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Investigating the Association Behaviour of Cetyltrimethylammonium Bromide as Affected by the Content of Non-steroidal Antiinflammatory Drug and Temperature

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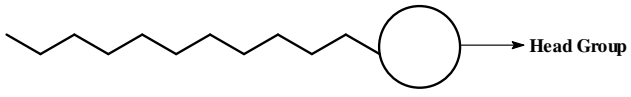
Critical micelle concentration of *N*-cetyl *N,N,N*-trimethyl ammonium bromide and its mixture with drug naproxen sodium were determined at different temperature by using surface tension technique. Naproxen sodium has been found to exhibit typical amphiphilic behaviour in aqueous solution in that they accumulate at interface, depressing the surface tension and form aggregate in solution at sufficiently high concentration. So critical micelle concentration of cetyltrimethylammonium bromide decreased as the concentration of drug increases and same is the case with temperature. Thermodynamic parameters like ΔG_{mic}, ΔH_{mic} and ΔS_{mic} of micellization of cetyltrimethylammonium bromide were also determined in the presence of naproxen sodium salt at different temperature, which shows that free energy of micellization, is favoured in the presence of drug and become more favourable with the temperature.

Key Words: Surfactant, Cetyltrimethylammonium bromide, Naproxen sodium, Effect of temperature, CMC determination.

INTRODUCTION

There are great varieties of surfactants available in the market. So due to widespread uses of surfactants and industrial applications the surfactants are used in almost every chemical industry[1-3] of which the following may be worth mentioning; detergents, paints, cosmetics, pharmaceutical, fibers and plastics. Water-soluble surfactants are used together in many formulations and industrial processes to determine the properties of the surfactant by the addition of polymer[4-14]. Moreover, surface active agents play vital role in the oil industry. They are also used for environmental protection *e.g.* in oil slick dispersants a fundamental understanding of physical chemistry of surfactants is vital for the preparation of emulsion and suspension in foams. In micro emulsion, in wetting and adhesion, *etc.*, the amphiphiles are of great importance in arriving at the right composition and control of the system involved.

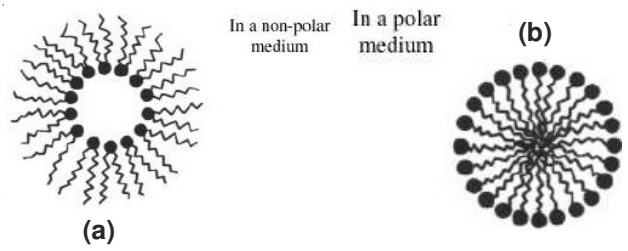
The basic characteristic of surfactants in a solution is that the concentration of the surfactants always remains high at the surface than in the bulk of liquid. The most common forms of surfactants are constituted of two portions that is non-polar or hydrophobic portion and a polar or hydrophilic portion[15,16].



Linear or poravahed hydrocarbon

The polar portion of the molecule is usually termed the head group and interacts strongly with surface active agents. Since the major applications of surfactants is detergency in G_{10} to G_{16} range. Therefore, the consideration for commercial point of view is the availability of hydrophilic groups of required length and the cost should be low. The hydrophilic group based on the hydrocarbon is basically available from the sources such as petrochemicals, natural vegetable and natural animal fats.

Surfactants are a group of material that have involved with growing and ever changing need of society. Substances contaiining in the same group, which are strongly hydrophobic (water repellent) and hydrophilic (water loving) orient themselves in different ways when dissolved or dispersed in water or non-aqueous solvents such orientation, which could also be in the form of aggregates of oriented molecules, termed micelles, is known as activity and materials exhibiting this are known as surface active agents often abbreviated as surfactants. Fig. (a, b) indicates orientation of surfactants in polar and non-polar system.



Bain *et al.*[17] suggested that when surfactants are dissolved in solvent the hydrocarbon groups are associated together and the polar head group orient themself towards aqueous media. In this way a big molecules or associated units are formed these associated units or big molecules are termed micelles.

Reychler and Kolloid[18] and Adam[19] proposed that micelles are spherical in shape. More current theories[20] on micelles from action are based on the assumption of a single micelles type in solutions of low ionic strength with the interior of the micelles thought to be in fluid state below the critical micelle concentration.

Spherical ionic micelles are contained on more than 10 surfactants ions formed initially in solution below the critical micelle concentration and the second is a larger lamellar weakly conducting. Micelles consisting of doubled leafly of soap molecules placed end to end and side by side.

The physico-chemical properties are well known of surfactants varies below and above the critical micelle concentration (CMC) values. Below the cmc value, the physico-chemical properties of ionic surfactants like SDS resemble those of strong electrolyte. Above the cmc value, these properties change dramatically; presenting that a strong cooperative association process is taking place.

Naproxen sodium is a widely used non-steroidal antiinflammatory drug, which inhibits prostaglandin biosynthesis, or more specifically the enzyme cyclooxygenase[1-3]. The compound is a sodium salt of naproxen, its absorption is claimed to be more rapid compared to its parent naproxen (Fig. A).

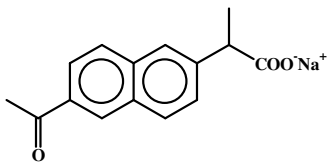


Fig. (A) Structure of naproxen sodium salt

EXPERIMENTAL

The surfactant used during this work was cetyltrimethylammonium bromide (CTAB), MW = 364.44 g/mol obtained from Merck Germany. Naproxen sodium (drug) having molecular formula $C_{14}H_{13}NaO_3$, MW = 252.24 g/mol, which was kindly supplied by Chong Kun Dang Co. Ltd.

Conductivity water was used as a solvent, whose conductance ranged from 5-7 μS/cm.

Sample preparation: Known concentration of CTAB was prepared in deionized water as a stock solution. Solutions of different concentration were obtained by diluting stock solution. Also prepared the solution of 0.001 M naproxen sodium. surface tension measurement.

TE3 LAUDA tensiometer, supplied by LAUDA, Germany to Dr. Musa Kaleem Baloch was used to measure the surface tension of solutions prepared. All measurements were made sufficiently slowly so as to ensure equilibrium conditions. The measurements were made for different concentrations and at different temperatures *i.e.* 20, 30 and 40 ºC. The temperature was maintained using ecoline circulation thermostat model E 015 T, Germany, which retained the temperature to ± 0.01 ºC.

RESULTS AND DISCUSSION

The results obtained from the surface tension measurement of surfactant CTAB in an aqueous media in the temperature range of 20-40 ºC are plotted in Fig. 1. It is clear from the data obtained that at first the surface tension decreases slowly till it reaches to a point, which we call as critical concentration of the surfactant (CC), further increase in concentration decreases the surface tension sharply and ultimately leads to a minimum value of surface tension which shows the adsorption of surfactant at the air-water interface and then becomes constant. This point at which surface tension become level off is known as critical micelle concentration[21,22]. Further increase in concentration of the surfactant does not alter the surface tension, however, it can increase size and change the shape of micelles[23].

It is clear from the plot of surface tension *vs*. log of concentration of CTAB (Fig. 1) that the surface tension of CTAB also decreases as the temperature increases,which is due to changes in the solvent-solute interactions and results in decrease in surface tension of CTAB[24].

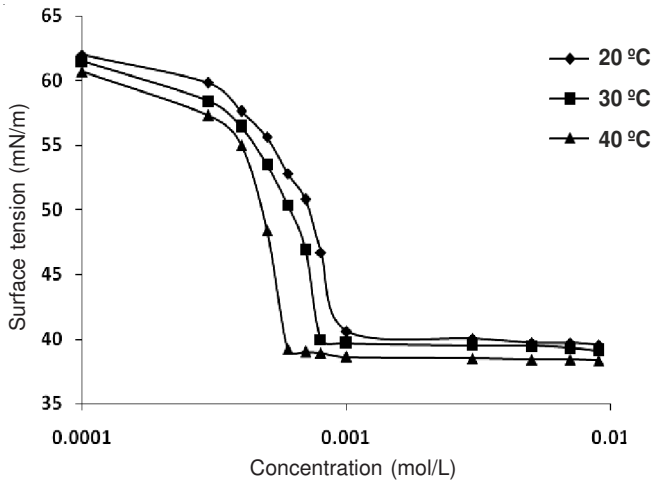


Fig. 1. Surface tension of CTAB as a function of its concentration

Surface tension of CTAB and its mixture with naproxen sodium were plotted as a function of log of concentration of CTAB and plotted in Fig. 2. This Fig. 2 shows the decreasing trend of surface tension with the increasing concentration, which is same as that of CTAB in aqueous solution *i.e.*, first surface tension decreases slowly, then in the second step surface tension decreases sharply with the increase in concentration and then levels off in the third step. The critical micelle concentration value is calculated from the point where two straight lines intersect.

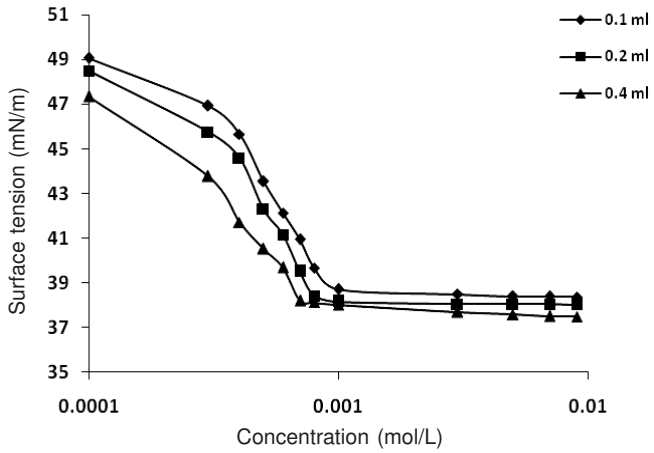


Fig. 2. Surface-active behaviour of CTAB in the presence of naproxen sodium

The critical micelle concentration values calculated from the intersection of two straight lines are presented in Fig. 3 and listed in Table-1, which shows that the critical micelle concentration of CTAB decreases with increase in temperature. This decrease in the critical micelle concentration of CTAB with temperature increase is possibly due to more hydrophobicity and dehydration of the monomers in the solution. However the effect of temperature on critical micelle concentration is complex, firstly temperature increase cause decreased hydration of the hydrophilic group, which favours micellization. Secondly, temperature increase also causes disruption of the structured water around the hydrophobic groups which opposes micellization[22,25]. Here in present data, it is observed that the first effect of temperature on the critical micelle concentration is more pronounced.

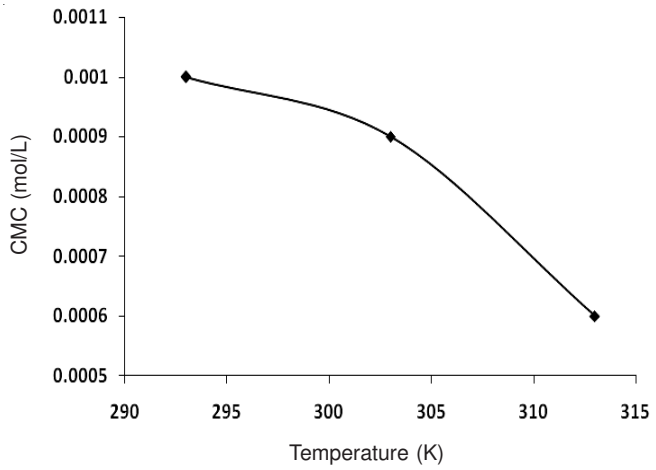


Fig. 3. Critical micelle concentration of CTAB as a function of temperature

TABLE-1
THERMODYNAMIC PARAMETERS OF MICELLIZATION OF CTAB AT DIFFERENT TEMPERATURE

Temp. (K)	CMC (mol L^{-1})	γ_{cmc} (mNm^{-1})	ΔG_{mic} ($KJmol^{-1}$)	ΔS_{mic} (KJ $mol^{-1}K^{-1}$)	ΔH_{mic} (KJ mol^{-1})
293	0.001	40.67	-26.61	0.242	44.296
303	0.0009	39.86	-27.785	0.243	45.819
313	0.0006	39.09	-29.757	0.246	47.241

The results obtained from the plot of critical micelle concentration of CTAB-naproxen sodium against volume of 0.001 M naproxen sodium added (Fig. 4) at a constant temperature shows that with increase in volume of naproxen sodium critical micelle concentration decreases which means that it favours micellization. The reason behind this is that the molecules solubilized in the outer portion of the micelle core which is effective in reducing the critical micelle concentration. Also the electrostatic interactions between CTAB and naproxen sodium decreases the repulsive forces between the head groups of surfactant molecules, which favour micellization process, therefore, cause decrease in the critical micelle concentration values as can be seen in Table-1. Due to decrease in the critical micelle concentration the solubility of naproxen sodium is enhanced in the micellar solution due to electrostatic forces of interactions[26].

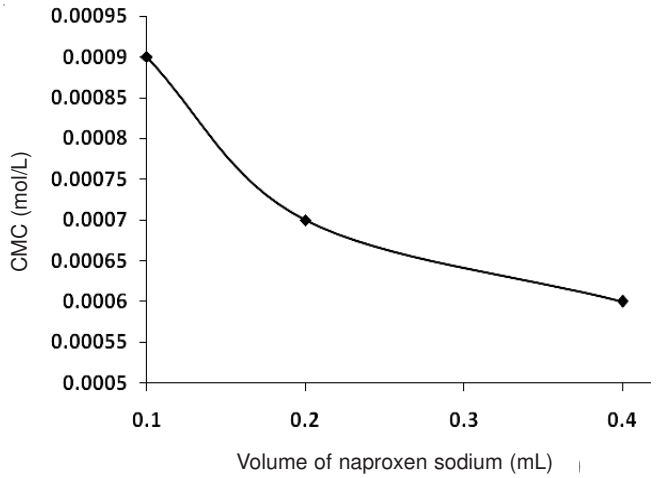


Fig. 4. Critical micelle concentration of CTAB-drug mixture plotted against volume of drug added

Thermodynamics of micellization: Different thermodynamic parameters of micellization of CTAB and its mixture with drug calculated are plotted in Figs. 3-6 and listed in Tables 1 and 2 respectively. Change in free energy of micellization calculated from the most common thermodynamic equation.

$$\Delta G_{mic} = RT \ln CMC \quad (1)$$

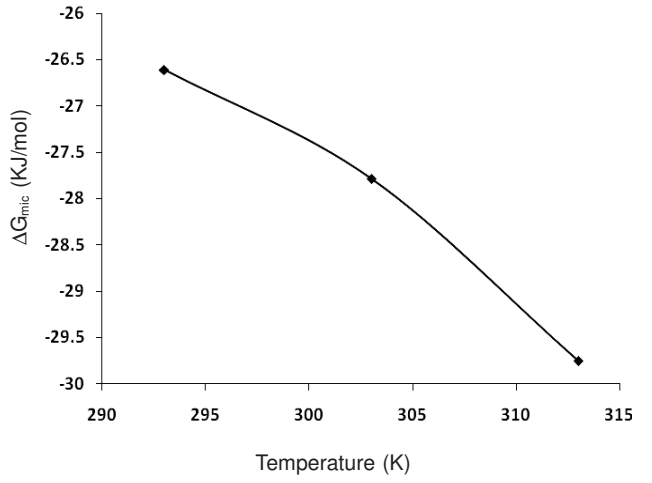


Fig. 5. Change in free energy of CTAB system in water plotted against temperature

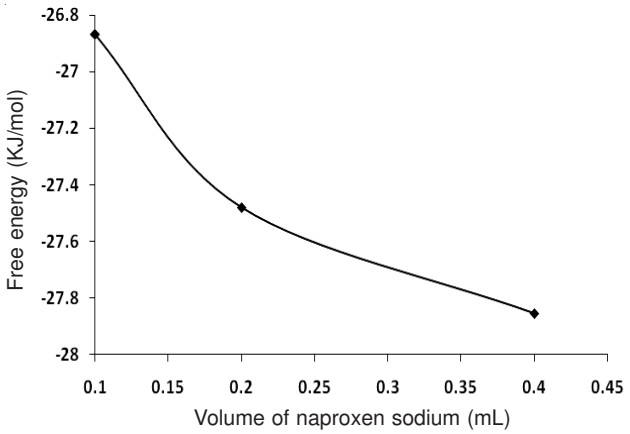


Fig. 6. Change in free energy of CTAB-Naproxen Sodium vs volume of drug added

TABLE-2
THERMODYNAMIC PARAMETERS OF MICELLIZATION OF CTAB-NAPROXEN SODIUM MIXTURE

Volume of 0.001 M Drug added (mL)	CMC (mol L^{-1})	γ_{cmc} (mN m^{-1})	ΔG_{mic} (KJ mol^{-1})
0.1	0.0009	38.69	-26.868
0.2	0.0007	38.42	-27.480
0.4	0.0006	38.26	-27.855

The negative value of ΔG_{mic} shows that micellization process is spontaneous and the negative value increases with increase in temperature, which shows that the micellization process becomes more spontaneous with increase in temperature[24]. Change in the free energy of micellization ΔG^{o}_{mic} of CTAB-naproxen sodium mixture calculated from eqn. 1 is illustrated in Fig. 6 and Table-2. The ΔG^{o}_{mic} values for each volume of naproxen sodium added in CTAB solution are negative, which shows that micellization process is spontaneous and it become more negative as the concentration of drug increase indicating the more spontaneous nature of micellization process in the presence of naproxen sodium, which shows that solubilization process is more favourable in this system due to decrease in the critical micelle concentration and increased negative value of free energy[26].

The enthalpy of micellization was calculated by using the Gibbs-Helmholtz equation:

$$\Delta H^{o}_{mic} = [\delta (\Delta G^{o}_{mic}/T)/\delta(1/T)] \quad (2)$$

Putting the value of ΔG^{o}_{mic} from eqn. 1 we get:

$$\Delta H^{o}_{mic} = R [\delta \ln CMC/\delta(1/T)] \quad (3)$$

In the above equation, the term $[\delta \ln CMC/\delta(1/T)]$ was calculated from the slope of the tangent to a plot of lnCMC *versus* 1/T. A slight increase in δH^{o}_{mic} values, with changing the temperature was observed. δH^{o}_{mic} is positive at all temperatures, which indicate the endothermic nature of micellization[22,24,27].

After knowing the values of ΔG^{o}_{mic} and ΔH^{o}_{mic} the values of entropy of micellization ΔS^{o}_{mic} were calculated from the well known thermodynamic relation which is as follows:

$$\Delta S^{o}_{mic} = \Delta H^{o}_{mic} - \Delta G^{o}_{mic}/T \quad (4)$$

The values so obtained are positive at all temperatures indicating greater disorder/randomness in the system upon micelle formation[27].

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