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CALORIMETRIC STUDIES ON THE INTERACTION OF SUGARS AND POLYOLS WITH THE NON-IONIC SURFACTANT TRITON-X-100 IN AQUEOUS SOLUTIONS

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ABSTRACT

The enthalpies of solution in the micellar state (ΔH_s) for the non-ionic surfactant Triton-X-100 in water and aqueous solution of 1-M glucose, sucrose, mannitol and sorbitol were measured at 298.15 K and 308.15 K by a Tronac titration calorimeter. The enthalpy data were used to evaluate the heat capacities for the surfactant in the micellar state ($\Delta C_{p,s}$) at 303.15 K in the systems studied. The heat capacities of transfer for the surfactant in the micellar state ($\Delta C_{p,tr}$) from water to aqueous solutions of sugars and polyols were found to be negative. The value of $\Delta C_{p,tr}$ for Triton-X-100 in the micellar state was more negative in glucose solution than in sucrose solution because of the relatively greater water-structure-making ability of glucose, whose hydroxyl groups have a better stereochemical compatibility with the structure of water than those of sucrose. Likewise, $\Delta C_{p,tr}$ for the surfactant micelles is more negative in mannitol than sorbitol solution because of the better fitting of mannitol than sorbitol with the tridymite structure of water.

INTRODUCTION

Surfactants in their micellar state show remarkable properties, for example solubilization of dyes, enhanced oil recovery and micellar catalysis [1]. Their formation in aqueous solution involves the hydrophobic effect, a property responsible for the stability of protein conformation and the formation of lipid-bilayer membranes [1–5]. In aqueous solutions, the structure of water plays an essential role in the micelle formation. The critical micelle concentration (cmc) of surfactants in water differs significantly from that in mixed aqueous solutions containing electrolytes and non-electrolytes.

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TABLE 1

Enthalpies of solution of Triton-X-100 in the micellar state (ΔH_s) as a function of concentration at 298.15 and 308.15 K in water and aqueous solutions of 1 M glucose, sucrose, mannitol and sorbitol

Concentration (mmol kg^{-1})	ΔH_s(298.15 K) (kJ mol^{-1})	Concentration (mmol kg^{-1})	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	−44.49	3.13	−32.31
2.09	−45.67	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 glucose			
2.52	−35.95	2.09	−35.26
2.53	−34.89	2.61	−35.24
2.72	−36.26	3.13	−34.98
3.19	−35.32	3.40	−35.41
4.15	−36.11	3.66	−36.08
4.81	−36.35		
Mean	−35.81 ± 0.61	Mean	−35.39 ± 0.51
1 M sucrose			
1.59	−34.35	2.09	−32.13
1.84	−35.92	2.61	−31.63
2.64	−35.61	2.72	−31.57
2.69	−35.90	3.13	−31.00
3.63	−36.03	3.66	−31.73
4.31	−36.22	4.18	−30.99
4.70	−34.76		
Mean	−35.54 ± 0.65	Mean	−31.51 ± 0.46
1 M mannitol			
2.12	−38.41	2.35	−35.85
2.69	−38.29	2.61	−36.97
3.13	−38.97	2.87	−37.20
3.76	−37.98	3.13	−36.53
4.70	−37.03	3.40	−36.19
4.78	−36.61	3.66	−36.90
5.33	−37.36		
Mean	−37.81 ± 0.77	Mean	−36.61 ± 0.54

TABLE 1 (continued)

Concentration (mmol kg^{-1})	ΔH_s(298.15 K) (kJ mol^{-1})	Concentration (mmol kg^{-1})	ΔH_s(308.15 K) (kJ mol^{-1})
1 M sorbitol			
2.09	−36.21	2.09	−33.37
2.35	−36.83	2.61	−33.19
2.87	−36.46	3.13	−33.60
3.11	−36.43	3.66	−33.77
3.66	−36.80	4.18	−33.95
		4.70	−33.37
Mean	−36.55 ± 0.33	Mean	−33.54 ± 0.30

In general, the cmc of non-ionic surfactants is much lower than the ionic ones, the former being predominantly hydrophobic in nature [6,7].

Thermodynamic parameters such as enthalpies and heat capacities are very sensitive to structural changes in aqueous solutions and can give significant insights into solute–solute and solute–solvent interactions [8–13]. In this paper we present the calorimetric studies on the interaction of two sugars, glucose and sucrose, and two polyols, mannitol and sorbitol, with the non-ionic surfactant Triton-X-100 in its micellar state. The sugars and polyols were selected as solvent additives because of their significant water-structure-making abilities [14–20]. Triton-X-100 is a *p*-(1,1,3,3-tetramethylbutyl) phenoxy polyoxyethylene glycol having an average of 9.5 oxyethylene units per molecule [21] and the structure
$(CH_3)_3C{-}CH_2{-}C(CH_3)_2{-}$⌬$-(O{-}CH_2{-}CH_2)_{9.5}OH$.
However, the structure of the Triton-X-100 micelle is unclear [22]. Non-ionic surfactants spontaneously form aggregates upon dissolving in water: the hydrocarbon portion forms the apolar micellar interior whereas the oxyethylene part (as in Triton-X-100) is preferentially partitioned into the aqueous phase. It has also been suggested that in such surfactants, the ether groups form highly directional hydrogen bonds with water molecules whereas the ethylene groups are accommodated in the overall water structure [23].

Because the sugars and polyols are expected to induce a greater degree of hydrogen bonding in water, they would also affect the nature of interaction of the micelle with water molecules surrounding it and such effects could be detected by changes in the enthalpies and heat capacities of the surfactant when it is transferred from an aqueous solution. The enthalpies of solution (ΔH_s) of Triton-X-100 in its micellar state at 298.15 and 308.15 K in water and in 1 M solutions of the sugars and polyols have been used to deduce the heat capacities of transfer ($\Delta C_{p,tr}$) of the micelle from an aqueous to a mixed aqueous environment. The results have been discussed in terms of the relative water-structure-forming abilities of the sugars and polyols.

EXPERIMENTAL

Electrophoresis grade Triton-X-100 (Bio-Rad laboratories) and analytical reagent grade glucose, sucrose, mannitol and sorbitol (BDH) were used. The enthalpies of solution were measured by a Tronac-450 titration calorimeter (Tronac Inc., UT). The set-up details and the operational procedure for the calorimeter have been described elsewhere [24].

The bath temperature of the calorimeter was controlled by a Tronac PTC-40 proportional temperature controller and an ultracryostat. The thermal stability of the bath temperature was better than 0.005 K. The design of the calorimeter permits the motor-driven buret and the reaction vessel, which in this case was an adiabatic dewar vessel of 25 ml capacity, to be completely submerged inside the constant temperature bath. All the voltages indicating changes in temperature inside the reaction vessel and the calibration heater voltage were measured using a digital multimeter. The output voltage was recorded on a potentiometric strip-chart recorder.

The buret delivery rate was determined by weighing the sample of water delivered by the buret as a function of time and was found to be 0.39 ml min^{-1}. The calibration of the calorimeter was performed by measuring the heat of protonation of an aqueous solution of THAM (tris-(hyroxymethyl) aminomethane) with aqueous hydrochloric acid solution. Our ΔH values agreed to within 0.3% of those published [25].

RESULTS

The enthalpies of solution (ΔH_s) for Triton-X-100 in the micellar state in water and aqueous solutions of 1 M glucose, sucrose, mannitol and sorbitol at 298.15 and 308.15 K are present in Table 1. The final concentration of the surfactant solution ranged from 0.91 to 5.53 mmol kg^{-1} indicating that the

TABLE 2

Heat capacities of Triton-X-100 in the micellar state ($\Delta C_{p,s}$) in water and aqueous solutions of 1 M glucose, sucrose, mannitol and sorbitol and heat capacities of transfer of Triton-X-100 in the micellar state ($\Delta C_{p,tr}$) from water to aqueous solutions of 1 M glucose, sucrose, mannitol and sorbitol

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})	$\Delta C_{p,tr}$(303.15 K) (J K^{-1} mol^{-1})
Water	-44.60 ± 0.54	-31.86 ± 0.43	1274 ± 69	
1 M glucose	-35.81 ± 0.61	-35.39 ± 0.51	42 ± 79	-1232 ± 105
1 M sucrose	-35.54 ± 0.65	-31.51 ± 0.46	403 ± 80	-871 ± 106
1 M mannitol	-37.81 ± 0.77	-36.61 ± 0.54	120 ± 94	-1154 ± 117
1 M sorbitol	-36.55 ± 0.33	-33.54 ± 0.30	301 ± 45	-973 ± 82

measurements were done well above the cmc for the surfactant which is 0.33 mmol dm^{-3} [26]. Using the enthalpy data, the heat capacities of solution ($\Delta C_{p,s}$) for the surfactant in water and in mixed aqueous solvents were evaluated at 303.15 K. Because there was no observable concentration dependence in ΔH_s, an average of all the experimental data points was taken and was expressed as the 95% confidence limit. The slight variation in ΔH_s values with concentration is the result of experimental uncertainties rather than because of concentration dependence.

The values of the enthalpy of solution and of the heat capacity of solution at 303.15 K, including their standard deviations, are presented in Table 2. The heat capacities of transfer ($\Delta C_{p,tr}$) for the Triton-X-100 micelles from water to 1 M aqueous solution of sugars and polyols are also included in Table 2. Uncertainties in $\Delta C_{p,s}$ values at a temperature "T" were estimated as follows:

$$e_{\Delta C_{p,s}(T)} = \left\{ \left[e_{\Delta H_s(T_1)} \right]^2 + \left[e_{\Delta H_s(T_2)} \right]^2 \right\}^{1/2} / (T_2 - T_1) \tag{1}$$

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

All the $\Delta C_{p,tr}$ values for Triton-X-100 from water to 1 M aqueous solution of sugars and polyols were found to be negative and in the order: glucose > mannitol > sorbitol > sucrose.

DISCUSSION

All the $\Delta C_{p,s}$ values observed in water and in aqueous solution of sugars and polyols are positive, that in water being the highest. This shows that Triton-X-100 has a strong tendency to order water molecules. It can be expected that, even though Triton-X-100 is predominantly hydrophobic, it is probable that not all of its hydrophobic moieties may be able to pack into the core of the micelle because of stereochemical constraints and that there could be partial exposure of some hydrophobic residues to water. The hydrophobic hydration of these residues as well as the hydrogen-bonding tendency of the ether groups with water [23] probably causes the highly positive $\Delta C_{p,s}$ value in water.

In the sugars and polyols, $\Delta C_{p,s}$ is less than that in water. This can be explained by considering the water-structure-making tendencies of the compounds as has been demonstrated on the basis of thermodynamic [27–29] and spectroscopic [30–32] data. Thus, when Triton-X-100 liquid is introduced into the sugar and polyol solutions, because of the energetically unfavorable environment produced by these additives in water, the monomers of the surfactant pack more tightly to form the micelles and there is less exposure of the hydrophobic moieties to the external solvent compared to the situation in pure water. Moreover, residues remaining exposed to the solvent are unable to interact with it as much as in pure water because of the considerable effect of the additives on the water. Thus, the $\Delta C_{p,s}$ value of Triton-X-100 in the sugar and polyol solutions, although positive, is much less than that in water.

The relative decrease in $\Delta C_{p,s}$ in these sugars and polyols can be explained on the basis of their relative water-structure-making abilities or water-structure compatibilities. $\Delta C_{p,s}$ values for the micelles of Triton-X-100 in 1 M glucose and sucrose solutions are 42 J K^{-1} mol^{-1} and 403 J K^{-1} mol^{-1}, respectively (Table 2). Glucose has been found to have a better water-structure compatibility than sucrose. This is because it has more equatorial hydroxyl groups than sucrose. Equatorial hydroxyl groups are believed to fit better with the water structure than axial ones [14–16]. In addition, sucrose has one hydroxyl group less than glucose because its structure includes a glycosidic linkage. Thus it is expected that sugar–solvent interaction would be more pronounced with glucose than sucrose making it more difficult for the hydrophobic groups of Triton-X-100 to be exposed to the solvent. This would enhance the water-structure-making abilities of glucose and eventually lead to a drastic decrease in $\Delta C_{p,s}$. Adderson and Butler [15] studied the cmc of some cationic surfactants in glucose solution and sucrose solution and from it deduced the enthalpies of micellization in these solvents. The signs and magnitudes of the enthalpies of micellization they observed have also been explained on the basis of the greater water-structure-making property of glucose than sucrose. However, in the case of the ionic surfactants, there is interference from the ionic groups surrounding the micelle [15,33].

Polyols are acyclic structures and it is believed that they would fit less well with the tridymite structure of water than the cyclic sugars [14,34]. Thus polyols would order the water structure less than those sugars with similar molecular formulae. In support of this, we have observed less decrease of $\Delta C_{p,s}$ values in mannitol and sorbitol than in glucose. $\Delta C_{p,s}$ values in mannitol and sorbitol solutions are 120 J K^{-1} mol^{-1} and 301 J K^{-1} mol^{-1}, respectively. Because sorbitol is believed to have a bent zigzag conformation and mannitol a planar one, water would tend to fit less well into sorbitol than into mannitol [35,36]. This would again explain our $\Delta C_{p,s}$ for Triton-X-100 in mannitol and sorbitol solutions.

Gratzer and Beaven [37] have observed that the cmc for Triton-X-100 in aqueous sucrose solution is less than that in water. This has been explained on the basis of the water-structure-making ability of sucrose which enables the monomers to come closer at lower concentration in sucrose solutions than in water and, hence, lowers its cmc. Janado and Nishida [38] have determined the solubility of n-octanol in glucose solution and observed it to be less than in water at 298.15 K. Also, Ueda et al. [39] have noted that the solubility of toluene in water decreases more in inositol which is cyclic. Our $\Delta C_{p,s}$ results support these findings.

Although it would appear from Table 2 that large uncertainties are involved with these data, the $\Delta C_{p,s}$ or $\Delta C_{p,tr}$ values are significantly different for sugars and polyols and show that water-structure-mediated effects are important as far as the micelle-additive interactions are concerned. Work on the Triton-X-100 micelle in water-structure-breaking solvents is in progress in our laboratory to further this research.

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