

# The effect of sugars on the temperature dependence of the critical micelle concentrations of cationic surfactants

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The temperature dependence of the critical micelle concentrations (cmc) of decyl, dodecyl and tetradecyl trimethylammonium and dodecyl benzyl dimethylammonium bromides in the presence of glucose or sucrose is reported. Thermodynamic parameters have been calculated using the uncharged phase-change model. An interpretation of the changes in cmc values, relative to those in simple aqueous solutions, is offered in terms of the resultant of two effects, namely modifications in water-structure and reduction of dielectric constant.

The occurrence of hydrocarbon-stabilized water-structure is commonly held to be an important factor in the micellization of surface-active agents (Anacker, 1970 and references therein). The change in cmc consequent upon the incorporation of a second solute into an aqueous surfactant solution has been used to investigate the role of such water-structure. As there may be no conclusive evidence for denoting such an added solute as a structure-promoting or structure-breaking agent, the observed effects are open to conflicting interpretations. Thus, the effects caused by the widely used additive, urea, have been described in terms of urea acting as a destructuring agent (Schick, 1964), a structure promoting agent (Abu-Hammdiyah, 1965) or as a competitive structuring agent (Benjamin, 1966).

The concept of hydrocarbon-stabilized water has been invoked to explain the chain-length dependence of the temperature of minimum cmc (Adderson & Taylor, 1970). The present investigation reports an examination of the changes in derived thermodynamic parameters consequent upon the incorporation of carbohydrates into aqueous surfactant solutions. Initial investigations showed that amides, such as the commonly used urea and malonamide, underwent slow hydrolysis in solution at 298·2K in conductance cells having platinized plates. Sugars, which might be expected to show marked interactions with water through the presence of multiple hydroxyl groups (Kay & Evans, 1966), were free from this defect.

## MATERIALS AND METHODS

### *Materials*

The preparation and characters of tetradecyl trimethylammonium bromide has been previously described (Adderson & Taylor, 1967). Decyl and dodecyl trimethyl ammonium, and dodecyl benzyl dimethylammonium bromides were prepared from the corresponding alkyl bromides (initially prepared from Fluka purissima grade alcohols) by quaternization with trimethylamine and *NN'*-benzyl dimethylamine respectively.

Decyl trimethylammonium bromide, m.p. 224° (497 K); found: Br, 28·4%; calcu-

Table 1. Critical micelle concentrations, mol fractions

(a) Alkyl trimethylammonium bromides in 1 molal sucrose and 2 molal glucose.

Temp. K	C <sub>10</sub>		C <sub>12</sub>		C <sub>14</sub>	
	Sucrose	Glucose	Sucrose	Glucose	Sucrose	Glucose
278·2	$1.22 \times 10^{-3}$	$0.996 \times 10^{-3}$	$2.84 \times 10^{-4}$	$2.12 \times 10^{-4}$	—	—
283·2	1·20	1·00	2·82	2·15	$6.34 \times 10^{-5}$	$5.26 \times 10^{-5}$
288·2	1·22	1·01	2·83	2·18	6·61	5·48
293·2	1·23	1·01	2·88	2·25	6·84	5·59
298·2	1·24	1·02	2·96	2·32	7·11	5·76
303·2	1·25	1·07	3·03	2·45	7·35	5·93
313·2	1·32	1·14	3·31	2·69	8·03	6·85
323·1	1·41	1·24	3·64	3·04	9·14	8·02
333·2	1·53	1·35	4·08	3·42	10·6	9·50
343·2	1·65	1·51	4·52	3·93	12·2	11·4

(b) Dodecyl trimethylammonium bromide, (c) dodecyl benzyl dimethylammonium bromide.

Temp. K	(b)	(c)	(c)
	In 4 molal glucose	In 1 molal sucrose	In 2 molal glucose
278·2	$1.68 \times 10^{-4}$	—	—
283·2	1·75	$1.00 \times 10^{-4}$	$7.66 \times 10^{-5}$
288·2	1·87	1·02	7·74
293·2	1·95	1·05	8·16
298·2	2·08	1·10	8·43
303·2	2·23	1·14	8·98
313·2	2·56	1·27	10·3
323·2	2·99	1·44	12·1
333·2	3·54	1·67	14·4
343·2	4·24	1·95	17·4

lated: 28·51%. Dodecyl trimethylammonium bromide, m.p. 231° (504 K), found: Br, 25·9%; calculated: 25·92%. Dodecyl benzyl dimethylammonium bromide, m.p. 52° (325 K), found: Br, 20·8%; calculated: 20·79%. All melting points were sensitive to the presence of traces of moisture.

Sucrose: British Drug Houses, Analar. A molal solution had a specific conductance of  $1.6 \times 10^{-6}$  ohms<sup>-1</sup> cm<sup>-1</sup> at 298·2K; that is not markedly different from that of water.

Glucose: Hopkins and Williams, Analar. Specific conductances of 2 molal solutions were found to vary from 1·2 to  $2.5 \times 10^{-5}$  ohms<sup>-1</sup> cm<sup>-1</sup> at 298·2K. An attempt to remove traces of ionic impurities by ion-exchange was unsuccessful. Trap & Hermans (1955) data show that the amounts of impurity indicated by the conductance of these solutions would be insufficient to account for the observed decreases in cmc. Care was taken to ensure that for any given system of glucose-surfactant-water the same batch of glucose was used throughout.

Polarimetric observations showed that: (i) A 1 molal solution of sucrose containing dodecyl trimethylammonium bromide did not undergo inversion when heated to 343·2K or on subsequent cooling. (ii) After initial equilibration of the  $\alpha$  and  $\beta$  glucose content, conveniently achieved by storage of 2 or 4 molal glucose solutions at 276·2K for 12 h, the equilibrium was not markedly affected by alteration of temperature. At higher temperatures equilibration was more rapidly achieved, requiring 15 min at 323·2K. Changes in measured conductance suggested that

slight decomposition of glucose solutions occurred in cells having platinized plates at temperatures of 323·2K and above. Conductance measurements were therefore made 15 min after the solutions had reached thermal equilibrium.

#### *Determination of critical micelle concentrations*

Values of the cmc were determined by the conductance technique previously described (Adderson & Taylor, 1964).

### RESULTS AND DISCUSSION

#### *Thermodynamic parameters*

Thermodynamic parameters recorded in Table 2 have been calculated using the uncharged phase-change model. The chosen standard states are the hypothetical mol fraction of unity for the monomeric species and, for the micellar phase, the micelle at the cmc. Heats of dilution are assumed to be negligible compared to

Table 2. *Thermodynamic parameters for the micellization of surfactants in sugar solutions.*

(a) Alkyl trimethylammonium bromides in 1 molal sucrose.

Temp. K	C <sub>10</sub>		C <sub>12</sub>		C <sub>14</sub>	
	−ΔG <sub>m</sub> <sup>o</sup> kJ/mol	−ΔH <sub>m</sub> kJ/mol	−ΔG <sub>m</sub> <sup>o</sup> kJ/mol	−ΔH <sub>m</sub> kJ/mol	−ΔG <sub>m</sub> <sup>o</sup> kJ/mol	−ΔH <sub>m</sub> kJ/mol
278·2	31·1	0·54	37·8	−3·1	—	—
283·2	31·6	0·69	38·5	−0·11	45·4	7·4
288·2	32·2	1·3	39·1	+2·8	46·0	8·8
293·2	32·7	2·3	39·8	5·7	46·7	10
298·2	33·2	3·7	40·3	8·3	47·3	12
303·2	33·7	5·4	40·9	11	47·8	14
313·2	34·6	9·2	41·7	15	49·0	18
323·2	35·3	13	42·5	18	50·0	22
333·2	36·0	15	43·2	20	50·8	27
343·2	36·6	15	44·1	20	51·4	33

(b) Alkyl trimethylammonium bromides in 2 molal glucose.

Temp. K	C <sub>10</sub>		C <sub>12</sub>		C <sub>14</sub>	
	−ΔG <sub>m</sub> <sup>o</sup> kJ/mol	−ΔH <sub>m</sub> kJ/mol	−ΔG <sub>m</sub> <sup>o</sup> kJ/mol	−ΔH <sub>m</sub> kJ/mol	−ΔG <sub>m</sub> <sup>o</sup> kJ/mol	−ΔH <sub>m</sub> kJ/mol
278·2	32·0	−1·5	39·1	1·5	—	—
283·2	32·6	+0·56	39·8	4·2	46·4	1·8
288·2	33·1	2·6	40·4	6·8	47·1	5·5
293·2	33·6	4·7	41·0	9·3	47·8	9·2
298·2	34·1	6·7	41·5	12	48·4	13
303·2	34·5	8·6	42·0	14	49·0	16
313·2	35·3	12	42·8	18	49·9	23
323·2	36·0	16	43·6	22	50·7	29
333·2	36·6	18	44·2	24	51·3	33
343·2	37·1	20	44·8	25	51·8	37

(c) Dodecyl trimethylammonium bromide and (d) dodecyl benzyl dimethyl ammonium bromide.

Temp. K	(c) in 4 molal glucose		(d) in 1 molal sucrose		(d) in 2 molal glucose	
	$-\Delta G_m^\circ$ kJ/mol	$-\Delta H_m^\circ$ kJ/mol	$-\Delta G_m^\circ$ kJ/mol	$-\Delta H_m^\circ$ kJ/mol	$-\Delta G_m^\circ$ kJ/mol	$-\Delta H_m^\circ$ kJ/mol
278.2	40.2	12	—	—	—	—
283.2	40.7	13	43.4	3.8	44.7	5.0
288.2	41.2	15	44.0	6.6	45.4	8.5
293.2	41.6	17	44.6	9.3	46.0	12
298.2	42.0	19	45.2	12	46.5	15
303.2	42.4	20	45.7	15	47.0	19
313.2	43.1	24	46.7	20	47.8	25
323.2	43.6	28	47.5	24	48.5	30
333.2	44.0	32	48.2	28	49.0	34
343.2	44.4	36	48.8	31	49.4	36

heats of micellization. Thermodynamic values may be calculated—

$$-\Delta G_m^\circ = -2RT \ln \text{cmc}$$

$$-\Delta H_m^\circ = -\Delta H_m^\circ = 2RT^2 \left( \frac{\partial \ln \text{cmc}}{\partial T} \right)_p$$

$$-\Delta S_m^\circ = \frac{\Delta G_m^\circ - \Delta H_m^\circ}{T}$$

$$-\Delta S_m = \frac{-\Delta H_m}{T}$$

Polynomial expressions have been fitted, as previously recorded (Adderson & Taylor, 1970), to the data relating  $\log \text{cmc}$  and absolute temperature  $T$  and used to evaluate  $\left( \frac{\partial \ln \text{cmc}}{\partial T} \right)$

The present cmc values when compared with those previously reported for simple aqueous systems (Adderson & Taylor, 1967 and 1971) show that: (i) at all temperatures cmcs are increased by the incorporation of sucrose; (ii) glucose may depress or increase cmcs relative to the aqueous values according to the temperature. Glucose-containing systems exhibit the same cmc as the corresponding aqueous system at approximately 323.2K, irrespective of glucose concentration or surfactant used.

The derived free energy changes of micellization reflect these cmc changes, e.g., for dodecyl trimethylammonium bromide  $\Delta G_m^\circ$  kJ mol<sup>-1</sup>

Temp. K	Water	1 molal sucrose	2 molal glucose	4 molal glucose
298.2	-40.9	-40.3	-41.5	-42.0
323.2	-43.5	-42.5	-43.6	-43.6
343.2	-45.2	-44.1	-44.8	-44.4

as illustrated in Fig. 1.

The component enthalpic and entropic terms show, in general, progressive negative increments, thus, for dodecyl trimethylammonium bromide at 298·2K

$\Delta S_m^{\circ}$ J deg <sup>-1</sup> mol <sup>-1</sup> and $\Delta H_m$ ( $\equiv \Delta H_m^{\circ}$ ) kJ mol <sup>-1</sup>	Water	1 molal sucrose	2 molal glucose	4 molal glucose
	130	110	100	79
	-2·4	-8·3	-12	-19

The observation that, in glucose, the  $\Delta G_m^{\circ}$  values change from being greater to being less than the corresponding aqueous values, whereas  $\Delta H_m$  and  $\Delta S_m^{\circ}$  are more negative at all temperatures, must imply that the observed  $\Delta G_m^{\circ}$  values are the result of changes in the balance of these component enthalpic and entropic terms. The observed changes in  $\Delta H_m$  and  $\Delta S_m^{\circ}$  consequent upon the incorporation of sugar into an aqueous surfactant system are relatively large, but almost self compensating. Thus a change in  $\Delta H_{\text{water}}$  to  $\Delta H_{\text{glucose}}$  of  $-16\cdot6$  kJ mol<sup>-1</sup> is only accompanied by a change of  $-1\cdot1$  kJ mol<sup>-1</sup> in  $\Delta G_m^{\circ}$ .

Inspection of Fig. 1 indicates that any interpretation of the changes in  $-\Delta G_m^{\circ}$  with change of solvent and temperature must account for a number of observations:

(i) below 323·2K addition of glucose increases  $-\Delta G_m^{\circ}$  but sucrose causes a decrease, (ii) in all cases  $-\Delta G_m^{\circ}$  increases with increasing temperature, the greatest rate of increase being observed in aqueous systems, (iii) as a result of (ii) the value of  $-\Delta G_m^{\circ}$  in glucose solutions at higher temperatures is less than in water.

To satisfy the above observations, it appears necessary to consider at least two

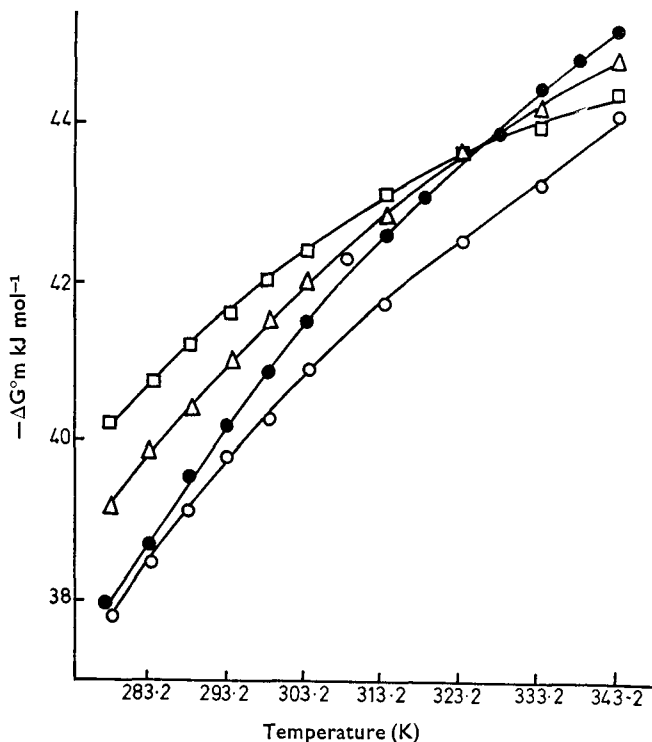


FIG. 1. The free-energy change,  $-\Delta G_m^{\circ}$ , upon micellization for dodecyl trimethyl ammonium bromide in water and in sugar solutions. ● Water. ○ 1 Molal glucose. △ 2 Molal glucose. □ 4 Molal glucose.

effects leading to a modification of the tendency of a surfactant to aggregate into micelles when a sugar is added. These effects should oppose each other, giving rise to a different balance at low temperatures in glucose compared to sucrose, and the component which tends to increase  $-\Delta G_m^\circ$  should be markedly reduced at higher temperatures.

The factors considered likely to assume the roles noted above, are: (i) water-structure promotion and (ii) a change in the dielectric constant of the medium, on incorporation of a sugar. It is suggested that the effect on dielectric constant is such as to tend to increase cmc values (relative to those in water) with both sugars over the entire range of temperatures reported. Enhanced water structure at low temperatures will tend to cause a slight decrease in cmc in sucrose solutions and a greater decrease in the presence of glucose whereas at higher temperatures changes in water structure will be of little significance. The net results of these changes will be to cause an increase in cmc relative to that in water in all instances except that of glucose at temperatures below 323-2K. In the latter instance the decrease in cmc associated with a change in water structure is sufficient to outweigh the increase due to a reduction in dielectric constant.

In support of the above contentions it may be noted:

(i) That water-structure promotional influence of glucose may be expected to outweigh that of sucrose.

Examination of the molecules of glucose and sucrose suggests that  $\beta$ -D-glucose where all the hydroxyl groups are in the equatorial configuration may be more readily incorporated into three dimensional water structure than  $\alpha$ -D-glucose. The equilibrium mixture contains about 62% of the  $\beta$ -isomer (Packer & Vaughan, 1958).

The glucose ring in sucrose is in the  $\alpha$ -configuration and, furthermore, absence of the glycosidic hydroxyl may well lead to reduced interaction with solvent in comparison with glucose. It is therefore to be anticipated that sugar-solvent interactions in 2 molal glucose would be higher than in 1 molal sucrose.

Kay & Evans (1966) designate both sugars as water structure-promoting agents. This suggests that these sugars would compete with the water-stabilization attributed to alkyl chains (cf. Benjamin, 1966). If glucose is more readily incorporated into three-dimensional water structure than sucrose it would be expected that its competitive effect would be greater and hence the changes in enthalpy and entropy accompanying micellization more markedly altered. Positive values of  $\Delta H_m$  and  $\Delta S_m^\circ$  have been previously attributed to loss of hydrocarbon-stabilized water accompanying micellization (Adderson & Taylor, 1970). Diminution of this unfavourable enthalpic change resulting from a reduction in the amount of hydrocarbon-stabilized water lost on micellization would promote aggregation at lower concentrations in sugar solutions than in water, that is, reduce the cmc.

It is noteworthy that the experimentally derived enthalpies of micellization are in the order—glucose more negative than sucrose which is more negative than water as solvent; this might be taken as indicating the validity of the above hypothesis. As there is no method of separately evaluating the changes in the other contributory enthalpic values, e.g. those associated with head group aggregation, loss of hydrocarbon-water interface and solvation of counterions, which would result from the incorporation of sugars, the above interpretation should be treated with due caution. Similarly, the standard state entropy changes should be water > sucrose > glucose. Such orders are observed in the experimental data. Reduction in the positive

enthalpic contribution to the heat of micellization due to a decrease in hydrocarbon-stabilized water would, in accordance with the considerations advanced for aqueous binary systems (Adderson & Taylor, 1970), be expected to lead to a reduction in the minimum cmc temperature. Such reductions are observed.

(ii) The reduction in dielectric constant on addition of sugars is expected to lead to a greater difficulty of assembling charged head groups, that is, to contribute unfavourably to micellization. Dielectric constants decrease with increasing temperature but with a relatively small temperature coefficient [0.2% degree<sup>-1</sup>, from 10° to 40°, 0.4% from 40° to 60°C, for water (Kaye & Laby, 1958)]. It is assumed that aqueous sugar solutions would behave similarly, so that the increased electrical work necessary for micellization in the presence of sugars would be largely independent of temperature.

Debye's (1949) relation, Electrical work  $\propto \frac{1}{\text{Dielectric constant}}$  where the effective dielectric constant is assumed to be the average of that of the solvent and hydrocarbon, may be used to indicate the likely effect of such a reduction. Using the values of 82 and 71 for water and 1 molal sucrose (International Critical Tables, 1929) respectively and 2.8 kT (Debye, 1949) for the electrical work term, the inclusion of sucrose into an aqueous solution would increase the electrical work necessary to assemble a micelle of dodecyl trimethylammonium bromide at 298.2K to 3.2 kT. This increase of 0.4 kT (i.e. approximately 1 kJ mol<sup>-1</sup>) is in excess of the difference of 0.6 kJ mol<sup>-1</sup> between the observed values of  $-\Delta G_m^0$  for dodecyl trimethylammonium bromide in water and 1 molal sucrose solution. This discrepancy may be attributed to the opposing effect upon  $-\Delta G_m^0$  of the changes discussed under water structure. If the same relative dielectric constant difference between water and 1 molal sucrose solution persists at 343.2K where water-structural effects should have a negligible effect upon the difference in  $-\Delta G_m^0$  in the two solvents, the calculated difference of 1.1 kJ mol<sup>-1</sup> is in good agreement with the observed change of 1.1 kJ mol<sup>-1</sup>. Thus, while it must be admitted that the above calculations are of necessity very approximate, changes in  $-\Delta G_m^0$  of the correct magnitude may be forecast as a result of reduction in dielectric constant.

The change in dielectric constant relative to the value in water at 298.2K is greater on the addition of 26.5% glucose (i.e. 2 molal) than 25.8% sucrose (i.e. 1 molal), being 42% and 13% respectively (International Critical Tables, 1929). If this reduction in dielectric constant was the only contributory factor to change in cmc, it would be expected that use of glucose solution as solvent would increase the cmc compared to the value in sucrose solution or water. Such is contrary to observation, suggesting the occurrence of at least one other factor, here presumed to be associated with the structure of water.

The above noted changes (i) and (ii) may satisfactorily account for the observed differences in  $-\Delta G_m^0$  but are less acceptable with respect to  $\Delta H_m$ . The increase in  $-\Delta H_{\text{sugar}}$  compared to  $-\Delta H_{\text{water}}$  has been attributed to the reduction of hydrocarbon-stabilized water and consequent reduction of the endothermic destruction of such structure. As this effect should largely vanish at higher temperature it might be expected that the values of  $\Delta H_m$  observed in sugar solutions would approach or become less negative than those in water. The present evidence is inconclusive

in that only five out of the nine systems studied show such a convergence. As this convergence is at the extreme end of the measured range of temperatures where it is admitted that less confidence may be placed in  $\Delta H_m$  values derived from the differentiation of approximating polynomial equations, it would be unwise to form any conclusions from such observations.

The micellization process in the presence of sugars involves factors that cannot be evaluated from the present observations. Such factors could involve solvation changes in head groups or counterions. Reduction in the solvation change accompanying micellization has been suggested as a factor in making the total enthalpy and standard entropy changes more negative (Corkill, Goodman & others, 1966). Solvation changes of the counterions could also affect the ease of counterion binding, which, if increased, would increase  $-\Delta H_m$  and decrease  $\Delta S_m^0$  relative to aqueous systems.

A further increase in the exothermic contribution to  $\Delta H_m$  would arise from the greater cohesive energy of sugar solutions, as shown by increases in surface tension relative to water (International Critical Tables, 1928). Removal of an alkyl chain from such a system would be accompanied by an increased value of  $-\Delta H_m$ .

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