Pakistan Journal of Pharmaceutical Science
Vol. 13(1), January 2000, pp.13-20

AN INVESTIGATION INTO THE BEHAVIOUR OF THE ELECTROLYTES IN PRESENCE OF IONIC URFACTANTS

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ABSTRACT:

The effect of various concentration of Sodium Chloride and Lithium Sulphate in presence of Carbonate-bicarbonate buffer at pH 9.20 on the base-catalyzed hydrolysis of procaine was investigated. The whole study was done in the presence of different concentration of cetyltrimethy l ammonium bromide (CTAB) and Sodium dodecyl Sulphate (SDS) at 60ºC. Addition of different electrolytes suppressed the maxima in the 'Surfactant Effect ratio (SER). The presence of these additives increase the inhibitory effect with a corresponding in their concentrations

SDS/ SO_4, appeared to be most effective inhibitory amongst SDS/ Li_2SO_4, SDS/Nacl, CTAB/ Li_2SO_4, and CTAB/NaCl systems.

INTRODUCTION

It is known that ionic surfactants in aqueous solutions change not only their micellar size but also their micellar shape when simple salts are added (Ozeki and Ikeda, 1940; Philips and Mysels, 1955). Addition of salts to an aqueous micelle solution will reduce the repulsive interaction between the polar head groups of the surfactant. The effect of inorganic electrolytes on the micellar rates of various substrates and the micellar properties have been for a long-time the subject of extensive investigation (Romsted *et al.,* 1967; Bunton and Robinson, 1968; Bonton, *et al.,* 1981; Amarson and Elworthy, 1981; Fadnavis and Engberts, 1982).

The addition of a wide *varie*ty of inorganic salts leads to changes in micellar structure and gives wide variation in the catalytic efficiency of the micelle. The salt effects were viewed as a type of competitive inhibition between solvent-derived ions and other ions for a restricted number of sites on the micellar surface. The extent of inhibition depends upon the nature of anion and is least *for* anions of high charge density, and greatest for anions which contain bulk organic residues which can assists hydrophobic bonding.

Added salts typically reduce micellar state enhancements and the extent inhibition increases with increasing hydrophobicity of added counterion to the micelle (Cordes, E.H. 1978; Bunton, 1979; Fadnavis and Engberts 1982). These inhibition were due to interactions between the anion and cationic micelle which make it more difficult for the OH^- ion to attack the organic substrate which is incorporated into the micelle, and the stronger the interaction the greater the ability to exclude OH^- ion.

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Akbas and Iscan observed that the addition of Sodium Chloride salts (Nacl) to aqueous solutions of sodium caprate and sodium laurate increased the solubility of dyes (Akbas and Iscan, 1994).

Inhibition by added electrolytes, however, does not explain the maxima on the rate constant surfactant concentration profiles for various types of surfactant concentration. Since little has been done to understand the mechanism of electrolytes.

MATERIALS AND METHODS

Procaine Hydrochloride (U.S.P), CTAB and SDS, inorganic salts (Nocl and Li_2SO_4) and other regents used in this study were all of A.R. Grade. The details of the procedure is given else where (Razvi, 1989). Water used throughout the work was double distilled through an all glass-still. The whole study was done in presence different concentration of CTAB and SDS to the see of the electrolytes. The effect of Nacl was done in the concentration range 0.1-1.0M in presence of SDS and 0.1-2.0M in presence of CTAB. From the previous study (Razvi, 1989) it has been shown that above these concentrations, turbidity appeared which was absent before pH adjustment. Similarly the effect of Li_2SO_4s in the concentration range 0.1-1.0M in presence of CTAB and between 01.-12 M in presence of SDS was also investigated. Above these concentration, turbidity appeared in the solution at pH 9.20 which remained constant at higher concentration.

RESULT AND DISCUSSIONS

In all the conditions i.e. in the presence of various concentrations of sodium chloride ranging from 0.1M – 2.0M in CTAB, 0.1M – 1.0M in SDS, and lithium Sulphate in the concentration range of 0.1M – 1.0M in CTAB and from 01.M – 1.2M in SDS found to decrease the rate of hydrolysis of ester and the inhibitory effect increased as the concentration of salts were increased. In order to compare the extent of its effect on hydrolysis it is generally convenient to present the data in term of the ‘Surfactant-effect ratio’ (SER) which has been define by Winterbom as the ratio of the rate constant in the presence of CTAB to that in the absence of CTAB (Winterborn, 1972). SER-CTAB and SER-SDS profiles in the presence of these salts has been shown in Fig (1-3) and (4-5) respectively. The observation is consistent with similar finding by many workers (Bunton and Robinson, 1968; Fadnavis and Engberts, 1982; Vera and Rodenas, 1984). This could be assigned that the size of the micelles increases with increasing surfactant concentration and it is expected that micellar molecular weight increases with the addition of neutral salt. Since the reduction of the repulsive forces between head group facilitates the formation of bigger micelles charge screening would be expected to increase the molecular weight. Therefore, it is suggested that the bigger the micelle, more is the possibility for the micelle to take up the substrate which can then become buried deeply in the micelle and the inhibition in the rate of hydrolysis in presence of electrolytes is expected. It can also be concluded that the rate constant for the reaction between procaine and electrolytes in presence of SDS is less them that of the hydrolysis in presence of electrolytes and CTAB. To explain this reduction free energy of the reaction by micelles could be taken into account which always retards reaction, but a cationic micelle should stabilize a bulky anion, such as the transition state, more than a small anion, such as hydroxide, relative to their stabilities in water, and therefore higher reaction rate in presence of a cationic micelle is expected. Moreover these ions are known to have different degree of influences on the value for the CMC and micellar polymerzation members for anionic and Cationic surfactants vera and Rodenas, 1986), therefore different degree in inhibition by the salts in presence of ionic surfactants in expected.

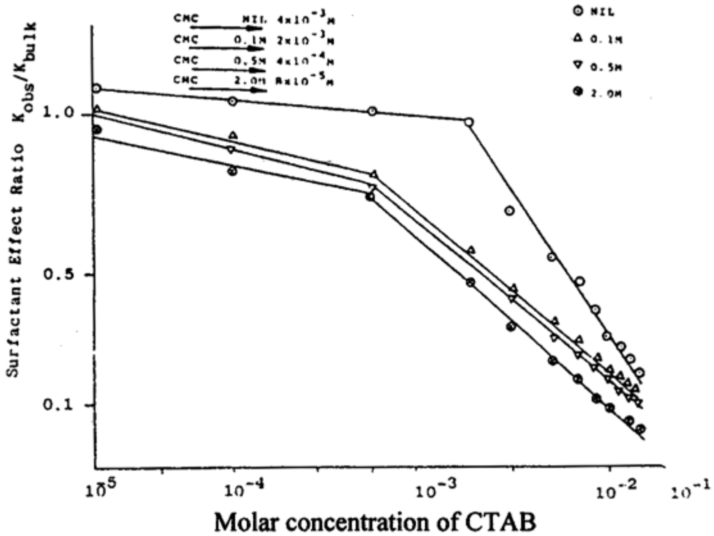

Fig. 1: SER plot for CTAB in absence and presence of 0.1, 0.5 and 2.0 Al concentration of Sodium Chloride in Carbonate-Bicarbonate Buffer at pH 9.20

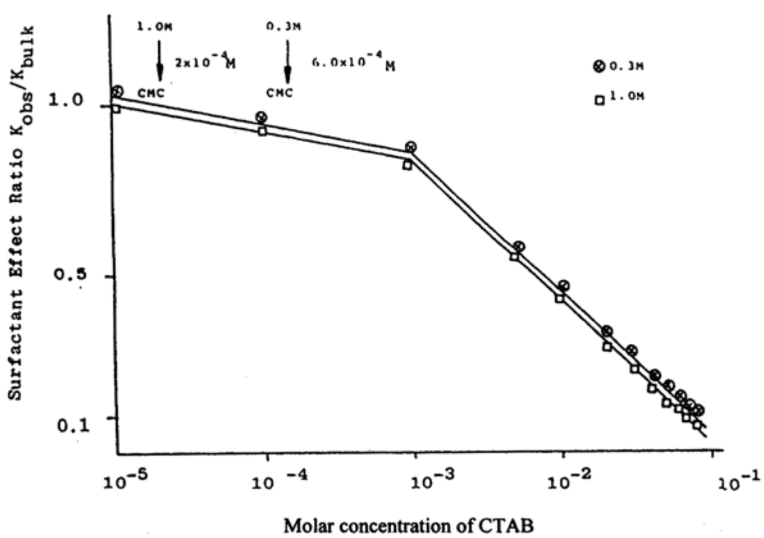

Fig. 2: SER plot for CTAB in absence and presence of 0.3, 0.5 and 1.0 M concentration of Sodium Chloride in Carbonate-Bicarbonate Buffer at pH 9.20

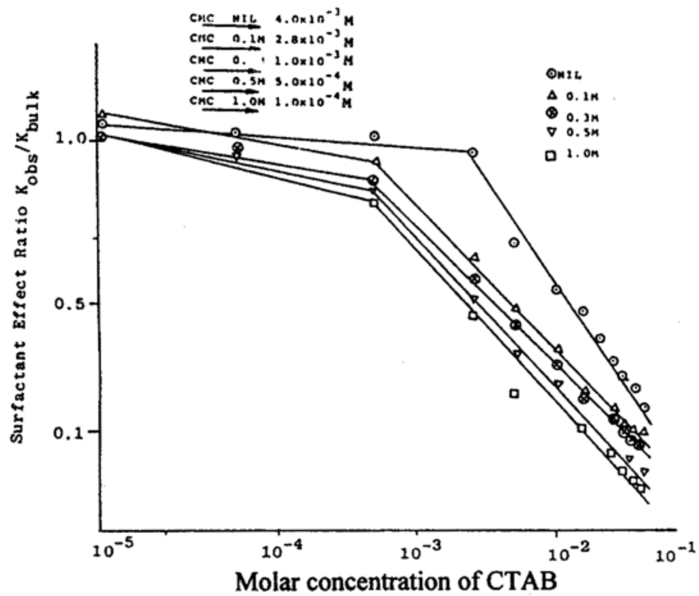

Fig. 3: SER plot for C7AB in absence and presence of various concentration of Lithuim Sulphate in Carbonate-Bicarbonate Buffer at pH 9.20

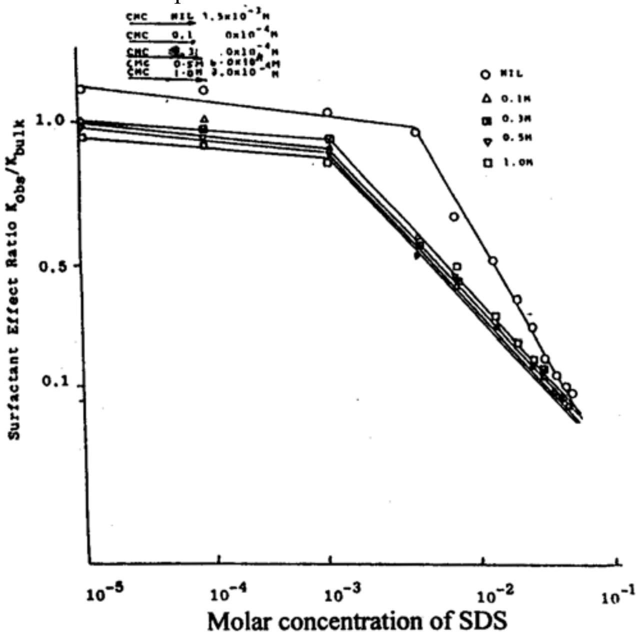

Fig. 4: SER plot for SDS in absence and presence of various concentration of Sodium Chloride in Carbonate-Bicarbonate Buffer at pH 9.20

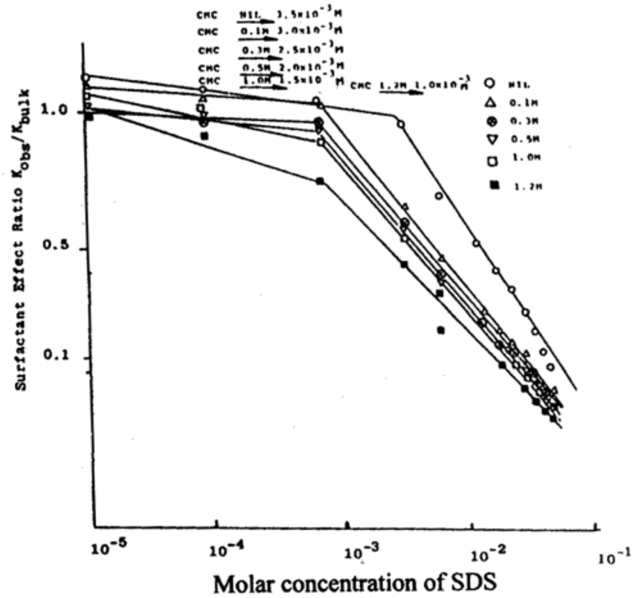

Fig. 5: SER plot for SDS in absence and presence of various concentration of Lithum Sulphate in Carbonate-Bicarbonate Buffer at pH 9.20

The uncreative chloride and sulphate ions from the added electrolytes, additional negatively charged species in the solution, also decrease the concentration of hydroide in stern layer which is already less in case of SDS micells due to the repulsion of the same charges available on hydrol ion and at the micelle surface resulting in presence of SDS CTAB with the added electrolytes.

More decrease of micellar rate inhibition by added salts in presence of SDS the CTAB can further be interpreted in terms of a decrease of protonating power of the solution, the anions of the electrolytes must inhibit the reaction to greater extent in SDS them CTAB by increasing protonating power in the micellar pseudo phase.

Cationic micelles do not effectively bind hydrogen ions, as shown by their effects on acid rates and equilibria (Fendler and Fendler, 1975; Cordes, 1978; Bunton, 1979; Funaski, 1979) and it equilibrium between hydrogen and hydroide ions is maintained in the micellar pseduophase of SDS (Vera and Rodenas, 1986), explusion of hydroxide ion from the micelle by chloride and sulphate ions from the electrolytes will increase acidity in the micellar pseudophase of SDS and therefore slow hydrolysis compared to CTAB is expected. Lithium is not a particular strong alkaline element as sodium and its hydroxide is not a very strong base like sodium hydroxide. Therefore this could be also one of the reason to show a less rate of hydrolysis of procaine compared to sodium chloride.

Micellar surface of CTAB could be more neutralized as compared to SDS by the electrolyte due to the attraction of oppositely charged ions, and therefore the more neutralized the micellar surface is the less penetration of the substrate and smaller the molar volume of micellar pseudophase (Vera and Rodenas, 1984; 1985; 1986.) This situation will favour the hydrolysis of the substrate to some extent and could be one of the reasons for less inhibitory effect of CTAB with added electrolytes than SDS electrolytes system.

Slower reaction in presence of SDS electrolytes than CTAB also suggests that other effects, e.g., changes in the structure of the micelles, or in their number, are of importance. Added salts cause micelles to grow and change their shapes from spherical and eventually to rodlike, and these changes could modify the rate of reaction in a different way to the micellar surface.

It should also be noted that the hydroxide ion is a 'structure maker' (Bunton and Robinson 1968) in that it orients water molecules about itself, these water molecules should become arranged differently when the hydroxide ion is incorporated into the transition state in presence of CTAB (due to positively charged surface of the micelle) and a 'structure breaking' on might be expected to assist the process and therefore there is higher rate, in presence of CTAB and salts with respect to SDS and added salts results.

Role of electrolytes in inhibiting anion-molecule reactions in micellar medium has also been investigated (Bunton and Robinson, 1968). Rate retardations have been attributed to the exclusion of the nuclephile by the an-ion of the added salt. Since in presence of SDS repulsion between the OH^- ions and the micellar surface takes place which will be further assisted by added electrolyte, more inhibition in the rate in presence of added salts is obvious compared to CTAB.

Figure 4 shows the adsorption of SDS with and without Nacl as a function of surfactant concentration. The strong electrostatic repulsion of the negatively charged hydrophilic moieties, both among them selves and also by the negatively charged adsorbent surface, which keeps the adsorption low unless concentrations are substantially higher than in the case of nonionic surfactants with the same hydrophobic group. For the same reason, the effect of electrolytes on SDS is generally very pronounced.

One could also compare the inhibitory effect between Li_2SO_4 and Nacl in ionic micellar environment and the tabulated results (Razvi, 1989) clearly indicate that SDS / Li_2SO_4 is the most effective inhibitor amongst SDS / Li_2SO_4, SDS/Nacl, CTAB / Li_2SO_4 and CTAB/Nacl. Several explanation for this behaviour can be given. In fact, it is the destabilization of the transition state which essentially dictates the overall salt effect of lithium sulphate compared to sodium chloride leading to decreased rates. Although sodium-chloride destabilizes the substrate, this destabilization could be less than the destabilization of transition state and it is a combined destabilization of the reacting ions, which predominates over even a very large destabilization effect on the transition state, leading to higher than Li_2SO_4 in presence of anionic surfactants. Larger destabilization of the transition state by Li_2SO_4 than Nacl could be due to high charge density of Li^+_2 and SO_4^{-2} and with higher charge density more destabilization of the transition state is expected.

The negatively charged surface of SDS micelle also facilitates the expulsion of the attacking hydroxyl ion and therefore Li_2SO_4 in presence of SDS could destabilize the transition slate more than the hydroxyl ion, and their net effect is to decrease the rate more than the same salt in presence of CTAB.

More inhibition in the rate by Li_2SO_4 and compared to Nacl in presence of SDS could further be explained on the basis of changing the micellar shape on reducing the charge density of the micelle, and therefore one would expected that decreasing the effective charge density of the micelle would retard the process more.

For molecules-molecule reaction both anions and cations of low charge density i.e. Na^+ and Cl^- compared to high charge density of Li^+ and SO_4^{2-} stabilize the transition state (Bunton and Robinson, 1968) and therefore higher rate is expected.

An increase in the concentration of electrolytes has also the effect of compressing the diffuse layer *of* the micelle. The thickness of this layer is decreased and the repulsive potential decays more rapidly. Thus according to the concept of electrical double layer, the energy barrier that opposes aggregation, decrease as the concentration of added electrolyse increases, and finally disappears. When the barrier ceases to exist, rapid coalescence of the particles occurs and large aggregates become visible in the system and in case of surfactants bigger micelles results.

The degree *of* compression of the diffuse layer depends not only on the concentration of added electrolyte but also on the valency of the ion of opposite charge to the micelle. They pronounced since lithium and sodium are both monovalent but the valency of the anion attached to these cations are different. Sulphate ions have two valency in case of Li_2SO_4 compared to chloride ion in Nacl. Thus as whole Li_2SO_4 would be expected to compress the diffuse layer of the micelle more than Nacl which could also account for more pronounced inhibitory effect in this kinetic study. The pronounced inhibitory effect on the rate of the hydrolysis of drug by Li_2SO_4, compared to Nacl in presence of ionic surfactants can further be understood in the light of the efficiency of hydrophobic interaction.

Energy can be lowered in the system by pushing the hydrocarbon chains out of the water content. This is affected by aggregation at the interface or by micellization. These phenomena could be said as the reversal of the dissolution of hydrocarbon chains in water (Rupprecht, 1976). The mechanism involved is called hydrophobic binding, or hydrophobic interaction (Linderbaum) and Boyd, 1964). These hydrophobic interactions are influenced by addition of water structure changing solutes. They become stronger in solutions of water-structure-making substances, like ions with small ionic radii and high surface charge densities (Ruppercht, 1976). On the contrary, typical structure breakers, like big monovalent ions or urea, diminish hydrophobic bonding and so weaken aggregation processes (Rupprrcht, 1976). If the ions are arranged in the order of their effectiveness to hydrophobic interactions the so called lyotropic series are obtained, with structure makers on the left side and the structure breakers on the right side, as for cations like (Bunton and Robinson, 1968).

$L_i^+ < Na^+ < K^+ < NH_4^+ < Rb_4^+ < C_s^+$ and for anions, like;
$SO_4^{2-} < F^- < C1^- < Br^- < No^- 3 < C1O^-{}_4 < I^-$

Therefore Li_2SO_4 in this study should demostrate greater inhibitory effect than Nacl in presence of ionic surfactants.

Thus in the light of foregoing discussion following characters of Li_2SO_4 could be taken into account: Lithium sulphate has like ions as SDS, both lithium and sulphate have high charge densities (Bunton and Robinson, 1968), lithium has highest specific heat in alkaline metal series (1.093 compared to sodium which has 0.297) and it is the structure-making ions. All these properties properties associated with Li_2SO_4 support it to be a potent inhibitor than Nacl for the micellar reactions.

Moreover the substrate which is already buried deep in the core of SDS micelles could be further protected by Li_2SO_4 Lithium ion has an enhanced effect on charge distribution (Bank and Dorr, 1987) and additional NMR methods have provided insight into the contributions of the several factors affecting more inhibition by Li_2SO_4 For example, hyberdization and delocalization in the lithium salts of aniline derivatives (Ide *et al.,* 1987) further strengthens our results.

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