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THERMODYNAMIC STUDIES ON THE INTERACTION OF SOME UREAS AND SALTS WITH MICELLAR TRITON-X-100 IN AQUEOUS SOLUTIONS

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ABSTRACT

We have determined the enthalpies of solution in the micellar state (ΔH_s) for Triton-X-100 in 1 m aqueous solutions of urea, 1,3-dimethyl urea, tetramethyl urea, sodium chloride and calcium chloride at 298.15 K and 308.15 K. These results were used to evaluate the heat capacities of solution ($\Delta C_{p,s}$) for Triton-X-100 micelles in these solvent systems. It has been observed that $\Delta C_{p,s}$ values of micellar Triton-X-100 decreases drastically upon transfer from water to these solutions but is positive in all cases. Thus, the heat capacities of transfer of Triton-X-100 micelles ($\Delta C_{p,tr}$) are negative in all the systems studied. A comparison of the effect of non-electrolytes (ureas) and electrolytes (salts) on the micelle has been presented. The results have been discussed in terms of the relative water-structure-disrupting tendencies of the ureas and the salts.

INTRODUCTION

Surfactants in aqueous solutions tend to aggregate above a particular concentration, called the critical micelle concentration (cmc), to form micelles in which all the non-polar groups tend to move closer to each other to form a micelle core while the ionic and hydrophilic groups remain exposed to the external medium. The aggregation behaviour takes place for the reason that the non-polar residues of the surfactant tend to have unfavorable contact free energy with the surrounding water. These aggregates or micelles possess some useful properties and can be used for solubilization of drugs and other small organic molecules, micellar catalysis, enhanced oil recovery, etc. [1].

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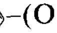
The formation of micelles in aqueous solution involves the hydrophobic effect which has been recognized as playing a key role in maintaining the native conformation of protein and the formation of lipid bilayer membranes [2,3].

In order to understand the nature of such interactions we have selected the non-ionic surfactant Triton-X-100, wherein the interference of the ionic groups on the micelle would be absent, and studied its interactions with urea, substituted ureas, sodium chloride, and calcium chloride. All these substances have been known to be significant water-structure-disrupting agents. The thermodynamic parameters studied were the enthalpies of dilution (ΔH_s) of the surfactant in the solvent system mentioned above at 298.15 and 308.15 K at concentrations at which Triton-X-100 exists in the micellar form. From these results, the heat capacities of solution ($\Delta C_{p,s}$) for the surfactant at 303.15 K were evaluated. Combining these with the $\Delta C_{p,s}$ data for Triton-X-100 in water, we evaluated the heat capacity changes in transferring micellar Triton-X-100 from an aqueous to a mixed aqueous environment. Enthalpies and heat capacities have been shown to be highly sensitive towards structure changes, especially the hydrophobic effects which are observed in aqueous solutions of compounds containing non-polar residues [4–9].

Urea has been believed to be a classical water-structure-breaker [10,11] although there is also some criticism of this view [12]. Methyl-substituted ureas, on the other hand, still have a urea-like structure-disrupting ability although this is somewhat reduced because of the hydrophobic nature of the methyl groups which are, in contrast supposed to be structure-ordering moieties. A study of the interaction of these diverse molecules of the same family of compounds with Triton-X-100 micelles may enable us to identify the solvent-mediated effects in the ternary system of surfactant–water–additive. The salts were selected in order to understand the different behaviours of electrolytes and non-electrolytes in aqueous solutions with respect to their interactions with water as well as the surfactant micelles. Furthermore, a comparison of the effect of calcium chloride and sodium chloride on the surfactant micelle should enable us to identify the effect of charge on such interactions. Triton-X-100 is a *p*-(1,1,3,3-tetramethylbutyl) phenoxypolyoxyethylene glycol with an average of 9.5 oxyethylene groups per molecule [13] and the structure $(CH_3)_3C–CH_2–C(CH_3)_2–$$–(O–CH_2–CH_2)_{9.5}OH$. The exact structure of the Triton-X-100 micelles is unclear [14]. In the case of such non-ionic surfactants, it has been observed that they spontaneously form aggregates upon dissolving in water, with the hydrocarbon portion forming the micellar core, while the oxyethylene part is preferentially partitioned into the aqueous phase. It has also been suggested that the ether groups of such surfactants form highly directional hydrogen bonds with water molecules and the ethylene groups are accommodated in the overall water structure [15].

MATERIALS

Triton-X-100 of electrophoresis grade was procured from Bio-Rad laboratories and was used as such without further purification. Analytical reagent grade urea, sodium chloride, and calcium chloride were from BDH and di- and tetramethyl urea were from Sigma. The distilled water used in the studies was further distilled and deionized by passing it over a Barnstead mixed-bed ion-exchange column.

EXPERIMENTAL

The enthalpies of solution were measured on a Tronac-450 titration calorimeter (Tronac Inc., Utah), the experimental details of which have been described elsewhere [16]. The solutions were measured in an adiabatic Dewar vessel of 25 ml capacity and the liquid Triton-X-100 was in a teflon burette. Both the reaction vessel and the burette could be completely submerged into the water bath, the temperature of which was controlled to ±0.005 K by a Tronac PTC-40 proportional temperature controller and a cryostat. The micro-thermistor immersed in the reaction vessel helped to sense the temperature changes and the resultant output voltages were measured using a digital multimeter. The output was also recorded on a potentiometric stripchart recorder.

The amount of liquid delivered from the burette was determined by calibrating the burette rate using water and was found to be 0.39 ml min^{-1}. The calorimeter was calibrated by measuring the heat of protonation of THAM [tris-(hydroxymethyl)amino methane] with aqueous hydrochloric acid solution. Our ΔH values agreed to within 0.3% of those in the literature [17].

RESULTS AND DISCUSSION

The enthalpy of solution (ΔH_s) values for Triton-X-100 in the micellar state in 1 m solutions of urea, 1,3-dimethyl urea, 1,1,3,3-tetramethyl urea, sodium chloride, and calcium chloride at 298.15 and 308.15 K are presented in Table 1. The concentrations of the surfactant solutions studied are in the range from 1.57 to 4.18 mmol dm^{-3}; hence, all the measurements were carried out considerably above the cmc of the surfactant which is 0.33 mmol dm^{-3} [18]. From these results, the $\Delta C_{p,s}$ values for Triton-X-100 in aqueous solutions at 303.15 K were evaluated. No concentration dependence in the

TABLE 1

Enthalpies of solution of Triton-X-100 in the micellar state (ΔH_s) as a function of concentration in water and in 1 M aqueous solutions of urea, 1,3-dimethyl urea, 1,1,3,3-tetramethyl urea, sodium chloride and calcium chloride at 298.15 and 308.15 K

Concentration (mol $kg^{-1} \times 10^{-3}$)	ΔH_s (298.15 K) (kJ mol^{-1})	Concentration (mol $kg^{-1} \times 10^{-3}$)	ΔH_s (308.15 K) (kJ mol^{-1})
Water			
0.91	−45.70	2.09	−32.17
1.04	−44.42	2.56	−32.21
1.25	−44.25	2.61	−31.58
1.49	−45.21	2.87	−31.43
2.04	−45.67	3.13	−32.31
2.09	−44.49	3.40	−31.48
2.51	−43.81		
2.59	−45.70		
3.03	−44.20		
4.21	−43.63		
4.66	−43.53		
Mean	−44.60 ± 0.54	Mean	−31.86 ± 0.43
1 m urea			
1.57	−42.60	2.61	−39.41
2.09	−41.65	2.87	−39.40
2.35	−42.62	3.13	−40.15
2.61	−41.75	3.39	−40.60
2.87	−42.11	3.65	−40.06
		3.92	−39.58
		3.92	−39.25
Mean	−42.15 ± 0.56	Mean	−39.78 ± 0.46
1,3-Dimethyl urea			
1.83	−38.84	1.57	−31.18
2.35	−39.23	2.09	−31.05
2.61	−38.54	2.35	−32.58
2.87	−38.84	2.61	−32.21
3.13	−38.76	2.87	−32.19
		2.87	−31.23
		4.18	−32.31
Mean	−38.84 ± 0.31	Mean	−31.82 ± 0.59
1,1,3,3-Tetramethyl urea			
1.83	−36.34	2.35	−28.35
2.09	−36.84	2.61	−29.35
2.35	−36.19	2.87	−28.98
2.61	−36.36	2.87	−29.12
2.87	−36.86	3.13	−28.52
3.13	−36.34	3.13	−29.57
3.59	−36.16	3.65	−28.58
Mean	−36.44 ± 0.33	Mean	−28.92 ± 0.42

TABLE 1 (continued)

Concentration (mol kg^{-1} × 10^{-3})	ΔH_s (298.15 K) (kJ mol^{-1})	Concentration (mol kg^{-1} × 10^{-3})	ΔH_s (308.15 K) (kJ mol^{-1})
Sodium chloride			
1.57	-40.18	2.09	-38.26
1.83	-40.71	2.35	-38.77
2.09	-40.26	2.61	-38.77
2.35	-41.61	2.87	-38.31
2.61	-40.39	3.13	-37.45
3.13	-41.22	3.92	-37.16
Mean	-40.73 ± 0.60	Mean	-38.12 ± 0.57
Calcium chloride			
1.57	-41.05	2.35	-35.50
1.83	-41.07	2.61	-35.60
2.09	-40.98	2.71	-35.80
2.09	-40.81	2.98	-36.16
2.61	-40.74	3.13	-35.53
2.87	-41.31	3.39	-35.50
		3.65	-35.78
Mean	-40.99 ± 0.21	Mean	-35.70 ± 0.21

ΔH_s values was observed and hence an average of all the experimental data points was taken and expressed as a 95% confidence limit.

The average enthalpy of solution values and the subsequently derived heat capacity of solution values are shown in Table 2 which also includes the heat

TABLE 2

Heat capacities of Triton-X-100 in the micellar state ($\Delta C_{p,s}$) in water and aqueous solutions of urea, 1,3-dimethyl urea, 1,1,3,3-tetramethyl urea, sodium chloride and calcium chloride, and heat capacities of transfer of Triton-X-100 in the micellar state ($\Delta C_{p,\mathrm{tr}}$) from water to 1 M aqueous solutions of urea, 1,3-dimethyl urea, 1,1,3,3-tetramethyl urea, sodium chloride and calcium chloride

Solvent	ΔH_s (298.15 K) (kJ mol^{-1})	ΔH_s (308.15 K) (kJ mol^{-1})	$\Delta C_{p,s}$ (303.15 K) (J K^{-1} mol^{-1})	$\Delta C_{p,\mathrm{tr}}$ (303.15 K) (J K^{-1} mol^{-1})
Water	-44.60 ± 0.54	-31.86 ± 0.43	1274 ± 69	
1 m urea	-42.15 ± 0.56	-39.78 ± 0.46	237 ± 72	-1037 ± 100
1 m 1,3-dimethyl urea	-38.84 ± 0.31	-31.82 ± 0.59	702 ± 67	-572 ± 96
1 m 1,1,3,3-tetramethyl urea	-36.44 ± 0.33	-28.92 ± 0.42	752 ± 53	-522 ± 87
1 m sodium chloride	-40.73 ± 0.60	-38.12 ± 0.57	261 ± 81	-1013 ± 106
1 m calcium chloride	-40.99 ± 0.21	-35.70 ± 0.21	529 ± 30	-745 ± 30

capacity of transfer ($\Delta C_{p,\mathrm{tr}}$) for the Triton-X-100 micelles from water to 1 m aqueous solutions which were used as additives. The uncertainties in the $\Delta C_{p,\mathrm{s}}$ values were evaluated as follows

$$\epsilon \Delta C_{p,\mathrm{s}}(T) = \left\{\left[\epsilon \Delta H_{\mathrm{s}}(T_1)^2\right] + \left[\epsilon \Delta H_{\mathrm{s}}(T_2)^2\right]\right\}^{1/2} / (T_2 - T_1) \qquad (1)$$

where ϵ is the uncertainty and $T = (T_1 + T_2)/2$.

The ΔH_{s} values for Triton-X-100, irrespective of the solvent system used, are all endothermic (Table 1). This shows that whatever the effect of the additive (ureas or salts) in the solvent system at post-micellar concentrations, Triton-X-100 always tends to structure the solvent water by increasing the hydrogen-bondedness of the neighboring water molecules. At 308.15 K as compared to 298.15 K, ΔH_{s} becomes less endothermic, which is obvious from the fact that at higher temperatures, the hydrogen bonds in water would be broken and Triton would, thus, structure fewer water molecules at 308.15 than at 298.15 K. One could also apply this kind of analogy to explain the ΔH_{s} results in the various solvent systems. But since the enthalpy of solution values also incorporate dilution effects, it is better to explain the results on the basis of $\Delta C_{p,\mathrm{s}}$ values. The dilution effects would be nullified when heat capacities rather than the enthalpies are used, because $\Delta C_{p,\mathrm{s}}$ is evaluated as the difference in enthalpies at two temperatures divided by the temperature difference.

The $\Delta C_{p,\mathrm{s}}$ of Triton-X-100 is positive in all the systems studied and has an enormously high value in water (1274 J K^{-1} mol^{-1}) (Table 2). Since Triton-X-100 is predominantly hydrophobic, it is expected that upon dissolution in water, Triton-X-100 would increase the water structure in its vicinity to a significant extent through the phenomenon of hydrophobic hydration, i.e. even in the micellar state some hydrophobic groups could be partially exposed to the solvent because stereochemical constraints prevent these groups from packing into the core. In addition, as mentioned earlier, the ether groups would form hydrogen bonds with the neighboring water molecules giving rise to an increase in the heat capacity of the system. When we go from water to 1 m urea, $\Delta C_{p,\mathrm{s}}$ decreases as compared to water but is still positive (237 J K^{-1} mol^{-1}).

It is well known that urea disrupts the water structure to a considerable extent [10,11]. Because of this effect, urea tends to interfere with the hydrophobic hydration sphere of water molecules around the non-polar groups of Triton-X-100. In the presence of urea, the urea–water environment is energetically more favorable for the non-polar residues of Triton-X-100 than is water alone. This could possibly lead to some dissolving out of the micelle core. Here, two effects need to be considered: (i) the exposure of the non-polar groups to the solvent which enhances the heat capacity of the system due to hydrophobic hydration; and (ii) the overlap of the hydration cospheres of the urea molecules with the non-polar residues of Triton. The latter effect has been found to give rise to a decrease in the $\Delta C_{p,s}$ of the system [19]. It appears that the net effect is in favor of (ii) and the resulting consequence is a decrease in the $\Delta C_{p,s}$ in 1 m urea solution as compared to water.

As far as the methyl-substituted ureas are concerned, there is ample evidence that they are water-structure-makers in contrast to the breaking effect of urea [11,20–23]. Thus, they should be able to make water structure in the hydrophobic hydration sphere of the partially exposed non-polar groups of Triton. At the same time, a direct interaction of the hydration cospheres of methyl ureas with the non-polar groups of Triton-X-100 would decrease the heat capacity of the system because when two hydrophobic moieties overlap there is a net decrease in heat capacity [19]. Thus the $\Delta C_{p,s}$ of Triton-X-100 is lower in 1,3-dimethyl urea than in water but higher than in urea. The substitution of two more methyl groups in dimethyl urea further increases its structure-making propensity and, hence, $\Delta C_{p,s}$ of Triton-X-100 in tetramethyl urea is higher than in dimethyl urea, considering the type of interactions mentioned above.

In the transfer of micellar Triton-X-100 from water at aqueous solutions of sodium chloride and calcium chloride, it has also been observed that the $\Delta C_{p,s}$ value of Triton-X-100 decreases drastically in these salt solutions compared with its value in water. The magnitude of $\Delta C_{p,s}$ values in 1 m sodium chloride is comparable to that in 1 m urea. However, owing to the difference in the chemical nature of these two compounds, the mechanism must be totally different. Ions of salts with low charge density have been known to be net water-structure-breakers while those with high charge density have the opposite effect [24,25]. Sodium chloride would thus belong to the former category. Therefore, the presence of sodium chloride in the vicinity of micelles of Triton-X-100 would lead to the loosening of the micelles, giving rise to a decrease in heat capacity. In addition, the overlap of the hydration cosphere of an ion and a hydrophobic moiety is also believed to result in a decrease in heat capacity [19]. A combination of these two effects would thus decrease the $\Delta C_{p,s}$ value of Triton-X-100 micelles in sodium chloride to a considerable extent. This is what has been observed.

The $\Delta C_{p,s}$ value for Triton-X-100 in 1 M calcium chloride is also much less than in water but higher than the value in 1 M sodium chloride. In contrast to sodium chloride, calcium chloride behaves as a water-structure-forming agent; this should increase the $\Delta C_{p,s}$ for Triton-X-100 in its solution. However, the overlap of the hydration cosphere of calcium ions and the non-polar groups of Triton decreases such an effect more than in sodium chloride. Thus, it seems that the structure-making propensity of calcium chloride overwhelms the negative combination due to ion–hydrophobic-group interaction resulting in a higher $\Delta C_{p,s}$ for Triton-X-100 in calcium chloride than in sodium chloride.

In conclusion, it can be said that the thermodynamics of the interactions between various additive molecules and the Triton-X-100 micelles is governed by a fine balance between the interaction of the individual groups present, both in the additive as well as in the surfactant itself.

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