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Dielectric Relaxation studies of aqueous Cetyl Trimethyl Ammonium Bromide with some additives as co-solvents in TDR Technique

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Abstract: Understanding the effect of external additives on the properties of aqueous surfactant solutions is of utmost importance due to widespread applications of surfactant-based systems. Dielectric relaxation studies of aqueous sodium dodecyl sulphate with nitriles, 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. We have determined the relaxation time using the Cole-Cole method. The relative viscosity of the micellar solutions was also determined. 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.

Keywords: Dielectric relaxation spectroscopy, Time Domain Reflectometry, Surfactants, SDS.

Introduction

Surfactants are compounds that lower the surface tension (or interfacial tension) between two liquids or between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants. Surfactants like hexadecyl (or cetyl) trimethylammonium bromide (CTAB) also belong to this category. Many methods have been proposed to determine the behaviour of cationic surfactants[1-10] Micellar catalysis in organic reactions has carried out evoked great interest among the research workers.

The aim of the present study is to investigate the dielectric behaviour of aqueous surfactants especially in the presence of certain additives of polar nature. There is an equilibrium between ‘hydrated water’ and ‘free water’ at a given temperature with a dynamic exchange rate K, which depends on the concentration of the surfactant and its ionic character. This is reflected in the dielectric relaxation time of the aqueous solution. Dielectric dispersion of aqueous solutions of materials are well studied. In micellar solutions, the dielectric dispersion in the region 2GHz to10GHz is particularly important since this region is related to the 'bound' water relaxation.

Hence in the present study, dielectric measurements were made on cationic CTAB aqueous solutions with cosolvents to obtain information on the micellar structure and the influence of polar additives on the hydration properties of micellar solutions. The emphasis is mostly on 'bound water relaxation' and hence the frequency dependence of $\varepsilon'$and ε'' of the micellar solutions in the region of 2GHz to 10GHz was studied in detail.

Materials and methods:

The surfactants CTAB is the product of BDH 99% pure and is used 'as such' without further purification. The co-solvents acetonitrile and benzonitrile 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 a HP54750A sampling oscilloscope and HP54754A TDR plug-in-module[11.] 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 on open load conditions. The sampling oscilloscope monitored the change in the pulse shape after reflection from the sample placed in the cell. A time window of 5ns was used. The reflection pulse with Rx(t) and without sample R1(t) were digitized in 1024 points and transferred to a computer through GPIB. A water circulated thermostat controlled bath was used to maintain constant temperature within ±1ºC. The sample cell is surrounded by a heat-insulated container through which the water from the bath is circulated.

A Fourier transform of $\{R_1(t) - R_X(t)\}$ and $\{ R_1(t) - R_X(t)\}$ namely p(ω) and q(ω) 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. 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 [12]. The ε_∞ is taken as an adjustable parameter but ε^* is not sensitive to small changes in ε_∞ in the similar class of liquid systems.

Results & Discussion

The Critical Micelle Concentration (CMC) of both anionic and cationic surfactants is found lowered in the presence of nitriles it promotes stability of micelles. Earlier several explanations were given for this phenomenon. Any addition of non-electrolyte to water should result in a decrease in the 'molecular order' of water due to the interference of the solute species. The cohesive forces between the water molecules get stronger in the presence of additives to repel the hydrophobic portion of the surfactants, with the result the surfactant molecules start to aggregate at lower concentrations. The aggregation is governed by a delicate balance between the reduction of hydrocarbon-water interface (hydrophobic interactions among the molecules of non-polar alkyl chains) and the coulomb interactions of the polar/ionic head groups with the counterions and the solvent. The size of the limiting factor is the area per head group in the Stern layer.

If the aggregation number increases, this area per head group reduces and the coulomb interaction between the head group increases, which disturbs the balance. This act of counter balancing, limits the size distribution of aggregates. However introducing more counterions in the stern layer can reduce the coulomb interaction between the head groups. Then the aggregation number will increase. Yet, another way is to alter the 'water structure'. For this purpose, small quantities of additives of varying chain lengths can be added. However, additives not only influences micellization through modification of 'water structure' but also incorporate itself into the micelles[13] other organic liquids especially aprotic solvents have occasionally been used as co-solvents for this type of investigations [14-15].

It is obvious that the dielectric relaxation spectroscopy is a technique that monitors a wide range of dynamical processes of micellar systems with relaxation on the pico and nano second time scale. However the number of investigations is rather few. The frequency range is always limited. Toshiyuki Shikata[16] covered a range of 30 to 300MHz, which excluded the relaxation range of the solvent water. Kaatze et al.[17] covered the frequency range of $5 \leq \gamma / \mathrm{GHz} \leq 38$, where the solute relaxation region (<5 GHz) was not covered.

In the case of ionic micellar aggregates, systematic studies of their dielectric properties are very few. Presently, an attempt is made to study for ionic solutions.

The strong interrelation between the dielectric relaxation and other process like the viscosity is quite well known. The classical Debye's theory envisages the dielectric relaxation as the hindred reorientations of spherically shaped polar molecules. The theory relates the dielectric relaxation time to the viscosity as $\tau = \frac{4\pi\eta a^3}{kT}$ where 'a' denotes the molecular radius for a system belonging to the same class. In the present study dielectric spectroscopic measurements are made on micellar solutions of cationic cetyl trimethyl ammonium bromide with organic polar solutes such as acetonitrile and benzonitrile,

The values of density, static dielectric constant and relative viscosity data of the CTAB solutions are given in Table 1. The calculated values of volume fraction of the hydrated micelles, the molar volume of the hydrated micelle and the activation energies for the dielectric and viscous relations are given in Table 2.

In the case of CTAB solutions, the range of our study is 10mM to 100mM. In cationic micellar solutions, the properties of head group and the micelle counterions play a leading role in relaxation phenomenon. We have chosen cetyl trimethylammonium bromide as a cationic group for study. However, the rate of dissolution of CTAB in water at room temperature is relatively low. CTAB offers a large volume for solubilization of additives[18]

An important observation made in our study is that on increase of CTAB concentration, the average relaxation time increases. On the other hand increase of acetonitrile concentration, for given concentration of CTAB, the relaxation time decreases. Similarly the static dielectric constant ε_0 increases with increase of surfactant concentration but decreases with increase of additive concentration. It is known that the amine contribution to the dielectric relaxation in a mixture of water + amine is atleast one order of magnitude smaller than that of pure water molecules and that hydrated water has a relaxation time about two times higher than bulk water. Hence at such low concentration of amines, the addition of amines to the solution is expected to increase the hydrated water; which in turn, must result in an increase of relaxation time of the mixture. On the other hand the trend is opposite. (i.e.,) the hydration-water content seems to decrease on increase of amine concentration though nominal. Also the fact that there is no abnormal change in shear viscosity indicates that there is no drastic change in micellar size. Hence one can conclude that the additives are mostly solubilized in the bulk water, leaving only a fraction at the micelle-water interface layer. These additives are mainly hydrophilic and do not affect the micellar structure, but the dynamics of the micelle is affected.

Table: 1 Dielectric relaxation of aqueous CTAB with nitriles and related parameters at 303K

Benzonitrile	Conc mM	Density kg m^{-3}	ε_0	η_r	τ ps	Acetonitrile	Conc mM	Density kg m^{-3}	ε_0	η_r	τ ps
0.05	10	996.1	78.19	1.001	13.2	0.05	10	996.3	78.25	1.002	12.86
	20	999.3	78.97	1.004	14.18		20	1005.4	79.02	1.005	13.57
	40	1005.2	79.84	1.006	15.45		40	1009.2	79.98	1.007	14.61
	60	1010.7	80.58	1.008	16.11		60	1011.1	80.69	1.008	15.56
	80	1016.4	80.91	1.009	16.71		80	1016.2	80.92	1.011	15.92
	100	1021.2	81.24	1.011	16.94		100	1021.1	81.37	1.013	16.36
0.10	10	997.3	77.71	1.001	12.25	0.10	10	995.2	77.83	1.002	12.21
	20	999.6	78.51	1.003	13.62		20	1004.9	78.52	1.005	12.98
	40	1004.2	79.21	1.006	14.10		40	1008.5	79.56	1.006	13.82
	60	1014.2	79.81	1.007	14.81		60	1010.7	80.17	1.008	14.91
	80	1016.5	80.11	1.009	15.09		80	1016.2	80.26	1.011	14.98
	100	1020.5	81.17	1.011	16.86		100	1020.8	80.55	1.014	15.42
0.15	10	997.1	77.11	1.001	11.01	0.15	10	994.8	77.22	1.002	10.91
	20	998.9	77.35	1.002	12.45		20	1004.6	77.69	1.005	12.02
	40	1004.2	78.31	1.006	13.01		40	1007.5	78.32	1.006	13.19
	60	1012.2	78.92	1.007	14.07		60	1010.2	79.53	1.007	13.81
	80	1015.8	79.23	1.009	14.14		80	1015.4	79.65	1.011	13.82
	100	1019.9	79.86	1.011	15.92		100	1020.4	79.76	1.013	14.51
0.20	10	996.4	75.96	1.001	09.96	0.20	10	994.3	76.25	1.001	9.67
	20	998.2	76.62	1.002	10.71		20	1004.2	76.83	1.005	10.65
	40	1008.4	76.82	1.006	11.18		40	1006.5	77.63	1.006	11.06
	60	1011.7	78.06	1.007	11.45		60	1010.2	78.69	1.007	11.41
	80	1015.2	78.86	1.009	11.81		80	1015.3	79.02	1.011	11.97
	100	1017.3	79.02	1.011	15.74		100	1020.4	79.35	1.013	12.11

CTAB showed distinctly two relaxation modes. The slow relaxation (τ=5ns) time is due to that of the distribution of the dissociated cationic surfactant head groups on the micellar surface or it's fluctuations on the micelle surface. The fast relaxation (τ=0.5ns) time is due to the rotational motion of ion pairs consisting of surfactant cations and counterions of the spherical micelle. The dielectric dispersion in aqueous CTAB is best described by a Cole-Cole type The 'τ' values decrease from 0.3 to 0.1 on varying the concentration of CTAB from 10 to 120mM[16].

Table:2 Activation energies for dielectric and thermo dynamic parameters for SDS micellar solutions at 303K

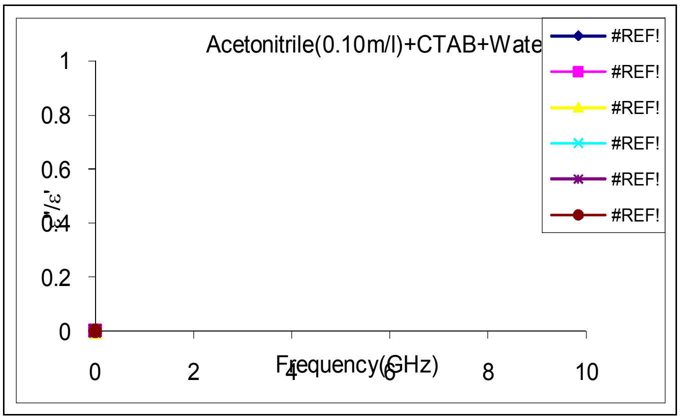
Acet M/l	Conc mM	τ/η_ρ ps	ϕ_μ	V_h(ml) x10^{-20}	ΔF_τ kJ mol^{-1}	ΔF_η kJ mol^{-1}	Benz M/l	Conc mM	τ/η_ρ ps	ϕ_μ	V_h(ml) x10^{-20}	ΔF_τ kJ mol^{-1}	ΔF_η kJ mol^{-1}
0.05	10	12.83	0.002	0.33	11.07	15.02	0.05	10	13.19	0.003	0.49	11.14	13.96
	20	13.51	0.003	0.07	11.21	15.22		20	14.12	0.004	0.06	11.32	14.11
	40	14.51	0.004	0.06	11.41	15.52		40	15.35	0.006	0.04	11.54	14.36
	60	15.43	0.004	0.05	11.56	15.87		60	15.98	0.007	0.03	11.65	14.57
	80	15.74	0.005	0.01	11.62	15.96		80	16.56	0.009	0.03	11.74	14.88
	100	16.15	0.006	0.01	11.68	16.01		100	16.75	0.012	0.02	11.78	15.01
	10	12.18	0.002	0.34	10.95	14.98		10	12.23	0.003	0.51	10.95	13.88
	20	12.92	0.003	0.06	11.11	15.06		20	13.57	0.004	0.06	11.22	13.99
	40	13.73	0.004	0.05	11.25	15.42		40	14.01	0.006	0.04	11.31	14.26
	60	14.79	0.004	0.04	11.45	15.81		60	14.71	0.007	0.04	11.43	14.48
	80	14.82	0.005	0.02	11.46	15.95		80	14.95	0.011	0.03	11.48	14.69

	100	15.21	0.006	0.01	11.52	15.98		100	16.68	0.013	0.02	11.75	14.87
0.15	10	10.88	0.002	0.35	10.66	14.89	0.15	10	10.98	0.003	0.51	10.68	13.86
	20	11.96	0.004	0.06	10.91	14.99		20	12.42	0.004	0.07	10.99	13.97
	40	13.11	0.005	0.05	11.14	15.09		40	12.93	0.006	0.06	11.11	14.21
	60	13.72	0.006	0.04	11.26	15.38		60	13.97	0.007	0.05	11.31	14.43
	80	13.66	0.007	0.02	11.28	15.79		80	14.01	0.011	0.05	11.32	14.61
	100	14.33	0.008	0.02	11.38	15.96		100	15.74	0.013	0.03	11.62	14.83
0.20	10	9.66	0.003	0.36	10.36	14.88	0.20	10	9.95	0.003	0.51	10.43	13.78
	20	10.59	0.004	0.07	10.61	14.89		20	10.68	0.004	0.07	10.62	13.86
	40	10.99	0.005	0.06	10.71	14.98		40	11.11	0.006	0.06	10.72	13.99
	60	11.33	0.006	0.06	10.78	15.16		60	11.13	0.007	0.06	10.78	14.06
	80	11.83	0.007	0.05	10.91	15.47		80	11.71	0.012	0.05	10.86	14.31
	100	11.96	0.008	0.02	11.61	15.87		100	15.57	0.013	0.03	11.59	14.56

This corresponds to decrease of the magnitude of slow relaxation mode with increasing surfactant concentration. As we have seen earlier the organic additives do not disturb the head group structure on the micellar surface[12]. The dissolution of amines in CTAB solutions results in electrostatic and hydrophobic effects due to dissolution of NH_3^+ ion and interfaces with the cationic micelle head group and affects the micelle rotation. It is logical to conclude that increase of the concentration of the additives could only disturb the fast relaxation time (i.e.,) the time of relaxation of the rotational motion of the counterions on the micelles surface. The bound water relaxation time is about 26-30ps (i.e.,) more than twice that of pure water. In the case of CTAX surfactants, a relaxation time of 20-30ps is unequivocally assigned to water adjacent to the hydrophobic surface.[18] The H-bond network is disturbed by the screening effect of the organic additives, this influence the mobility of the hydration of water.

We have drawn ε''/ε' *Vs* frequency curve for all systems investigated. The region 2GHz to 8GHz is highlighted in (Fig.1). The amplitude of the relaxation in this region is a maximum at 25ps and 35ps. They are characteristic relaxation times for the hydrated water 'h' bonded with the ionic head groups and that around the interface of the ionic head group and bulk water.

The surfactant concentration dependence of the amplitude of the peak around 35ps is much less than that around 25ps. Hence the peak around 25ps may be assigned to the hydrated water around the micelle head group and that around 35ps is attributed to the h-bonded water with the ionic head groups. We also found that the increase of the additives concentrations do not result in any change in the ε''/ε' values of the 6GHz peak, (i.e.,) the volume of the hydrated-water around the micelle is almost not altered by the addition of these organic solutes.



The values of τ/η_r for all these systems recorded. τ/η_r is found to vary linearly with CTAB concentration but the increase is very small, showing that the hydrated micellar volume does not very much with the concentration of CTAB. It is found that increase of the concentration of the organic additives slightly increases the volume of the hydrated micelles as seen from the graph τ/η_r *Vs* concentration. However the effect is minimal. This effect is again in conformity with the observation that in CnTAX micelles the hydrated water mostly reside inside the Grosse sphere[17] and an appreciable amount of this water is irrotationally bound by an interaction with the cations. The molar activation of free energy for viscous flow ΔF_η is greater than ΔF_τ, the free energy of activation of dielectric relaxation[18]. 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.

References

1. Ganesh T, Sabesan R, Krishnan S. Dielectric relaxation studies of alkanols solubilized by cationic surfactants in aqueous solutions. Journal of Molecular Liquids, 2008, 137;31-35
2. Ganesh T, Sabesan R, Krishnan S. Dielectric relaxation spectroscopic studies of ionic surfactants in aqueous solutions. Journal of Molecular Liquids, 2006, 128;77-80
3. Castedo A, Del Castillo J L, Suarez-Filloy M J , Rodriguez J R. Effect of temperature on the mixed micellar tetradecyl trimethylammonium bromide – butanol system. J. Colloid interface Sci. 1997, 196; 148-156.
4. Gharibi H., Razavizadeh B M, Hashemianzeheh M. New Approach for the studies of physicochemical parameters of interaction of Triton X-100 with cationic surfactants. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2000,174; 375-386.
5. Kaatze U, Neumann Chr, Pottel R, Dielectric Spectroscopy on Aqueous Solutions of Pyridine and its Derivatives. J. Mol. Liq. 1986. 202-203.
6. Kshipra V. Padalkar, Omprakash R. Pal, Vilas G. Gaikar. Rheological characterization of mixtures of cetyl trimethylammonium bromide and sodium butyl benzene sulfonate in aqueous solutions. Journal of Molecular Liquids, 2012, 173;18-28
7. Katerina Bílková, Egil Gulbrandsen. Kinetic and mechanistic study of CO2 corrosion inhibition by cetyl trimethyl ammonium bromide. Electrochimica Acta, 2008, 53; 5423-5433
8. Dipak Kumar Rana, Soumyadipta Rakshit, Sayaree Dhar, Subhash Chandra Bhattacharya. Spectroscopic probing of the microenvironment of 7-oxy(5-selenocyanato-pentyl)-2H-1-benzopyran-2-one in ionic and nonionic micelles. Journal of Photochemistry and Photobiology A: Chemistry, 2013, 270; 67-74
9. Debabrata Mandal, Sobhan Sen, Kankan Bhattacharyya, Tahei Tahara. Femtosecond study of solvation dynamics of DCM in micelles. Chemical Physics Letters, 2002, 359; 77-82
10. Bornali Boruah, Palash M. Saikia, Robin K. Dutta Binding and stabilization of curcumin by mixed chitosan–surfactant systems: A spectroscopic study. Journal of Photochemistry and Photobiology A: Chemistry, 2012, 245; 18-27
11. Achole B D, Patil A V, Pawar V P, Mehrotra S C. Study of interaction through dielectrics: Behavior of − OH group molecules from 10 MHz to 20 GHz. Journal of Molecular Liquids, 2011, 159; 152-156
12. Kalaivani T Prabhakar Undre Sabesan R Krishnan S. Dielectric relaxation studies of nitriles solubilized by Sodium dodecyl sulphate in aqueous solutions. Journal of Molecular Liquids, 2012, 176;76-80
13. Singh H.N. and S. Swamp, Effect of monohydroxy alcohols and urea on the CMC of surfactants. Bull. Chem. Soc. Japan 1978 51: 1534-1538.
14. Marilyn F. Emerson and Alfred Holtzer, Hydrophobic bond in micellar systems. Effects of various additives on the stability of micelles of sodium dodecyl sulphate and of n-dodecyl trimethyl ammonium bromide. J. Phys. Chem. 1967.10;3320-3330.
15. Inoesch L.G. and V.T. De Favere, In solution behaviour of surfactants eds. Mittal K.L. & E.J. Fendler I, Plenum Press, New York. 1982;407
16. Toshiyuki Shikata and Shin-ichiro-Imai, Dielectric Relaxation of surfactant Micellar solutions. Langmuir 1998, 14: 6804-6810.
17. Kaatze U., Neumann Chr. and R. Pottel, Dielectric Spectroscopy on Aqueous Solutions of Pyridine and its Derivatives. J. Mol. Liq. 1986, 202-203.
18. Buchner R, Baar C, Fernandez P, Schrodle S, Kunz W. Dielectric spectroscopy of micelle hydration and dynamics in aqueous Ionic surfactant solution. J. Mol. Liq. 2005 118: 179-187.

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