

## The temperature dependence of the critical micelle concentrations of cationic surface-active agents

The temperature dependence of the critical micelle concentrations, CMC values, of dodecyl pyridinium bromide (Adderson & Taylor, 1964), tetradecyl pyridinium, trimethyl ammonium and benzyl dimethyl ammonium bromides (Adderson & Taylor, 1967) and alkyl  $\alpha$ -picolinium bromides (Adderson & Taylor, 1970) has been previously reported and an explanation of the micellization process advanced. The present data are complementary and reinforce this explanation.

Dodecyl benzyl dimethyl ammonium bromide, decyl and dodecyl trimethyl ammonium bromides were prepared by methods previously reported. CMC values were determined by conductance technique and are recorded in Table 1.

The fraction of theoretical charge,  $p/N$  has been calculated both for these salts and from the conductance-concentration data for the tetradecyl homologues (Adderson & Taylor, 1967), using the method of Evans, (1956). Aggregation numbers,  $N$ , of  $C_{10} = 36$ ,  $C_{12} = 50$  &  $C_{14} = 75$  (Debye 1949) have been used throughout (Table 2).

As observed for alkyl picolinium bromides, (Adderson & Taylor, 1970) the degree of dissociation increases with temperature and decreases with increase in length of the principal alkyl chain. The dissociation is less in the alkyl trimethyl salts than in the corresponding compounds containing a cyclic structure, suggesting that the benzyl screens the charged nitrogen to a greater extent than a methyl group.

Thermodynamic parameters, Fig. 1a and b, have been calculated as previously, using the uncharged phase-change model and standard states of a mol fraction of unity for the monomeric species and the micelle itself for its species, and assuming that the heats of dilution from standard state to CMC are negligible compared to the heat of micellization. Hence,  $\Delta G_m^0 = 2RT \ln \text{CMC}$ , and  $\Delta H_m = \Delta H_m^0 = -2RT^2 (\partial \ln \text{CMC} / \partial T)_p$ .

Table 1. *Critical micelle concentrations, mol fractions.*

Temperature °C	Trimethyl ammonium bromides		Benzyl dimethyl ammonium bromides
	Decyl	Dodecyl	Dodecyl
5	$1.19 \times 10^{-3}$	$2.76 \times 10^{-4}$	—
10	1.16	2.70	$1.01 \times 10^{-4}$
15	1.15	2.64	0.989
20	1.13	2.63	0.983
25	1.12	2.64	0.994
30	1.13	2.69	1.02
35	1.14	2.75	1.06
40	1.15	2.82	1.11
45	1.18	2.89	1.15
50	1.22	3.01	1.22
55	1.25	3.15	1.28
60	1.28	3.33	1.38
65	1.31	3.48	1.51
70	1.35	3.71	1.62

Table 2. *The fraction of the theoretical charge,  $p/N$ .*

Temperature °C	Trimethyl ammonium bromides			Benzyl dimethyl ammonium bromides	
	$C_{10}$	$C_{12}$	$C_{14}$	$C_{12}$	$C_{14}$
5	0.26	0.16	—	—	—
15	0.27	0.17	0.14	0.21	—
25	0.28	0.18	0.16	0.22	—
35	0.29	0.19	0.17	0.23	0.19
45	0.30	0.20	0.18	0.24	0.20
55	0.31	0.21	0.19	0.25	0.20

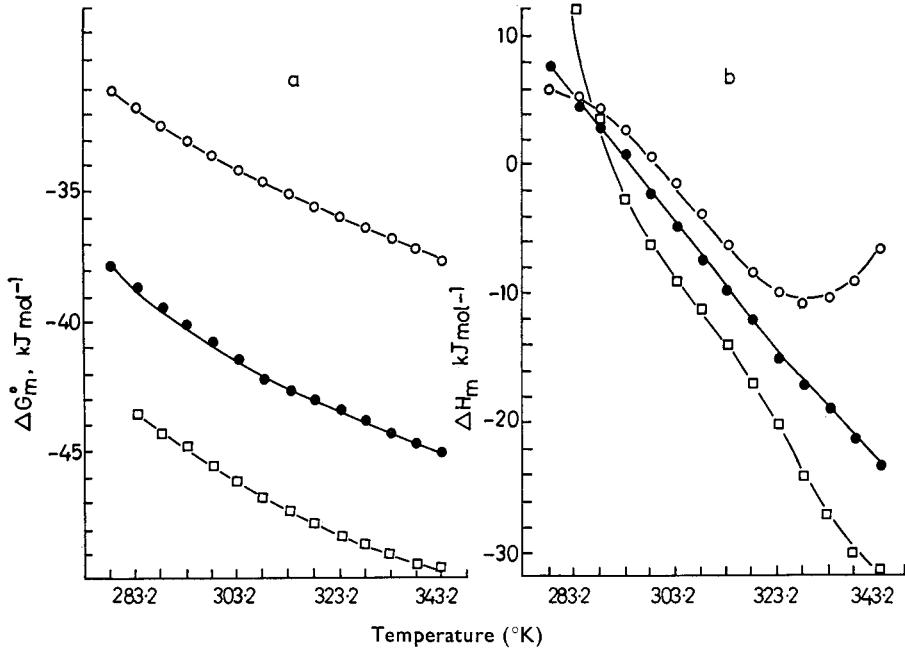


FIG. 1. a. Energy changes accompanying micellization. ○ Decyl trimethylammonium bromide; ● dodecyl trimethylammonium bromide; □ dodecyl benzyl dimethylammonium bromide. b. Heats of micellization. Symbols as in a.

These derived enthalpy changes are very similar to those formerly reported and are in accord with the previously suggested energy changes accompanying micellization.

At least three factors contribute to the enthalpy changes, namely those associated with head-group aggregation, those with breakdown of hydrocarbon-stabilized water-structure and changes due to transfer of hydrocarbon from water to micelle. The first two are endothermic, the latter exothermic. The temperature at which micellization changes from an endo to an exothermic reaction, shown by the chain-length dependence of temperature of minimum CMC, varies with the summation of these effects. The major variable between members of a homologous series is the area of hydrocarbon-water interface associated with the alkyl chain. Increase in the associated exothermic component of micellization accompanying increase in chain length depresses the temperature at which a favourable enthalpic change first occurs.

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