

[29] D.E.Guveli; J.Chem.Soc.Faraday Trans., **78**, 1377 **(1981)**.

[30] R.H.Cole; J.Chem.Phys., **23**, 493 **(1955)**.

[31] D.Fioretto, A.Marini, M.Massorotti, G.Onori, L. Palmieri, A.Santucci, G.Socino; J.Chem.Phys., **99**, 8115 **(1993)**.

[32] R.Buchner, C.Baar, P.Fernandez, S.Schrodle W. Kunz; J.Mol.Liq., 118, 179 (2005).

[33] M.Salim Akhter; Colloids, Surfaces A: Physicochemical and Engineering Aspects, **121**, 103 **(1997)**.

[34] P.Mukherjee, K.J.Mysels; NSRDS-NBS-36, Superintendent of Documents, US Government Printing Office, Washington D.C., 20402, **(1971)**.