

## Physico-chemical and dielectric relaxation studies of ionic surfactants in Time Domain Reflectometry (TDR)

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**Abstract**—The properties of aqueous surfactant solutions with external additives are extensively useful in surfactant-based systems. To study the dielectric relaxation studies of aqueous ionic surfactants (SDS, CTAB, DPC) and aqueous butanol, benzyl alcohol, aniline and tributylamine were carried out for different concentrations at 303K. Dielectric relaxation spectroscopy (DRS) is valuable for understanding the dynamic process mainly in micellar systems. Time domain dielectric data were obtained through HP54750A oscilloscope and TDR plug-in-module. The relaxation times were determined through the well-known Cole-Cole method. The superposition of two relaxation times gives the dielectric relaxation time obtained from the hydrated water molecule with rotations around the micelle, ions and another hydrophobic inner side of the micelle. Viscosity measurements were used to correlate the dielectric data. The Kirkwood correlation factor ( $g_f$ ), effective Kirkwood correlation factor ( $g_{eff}$ ), Bruggeman Factor ( $f_B$ ), excess inverse relaxation time  $(1/\tau)^E$ , excess dielectric constant ( $\epsilon^E$ ) and free energy of activation ( $\Delta F_i$ ) were also calculated. The effects of dielectric relaxation and viscous flow were interpreted and discussed.

Keywords: Dielectric Relaxation Spectroscopy, Time Domain Reflectometry, Surfactants, SDS, CTAB, DPC, Micelle

### INTRODUCTION

There has been considerable interest in micelle aggregates of surfactants in many areas like technology, biology and pharmacology [1]. To realize the properties of the dielectric system of any medium, mainly in colloids, the theory is based on single step and continuous distribution of relaxation times [2-7]. Further, the relaxation data are not sufficient to describe the dielectric behavior of fluids and surfactant. The required additional data, due to their entropic attraction in solute-solvent molecules with their additives, are important [8-15]. These are necessary to understand the insight nature of hydration phenomenon and H-bond of some mixtures of solute and solvent (not all). "There is a great interest to study the dielectric relaxation behavior in alcohol system to understand the role of hydrogen bond in liquid alcohol system. This study provides better values of dielectric parameter because of large frequency range covered in a single measurement. The importance of measuring the dielectric constant of liquid lies in the fact that it provides valuable information about ordering of the liquid state."

Hence in the present study, dielectric, spectroscopic measurements are made on aqueous (i) anionic sodium dodecyl sulfate, (ii) cationic cetyltrimethylammonium bromide solutions, (iii) cationic dodecyl pyridinium chloride and organic solutes such as n-

butanol, benzyl alcohol, aniline, tributylamine, acetonitrile, benzonitrile, acetamide and formamide in aqueous media to obtain the hydrophobic and hydrophilic nature of micelle structure. The study of Kirkwood correlation factor provides valuable information regarding the solute-solvent interactions in binary mixture especially when one of the components has anti-parallel orientation of dipoles [12]. The viscosity measurements were carried out to correlate the dielectric data. Kirkwood correlation factor, effective Kirkwood correlation factor, Bruggeman Factor, excess inverse relaxation time, excess dielectric constant and free energy of activation were also calculated [12-15].

### MATERIALS AND METHODS

Anal grade chemicals were purchased from Fluka and Aldrich with 99.7% pure and used without further purification. Doubly distilled, deionized water was used for the preparation of samples. The surfactants were 99% purity. The solutions were prepared by weight using a semi-micro Sartorius balance. The density and viscosity were measured through the pycnometer and Oswald's viscometer, respectively. The measurements were at 30 °C.

The dielectric measurements were made using time domain reflectometry in the frequency range of 10 MHz to 20 GHz using a HP54750A sampling oscilloscope and TDR plug-in-module 11. The workings of experimental set up are explained elsewhere [2].

Fourier transform of  $\{R_i(t) - R_x(t)\}$  and  $\{R_i(t) - R_x(t)\}$ , namely  $p(\omega)$  and  $q(\omega)$ , respectively, was obtained. Spectra  $\rho^*(\omega)$  over the fre-

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quency range of 10 MHz to 20 GHz were obtained through,

$$\rho^*(\omega) = \frac{c/j\omega d}{p(\omega)q(\omega)} \quad (1)$$

where ' $\omega$ ' is the angular frequency, ' $c$ ' is the velocity of light and ' $d$ ' is the effective pin length. The complex permittivity spectra  $\epsilon^*(\omega)$  were obtained from reflection coefficient  $\rho^*(\omega)$  by applying bilinear calibration method. The experimental values  $\epsilon^*$  were fitted with Debye equation with  $\epsilon_0$  and  $\tau$  as fitting parameters and fitted with least square method [13,14].

## EXPERIMENTAL FACTORS

### 1. Bruggeman Factor

Bruggeman mixture formula can be used for studying the interactions in molecules in binary liquids. It states the static permittivity of mixture ( $\epsilon_{om}$ ), solute ( $\epsilon_{os}$ ), and solvent ( $\epsilon_{ow}$ ) with volume fraction of solvent ( $V_{ow}$ ) in mixture as

$$f_B = \left( \frac{\epsilon_{om} - \epsilon_{ow}}{\epsilon_{os} - \epsilon_{ow}} \right) \left( \frac{\epsilon_{os}}{\epsilon_{om}} \right)^{1/3} = 1 - V_{ow} \quad (2)$$

According to the above equation a linear relationship is expected in Bruggeman factor  $f_B$  and  $V_{ow}$ . The molecular interactions are found through the deviation in linear relation; to fit the experimental data, the Bruggeman formula of mixture can be modified as

$$f_B = \left( \frac{\epsilon_{om} - \epsilon_{ow}}{\epsilon_{os} - \epsilon_{ow}} \right) \left( \frac{\epsilon_{os}}{\epsilon_{om}} \right)^{1/3} = 1 - [a - (a-1)*V]*V = 1 - f(V) \quad (3)$$

with ' $a$ ' as a fitting parameter and ' $f$ ' can be interpreted as fraction of effective volume  $V$ . The relative change in value of ' $a$ ' reveals the magnitude of interaction between solute and solvent.

### 2. Excess Parameters

The structural changes in the binary mixture were obtained through the excess dielectric properties and used to determine the static permittivity and inverse relaxation time. The excess permittivity ( $\epsilon^E$ ) and excess inverse relaxation time ( $(1/\tau)^E$ ) take the form

$$\epsilon^E = (\epsilon_0 - \epsilon_\infty)_m - [(\epsilon_0 - \epsilon_\infty)_A X_A + (\epsilon_0 - \epsilon_\infty)_B X_B] \quad (4)$$

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_A X_A + (1/\tau)_B X_B] \quad (5)$$

where  $X_A$  and  $X_B$  - are the mole fractions of solute and solvent, respectively, and  $m$  - is the mixture. The qualitative information for multimers formation in the mixtures is obtained through excess permittivity.

### 3. Kirkwood Correlation Factor

Kirkwood equation for the mixture can be written as

$$\frac{4\pi N}{9kT} \left( \frac{\mu_A^2 \rho_A g_A}{M_A} X_A + \frac{\mu_B^2 \rho_B g_B}{M_B} X_B \right) g_f = \frac{(\epsilon_{om} - \epsilon_\infty)(2\epsilon_{om} + \epsilon_\infty)}{\epsilon_{om}(\epsilon_\infty + 2)^2} \quad (6)$$

where  $g_f$  is a correlation factor for mixture. The values of  $g_{eff}$  will change from  $g_A$  to  $g_B$  as the fraction of component B increases from zero to one.

### 4. Thermodynamic Parameters

To determine the activation enthalpy, from the relaxation time it is obtained from the rate process theory is,

$$\tau = \frac{h}{kT} \exp\left(\frac{\Delta H_r}{RT}\right) \exp\left(\frac{-\Delta S_r}{R}\right) \quad (7)$$

where  $\Delta F_r = \Delta H_r - \Delta S_r$

Both dielectric relaxation and viscosity process require activating the potential barrier. The viscosity value can be obtained through the same type of rate process theory as,

$$\eta = \frac{Nh}{V} \exp\left(\frac{\Delta H_\eta}{RT}\right) \exp\left(\frac{-\Delta S_\eta}{R}\right) \quad (8)$$

where  $V$ ,  $H$  and  $S$  be the molar volume, enthalpy and entropy respectively, and all other notations having the usual meanings.

## RESULTS AND DISCUSSION

### 1. Ionic Surfactants in Water Media

The dielectric relaxation in pure water is mostly interpreted in

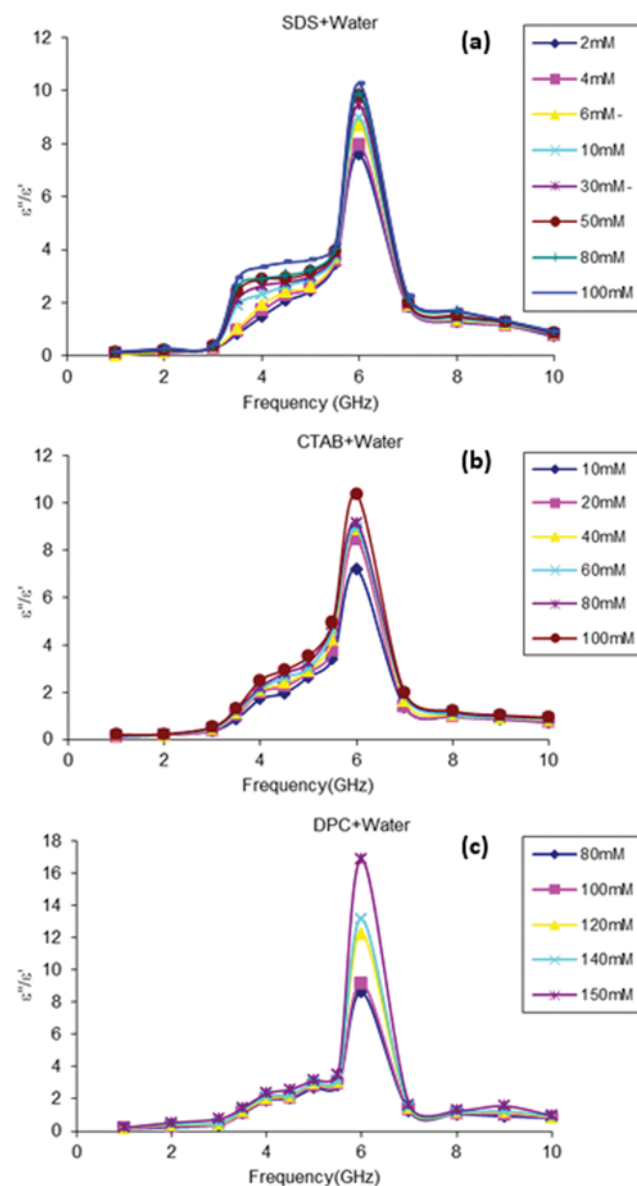


Fig. 1. Frequency Vs  $\epsilon''/\epsilon'$  for aqueous (a) SDS, (b) CTAB & (c) DPC.

terms of two close distinct relaxation times. (i) The breakage of H-bond in water is a rate-determining step in dielectric relaxation of water, the activation enthalpy  $\Delta H \approx 18$  KJ/mole. The frequency dependence of loss tangent ( $\tan \delta = \epsilon''/\epsilon'$ ) of the micellar solutions was

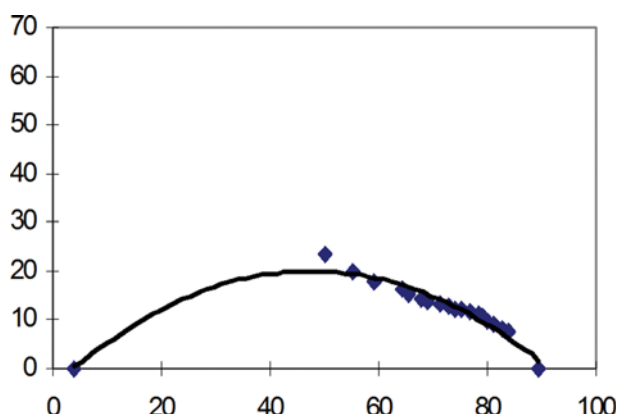


Fig. 2. Cole-Cole Plot  $\epsilon'$  Vs  $\epsilon''$  for 2 mM SDS.

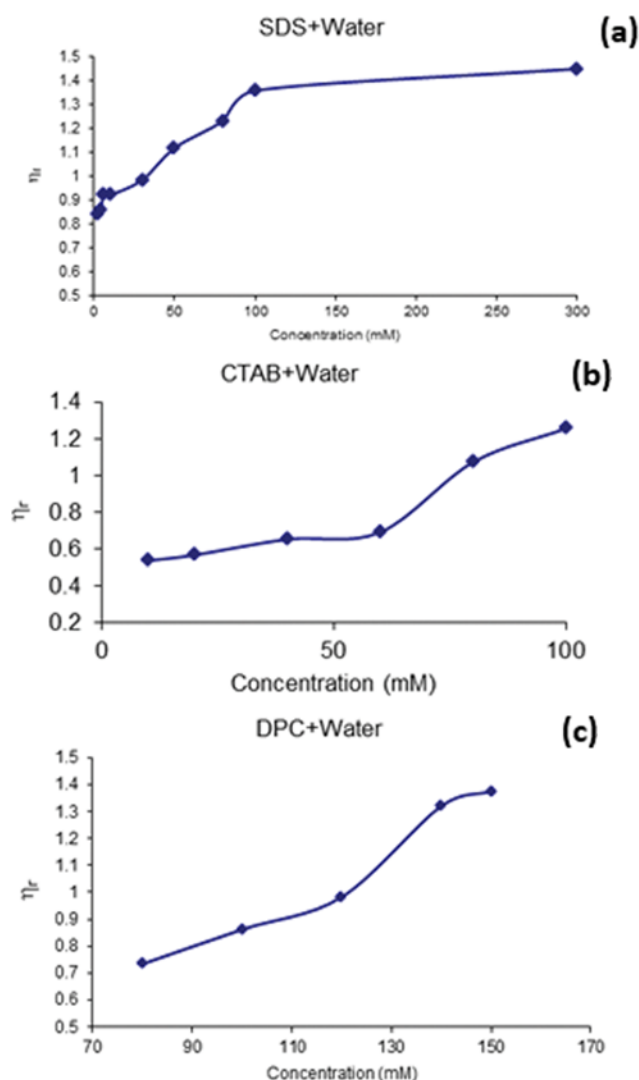


Fig. 3. Conc Vs  $\eta_r$  for aqueous (a) SDS, (b) CTAB and (c) DPC.

studied here (Fig. 1). The studies of excess enthalpy of mixtures showed large positive values due to the breaking of alcohol-alcohol interactions.

In SDS solutions in water the dispersion curves in the frequency are obtained highly different. Two different large different relaxation frequency regions are obtained through constant values. The lower frequency is due to relaxation of solute molecules and the higher frequencies the relaxation responsible for water molecules. The dispersion phenomenon in the relaxation process can be carried out in chemical stream. In this analysis the role of hydrophobic interaction involved the formation of micelle by bound or hydration of water molecules [15].

In SDS, a uniform increase in the dielectric absorption of water molecules is found till CMC and reaches a maximum  $\tau = 40$  ps. Beyond that, there is dispersion with relaxation time extending on  $\tau = 40$  ps to 25 ps. In this region the relaxation strength is found uniform. But the dispersion phenomenon is higher in SDS solutions rather than CTAB and DPC solutions.

Cole-Cole Plot is shown in Fig. 2.

The complex permittivity  $\epsilon^* = \epsilon' - j\epsilon''$  relaxation spectra were found that for all ionic surfactant-water systems under study,  $\epsilon''$  vs.  $\epsilon'$  is the superposition of two Cole-Cole distributions. In bound water

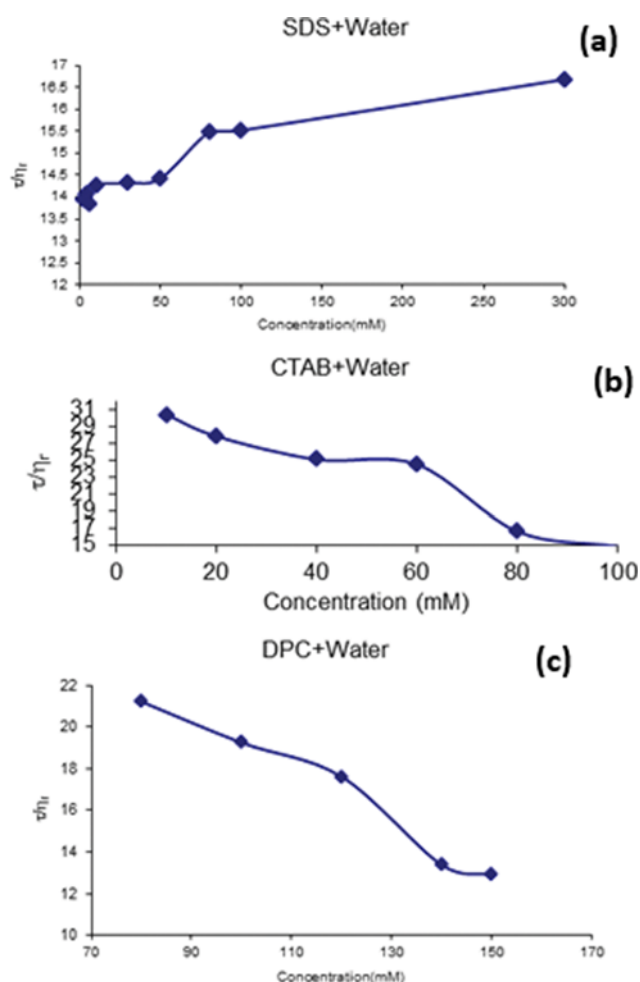


Fig. 4. Conc Vs  $\pi/\eta_r$  for aqueous (a) SDS, (b) CTAB and (c) DPC.

system the ideal nature is possible to discuss and in the case of micelle it is easy to describe, and the possible due to surface-active agents are localized at the interface. The micelle core surrounded by a homogeneous shell of bound water of uniform thickness is

**Table 1. Relative Viscosity, and dielectric constant dielectric relaxation data for SDS, CTAB and DPV micellar solutions in water at 303 K of various concentrations**

Concentration mM	$\eta_r$	$\epsilon_0$	$\tau$ ps		$\tau/\eta_r$
			Theoretical	Graphical	
SDS					
2	0.838	77.91	11.69	11.68	13.94
4	0.857	78.17	12.15	12.06	14.07
6	0.919	79.39	12.87	12.72	13.85
10	0.919	80.54	13.28	13.12	14.27
30	0.982	82.72	14.32	14.06	14.32
50	1.116	83.69	16.22	16.1	14.43
80	1.229	86.83	19.51	19.02	15.48
100	1.356	87.87	21.25	21.04	15.52
300	1.447	88.75	24.61	24.13	16.68
CTAB					
10	0.436	78.63	13.24	12.86	30.37
20	0.567	79.48	15.77	15.02	27.81
40	0.652	80.16	16.34	16.04	25.06
60	0.691	80.84	16.91	16.26	24.47
80	1.073	81.04	17.81	17.16	16.59
100	1.256	81.61	18.61	17.95	14.82
DPC					
80	0.734	80.75	15.58	14.89	21.22
100	0.862	81.67	16.6	15.87	19.25
120	0.983	82.41	17.31	16.71	17.61
140	1.321	82.89	17.65	17.03	13.37
150	1.375	83.26	19.11	18.82	13.91

referred to as hydrated micelle. The relaxation time of free water is 8 ps at 25 °C and approximately varies exponentially with temperature. The presently observed average relaxation time is certainly due to the 'bound water' as they are unable to rotate at frequencies near 1 GHz to 2 GHz, and it is difficult to obtain the water of hydration through the decrement in dielectric constant as pointed out by many authors [16,17].

The conductivity measurement varies increasingly with the volume fraction of the hydrated micelle as shown in Fig. 2. In our concentration range it may be presumed to a first approximation the distribution of the relaxation time in a Cole-Cole type in the same Fig. 2. The relaxation time ( $\tau$ ) for all concentrations using Cole-Cole plot was determined. This relaxation time reflects mostly that of the bound water. It was suggested that the experimental relaxation time reflects the only average dynamics of water molecules in the micelle and not for concentrations [16,17].

**Table 2. Relative Viscosity, dielectric constant and dielectric relaxation data for n-butanol and benzyl alcohol solutions in water at 303 K**

Concentration m/l	$\eta_r$	$\varepsilon_0$	$\tau$ ps		$\tau/\eta_r$
			Theoretical	Graphical	
n-Butanol					
0.2	0.907	80.42	23.31	22.14	25.71
0.5	1.027	79.17	25.51	23.92	24.83
1.0	1.181	78.62	27.82	25.64	23.55
2.0	1.294	77.04	28.54	26.81	22.05
3.0	1.434	76.82	29.13	27.92	20.31
Benzyl alcohol					
0.2	0.984	79.84	25.81	27.64	26.23
0.5	1.064	78.73	26.43	26.32	24.84
1.0	1.223	77.54	28.63	24.21	23.41
2.0	1.359	77.32	29.36	23.32	21.61
3.0	1.551	76.38	30.82	21.23	19.87

**Table 3. Kirkwood Correlation factor, Bruggeman factor, Excess Inverse Relaxation time, Free energy of activation of aqueous solution of n-butanol and benzyl alcohol for various concentrations**

Concentration m/l	Fractional volume $\phi_m$	$g_{eff}$	$F_{BM}$	$\epsilon^E$	$g_f$	$(1/\tau)^E$	$\Delta F_\tau$ KJ/mole	$\Delta F_\eta$ KJ/mole
n-Butanol								
0.2	0.019	1.155	0.018	-0.41	0.997	-0.089	12.57	13.91
0.5	0.043	1.165	0.023	-0.13	1.004	-0.087	12.81	14.33
1.0	0.083	1.198	0.028	-1.33	1.031	-0.086	13.02	14.87
2.0	0.156	1.266	0.038	-4.12	1.086	-0.079	13.09	15.03
3.0	0.216	1.331	0.058	-6.56	1.138	-0.074	13.14	15.98
Benzyl alcohol								
0.2	0.02	1.153	0.019	-2.09	0.997	-0.092	12.93	15.61
0.5	0.038	1.159	0.021	-3.57	1.001	-0.091	12.99	15.87
1.0	0.078	1.191	0.026	-5.43	1.029	-0.086	13.09	15.96
2.0	0.091	1.232	0.036	-6.92	1.036	-0.085	13.15	16.32
3.0	0.134	1.291	0.061	-8.67	1.063	-0.081	13.28	16.87

The viscosity values of solutions gradually increase with concentration, up to the 60 mM and become a plateau (Fig. 4). It is indicating that the monomers are aggregates up to 60 mM as spherical micelles; then these transit to rot shape, and an increase in the concentration of surfactant is expected. The  $\tau/\eta_r$  values increase continuously over the entire region in the case of SDS (Fig. 4(a)), whereas in CTAB and DPC a decreasing trend with concentration is observed (Fig. 4(b)) [18].

## 2. Organic Solutes in Water

In Table 2, the authors took the water-rich region binary mixtures formed by the addition of 0.2 m/l of n-butanol; the absorption at 34.5 ps for water was not shifted and so the structure-making nature of n-butanol made stable structure of water, and so the fluid structure was not disturbed with increase the concentration of n-butanol; the larger dispersion with frequency variation up to  $\tau=28$  ps indicated that larger 'structure breaking' property.

Also from Table, for the case of benzyl alcohol, we find that there is hydrogen bonding (OH) between the alcohol and water molecules of frequency around 25 ps. Similar behavior was observed in case of benzyl alcohol. Even though the addition of aniline, tributylamine, makes the peak absorption at 35 ps most dominant, there is no dispersion around this frequency as given in Table 4, and the addition of these compounds strengthens the structure of water [19].

The viscosity measurements on addition of n-butanol and benzyl alcohol indicate a steep increase in relative viscosity up to about 1 m/l of additives, but in all other cases the viscosity is linearly increasing with increasing concentration (Table 2) [20].

The effective Kirkwood correlation factor increases from 1.15 to 1.35 as the n-butanol and benzyl alcohol (Fig. 3), the concentration is increased and the structure of water is disturbed and more intramolecular stable hydrogen bonds are broken and new intermolecular stable hydrogen bonds are formed with alcohol molecules. Also from Table 3, the  $g_{\text{eff}}$  values of water are almost constant for all other additives with all concentrations. It is evident that these additives strengthen the fluid structure of water.

The measurement of  $\tau/\eta_r$  is the ratio of translational and rotational motion of fluids and it falls rapidly with addition of n-butanol and benzyl alcohol (Fig. 2), which shows that the hydrodynamic

**Table 4. Relative Viscosity, dielectric constant and dielectric relaxation data for Aniline and Tributyl Amine solutions in water at 303 K**

Concentration m/l	$\eta_r$	$\epsilon_0$	$\tau$ ps		$\tau/\eta_r$
			Theoretical	Graphical	
Aniline					
0.05	1.038	76.93	21.34	20.89	20.56
0.10	1.162	76.11	23.62	22.74	20.33
0.15	1.273	75.84	25.61	24.86	20.12
0.20	1.461	74.69	26.28	25.31	17.99
Tributylamine					
0.05	1.034	76.28	20.12	19.37	19.45
0.10	1.122	75.84	21.54	20.25	19.19
0.15	1.211	74.69	22.87	21.81	18.88
0.20	1.328	73.82	24.64	23.79	18.56

interactions are more rapid than the rotation of motion of the bulk water. But, from Table 4, in the case of aniline and tributylamine, the values of  $\tau/\eta_r$  are almost constant for small additions, whereas decreasing trend was observed for higher concentrations [21].

The information regarding the dynamics of solute-solvent interaction was obtained from the excess permittivity ( $\epsilon^E$ ) and the excess inverse relaxation time ( $(1/\tau)^E$ ). The excess permittivity may provide qualitative information about multimer formation in the mixture as follows: (i) indicates the solute and solvent do not interact at all, (ii) indicates the solute and solvent interaction is in such a way that the effective dipole moment gets reduced. The solute and solvent may form multimers, leading to the less effective dipoles, (iii) indicates the solute and solvent interact in such a way that the effective dipole moment increases [22].

From Tables 3 and 5, the values of  $\epsilon^E$  are negative and increase with increase of concentration of alcohol/amine/amide/nitrile species. Decreasing dipole character is evident for these observed trends. The antiparallel alignment of dipole is responsible for the cluster formation. Also from Tables 3 and 5, the values of  $(1/\tau)^E$  are also negative. These negative values further indicate the slow

**Table 5. Kirkwood Correlation factor, Bruggeman factor, Excess Inverse Relaxation time, Free energy of activation of aqueous solution of Aniline, TBA for various concentrations**

Concentration m/l	Fractional volume $\phi_m$	$g_{\text{eff}}$	$F_{BM}$	$\epsilon^E$	$g_f$	$(1/\tau)^E$	$\Delta F_\tau$ KJ/mole	$\Delta F_\eta$ KJ/mole
Aniline								
0.05	0.004	1.111	0.012	-1.61	0.987	-0.084	12.35	15.04
0.10	0.009	1.124	0.017	-2.02	0.981	-0.089	12.61	15.25
0.15	0.012	1.135	0.023	-2.59	0.973	-0.091	12.81	15.86
0.20	0.018	1.159	0.031	-3.53	0.961	-0.092	12.88	16.13
Tributylamine								
0.05	0.011	1.106	0.009	-0.987	0.989	-0.081	12.21	15.82
0.10	0.023	1.131	0.017	-1.98	0.987	-0.083	12.38	16.02
0.15	0.034	1.145	0.027	-3.19	0.973	-0.085	12.53	16.35
0.20	0.045	1.154	0.033	-3.42	0.972	-0.088	12.72	17.02

rotation of cluster of dipoles rather than in pure components [23].

From the Tables 3 and 5, the values of  $\Delta F_\eta$  are always greater than  $\Delta F_r$  [24]. These results suggest that the viscous flow involves more interference by the neighbors rather than dielectric relaxation due to rotation only. But, in the case of viscous flow, both rotational and translational motions were involved [25,26].

## CONCLUSIONS

Dielectric relaxation studies of some ionic surfactants were carried out 303 K. The relaxation of solute and water molecules was shown by loss tangent. The experimental relaxation time from the Cole-Cole plot showed the average dynamics of water molecules in the micelle. The additives strengthened the fluid structure. The excess inverse relaxation time shows the slow rotation of dipoles. Viscous flow offers more interaction rather than dielectric relaxation.

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