

RESEARCH PAPERS

THE CRITICAL MICELLE CONCENTRATIONS OF DOUBLE LONG-CHAIN ELECTROLYTES (AMINE SOAPS) IN AQUEOUS SOLUTION

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Micelle formation and gegenion binding have been studied in aqueous solutions of primary and quaternary ammonium dodecyl sulphates (amine soaps) by the conductivity method. Critical micelle concentrations decrease markedly with increase in the cation chain length; this phenomenon is due mainly to increase in the free energy of micelle formation. Gegenion binding also increases with increasing cation chain length and reaches 95 per cent for the octyl and higher ammonium salts.

DOUBLE long-chain electrolytes (amine soaps), in which both anion and cation are attached to long-chain organic groups are used as surface-active agents when good solubility is required in both water and organic phases; the hydrophilic-lipophilic balance is often modified advantageously when organic counterions are substituted in place of the more usual inorganic ions in such materials (Moilliet, Collie and Black, 1961; Clayton and Sumner, 1954; Winsor, 1954).

Organic counterions are also known to have a marked influence on micelle formation by colloidal electrolytes in solution; the critical micelle concentration (CMC) decreases markedly with increase in counterion length (Cushman, Brady and McBain, 1948; Goddard, Harva and Jones, 1953; Scott and Tartar, 1943). This phenomenon might also be advantageous in many practical applications (Clayton and Sumner, 1954; Winsor, 1954) and in this respect, amine soaps may constitute a new and distinctive class of surface-active agents.

Few detailed studies on the physical properties of these materials have been reported and a systematic investigation of micelle formation and allied phenomena in solution should be of theoretical and practical interest.

In this initial work, the CMC of a series of alkyl ammonium dodecyl sulphates have been determined by the conductivity method.

The effect of counterion size on micelle formation and counterion binding has also been studied.

EXPERIMENTAL

Materials

The "amine soap" solutions studied were prepared *in situ* by exact neutralisation of a prepared batch of aqueous dodecyl sulphuric acid solution (0.1M) with various organic bases.

Sodium dodecyl sulphate. "Sipons" W.D. product was used. This material contained less than 0.1 per cent free long-chain alcohols.

The sulphate was hydrolysed to "lauryl alcohol" and the latter analysed by gas chromatography (on a Celite—20 per cent Silicone E301 column) and shown to be a mixture of approximately 92 per cent dodecyl and 8 per cent tetradecyl alcohols.

Dodecyl sulphuric acid was prepared by passing a solution (0.1 M) of the sodium dodecyl sulphate through a column of "Zeo-Karb 215" (H).

The acid solutions were standardised by potentiometric titration with sodium hydroxide. Complete conversion to dodecyl sulphuric acid was checked by determination of the equivalent conductivity of the neutralised acid; unchanged sodium dodecyl sulphate would lead to high equivalent conductivity values.

Primary amines. Methylamine and ethylamine of above 99 per cent purity were supplied by British Drug Houses Ltd., redistilled butylamine and hexylamine of 98–99 per cent purity and octylamine of 95–98 per cent purity by L. Light and Co., Ltd.

Purity was checked by equivalent weight determination and boiling-point (or melting-point).

Tetramethyl ammonium bromide was supplied by British Drug Houses Ltd., and recrystallised from alcohol.

Alkyl trimethylammonium bromides were prepared by reacting the alkyl bromide with excess alcoholic trimethylamine (Scott and Tartar, 1943).

Ethyl and butyl bromide (of above 99 per cent purity) were supplied by British Drug Houses Ltd. Hexyl, octyl and decyl bromide (of 95–96 per cent purity) were supplied by L. Light and Co., Ltd. Their purity was checked by gas chromatographic analysis on a Celite—10 per cent tricresyl phosphate column. These bromides contained up to 3 per cent isomers, about 0.5 per cent of lower homologues and about 2 per cent of higher homologues; this distribution should have little effect on CMC values (Harkins, 1953).

Alcohol and excess trimethylamine were removed by evaporation on a water bath. The quaternary bromides were then recrystallised from alcohol or acetone.

Quaternary ammonium hydroxide solutions were prepared by treating the corresponding halide salt solution (0.1 M) with a slight excess of silver oxide; the solution was then centrifuged and filtered free of silver halide. Complete conversion to hydroxide was checked by testing with acidified silver nitrate solution and by potentiometric titration of the prepared hydroxide with standard hydrochloric acid.

Alkyl ammonium dodecyl sulphates. Dodecyl sulphuric acid solutions (0.1 M) were standardised by potentiometric titration with sodium hydroxide.

These solutions were then titrated potentiometrically to pH 7.0* with the appropriate primary or quaternary ammonium hydroxide solution and the salt solutions were diluted as required.

* In the case of the primary amine soaps, a slight excess of free hydroxide was present in the titrated solution to prevent conductivity errors caused by hydrolysis at the higher dilutions.

CMC OF DOUBLE LONG-CHAIN ELECTROLYTES

The water used for the preparation of solutions and for conductivity measurements was prepared from freshly glass-distilled water (specific conductivity of $3\text{--}5 \times 10^{-6}$ ohms $^{-1}$) by passing through a bed of mixed ion-exchange resins (in an "Elgostat") and used immediately.

Its specific conductivity, at 25°, varied between 0.8 and 1.2×10^{-6} ohms $^{-1}$.

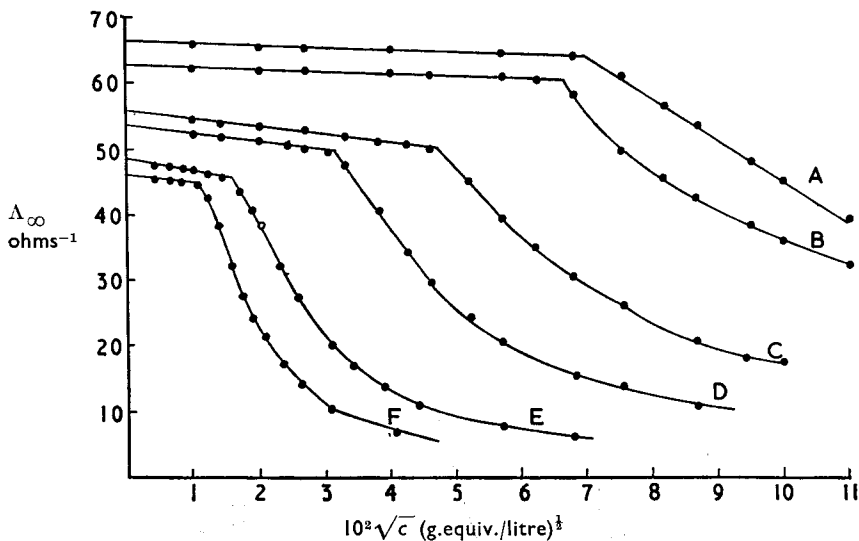


FIG. 1. Variation of equivalent conductivity of alkyl ammonium dodecyl sulphates with concentration (25°).

A, Tetramethyl; B, Ethyl trimethyl; C, Butyl trimethyl; D, Hexyl trimethyl; E, Octyl trimethyl; F, Decyl trimethyl.

Measurement of Critical Micelle Concentrations and Allied Properties

Critical micelle concentrations were measured by the conductivity method (Scott and Tartar, 1943; Evans, 1956).

A titration cell was used, with platinised platinum dipping electrodes, similar to that described by previous workers (Winsor, 1950; Evans, 1956); the cell constant was determined using standard potassium chloride solutions. Solutions were stirred with flowing nitrogen.

Conductivity measurements were made, at $25.0 \pm 0.1^\circ$, using a "Pye" Conductance Bridge (Model 11700) operating at 300 c./sec. and fitted with a cathode ray oscillographic detector; cell capacitance effects were balanced out by means of a variable condenser in parallel with the variable resistance. The Bridge operated with an accuracy of 0.1 per cent.

Measured volumes of the alkyl ammonium dodecyl sulphate solution were run into conductivity water, the solutions allowed to come to equilibrium at 25°, stirring stopped and the conductivity measured.

In all, 15 to 20 measurements were taken with each salt to provide a suitable range of conductivities for studies both below and above the CMC; generally, the range 10^{-4} N to $5 \times$ CMC was investigated.

RESULTS AND DISCUSSION

Determination of Critical Micelle Concentrations

Typical *equivalent conductivity—(concentration)^{1/2}* graphs for a series of alkyl ammonium dodecyl sulphate solutions studied are presented in Fig. 1. The Λ_{∞} values decrease regularly with increasing chain length and decreasing cation mobility.

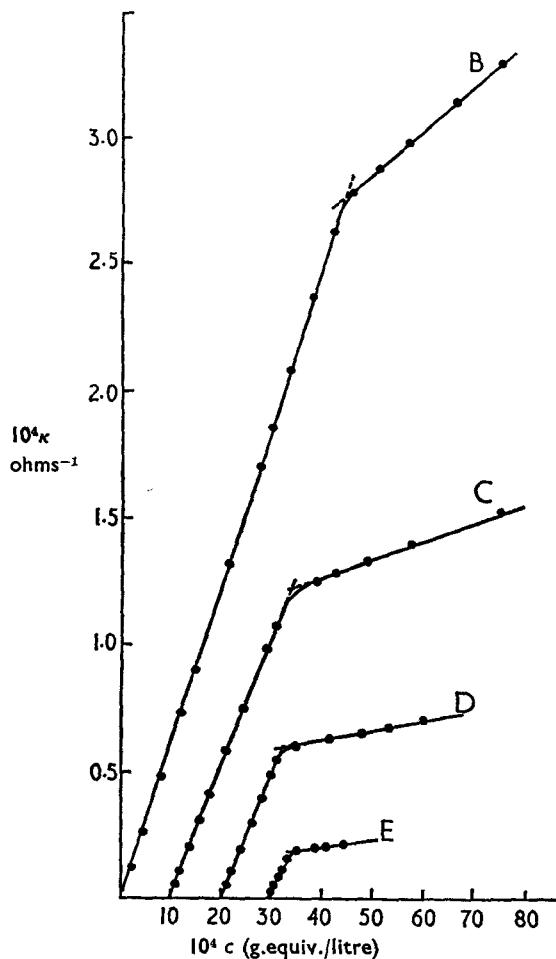


FIG. 2. Variation of specific conductivity of alkyl ammonium dodecyl sulphates with concentration (25°). For key, see Fig. 1. The origin has been shifted a scale division dexterwise for the concentration values of the butyl, hexyl and octyl trimethylammonium salts, to ensure greater clarity.

Formation of micelles in dilute aqueous solutions of these salts is demonstrated by the sharp breaks in these graphs (Scott and Tartar, 1943; Evans, 1956). The critical micelle concentration is seen to decrease markedly with increase in length of the cation chain.

CMC OF DOUBLE LONG-CHAIN ELECTROLYTES

Specific conductivity—concentration graphs were also plotted. The results presented in Fig. 2 are typical of those obtained for all the systems studied.

Below the CMC the slopes (S_1) decrease with increasing cation chain length and decreasing cation mobility. Above the critical range, the gegenion-micelle interaction is increasing with increase in cation chain length (Evans, 1956) and the slopes (S_2) decrease even more sharply.

Critical micelle concentrations were determined from the intersection of the two linear portions of the specific conductivity graphs.

The results are summarised in Table I. The limits of error were ± 0.02 mM for all CMC values.

TABLE I
CRITICAL MICELLE CONCENTRATION, OF ALKYL AMMONIUM DODECYL SULPHATES (25°)

	CMC (mM)	$-\frac{\Delta G^\circ}{RT}$
Tetramethylammonium	5.50	16.8
Ethyl trimethylammonium	4.30	17.5
n-Butyl trimethylammonium	2.38	18.9
n-Hexyl trimethylammonium	1.25	20.5
n-Octyl trimethylammonium	0.40	23.0
n-Decyl trimethylammonium	0.21	24.3
Ammonium	6.16	16.6
Methylamine	5.70	17.0
Ethylamine	5.00	17.3
n-Butylamine	2.92	18.5
n-Hexylamine	1.12	20.9
n-Octylamine	0.28	23.7
n-Decylamine	sparingly soluble	

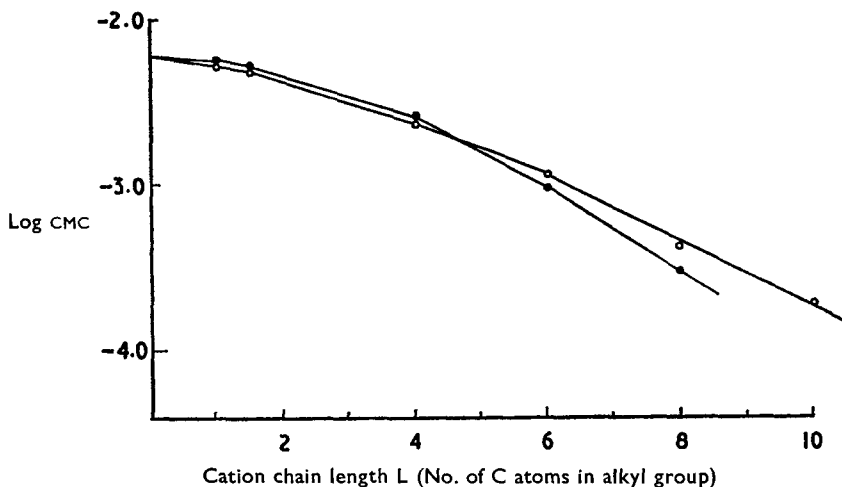


FIG. 3. Effect of cation chain length on critical micelle concentrations (25°).

The CMCs decrease markedly with increasing cation chain length. The hexyl- and octylamine salts have lower CMC values than the corresponding quaternary trimethyl ammonium salts. Log CMC values are plotted against chain length (L) in Fig. 3.

Micelle Formation and Structure

Phillips (1955) has proposed the following idealised equilibrium for micelle formation with long-chain electrolytes,



where X^- represents the dodecyl sulphate anion,

R^+ represents the smaller gegenion,

$[X_N R_{N-p}]^{p-}$ represents the micelle,

N represents the number of anions in the micelle,

$(N-p)$ represents the number of the smaller cations in the micelle,

p represents the net effective charge on the micelle.

The size and molecular weight of the micelle will be determined by the value of $(2N-p)$; while the ratio $(N-p)/N$ represents the fraction of gegenions bound on the surface or within the micelle or both. Phillips (1955), Stigter (1954) and Hoyer (1957) have shown that CMC values are hardly affected by micelle size but depend on the p/N ratio. In the absence of added electrolyte, CMC values are mainly determined by $-\Delta G^\circ$, the standard free energy decrease associated with the formation of one g. mole. of micelle from its constituent ions. Phillips (1955) has proposed the relation,

$$\log_{10} \text{CMC} = \frac{-\Delta G^\circ}{2.303 (2-p/N)RT} \quad \dots \quad (2)$$

Counterion Binding

Integral values of p and $(N-p)/N$ for the systems studied were estimated from the conductivity data, using Evans' (1956) equation.

$$\frac{p^2}{N^{4/3}} (1,000 S_1 - \lambda_{R^+}) + \frac{p\lambda_{R^+}}{N} = 1,000 S_2 \quad \dots \quad (3)$$

where S_1 is the gradient of the specific conductivity-concentration graph below the CMC, S_2 is the gradient above the CMC, λ_{R^+} is the cation mobility.

Since p and $(N-p)/N$ values are practically unaffected by large changes in N (Evans, 1956), e.g. from 40 to 120, Phillips' value of $N = 80$ for sodium dodecyl sulphate was used in all the calculations.

The values calculated for the alkyl ammonium dodecyl sulphate micelles studied are summarised in Table II: data for the ammonium salt are also included.

The micelle charge (p/N) decreases from 0.23 for the ammonium salt to 0.05 for the higher alkyl ammonium dodecyl sulphates; that is, the degree of binding $(N-p)/N$ of the organic gegenions increases from 77 to 95 per cent.

Energetics of Micelle Formation

The increase in $(N-p)/N$ ratios is insufficient to explain the marked reduction in CMC values; the latter effect must therefore be mainly attributed to a significant increase in the free energy change (ΔG°) of micelle formation.

CMC OF DOUBLE LONG-CHAIN ELECTROLYTES

The standard free energy decrease (ΔG°) of micelle formation in the systems studied was estimated from the CMC results using equation 2 (Phillips, 1955),

$$-\Delta G^\circ = 2.303 (2-p/N)RT \log_{10} \text{ CMC calories per g. mole.}$$

where CMC values are expressed in *mole fractions*.

The results are summarised in Table I.

The free energy change increases progressively with length of the organic cation. The estimated ($-\Delta G^\circ$) values for the alkyl ammonium salts are from 1 to $7RT$ calories per g. mole. greater than the value for the ammonium dodecyl sulphate and it is evident that organic cation—organic anion interactions must contribute to the overall free energy of micelle formation.

TABLE II

DEGREE OF CATION BINDING IN ALKYL AMMONIUM DODECYL SULPHATES ESTIMATED FROM SPECIFIC CONDUCTIVITY DATA AT 25° (CALCULATED FOR N = 80)

Salt	λ_{R+}	1,000 S_1	1,000 S_2	p	$\frac{(N-p)}{N}$
Ammonium	73.4	91.2	30.0	17.5	0.77
Tetramethylammonium	44.9	63.8	19.0	14.1	0.82
Ethyl trimethylammonium	40.5	57.0	17.0	13.3	0.83
n-Butyl trimethylammonium	33.3	50.0	9.2	9.9	0.88
n-Hexyl trimethylammonium	29.2	47.0	4.2	6.1	0.92
n-Octyl trimethylammonium	26.2	44.5	3.2	5.1	0.94
n-Decyl trimethylammonium	24.0	43.0	2.5	4.9	0.94
Methylamine	57.8	75.4	16.0	12.1	0.85
Ethylamine	44.9	65.0	15.0	11.3	0.86
n-Butylamine	35.5	55.5	9.5	9.6	0.88
n-Hexylamine	32.5	53.0	4.4	5.9	0.93
n-Octylamine	30.5	50.0	2.6	4.8	0.94

This could take place either as a result of changes in electrostatic effects at the anion heads or by enhancement of van der Waals' interactions within the micelle.

The electrostatic repulsion between adjacent anion heads is indeed not very marked, even in the case of sodium dodecyl sulphate micelles and reduction of this repulsion by ion-pair formation with organic cations would lead at most to an increase in ($-\Delta G^\circ$) of 0.6 RT calories per g. mole (Phillips, 1955). However, the large increase in free energy change observed could be explained by a closer packing of the organic sections of the long-chain anions inside the micelle, which might occur as a result of the reduction of repulsive forces at the anion heads. Such closer packing would in turn lead to an increase both in ($-\Delta H$), the heat of interaction of the hydrocarbon chains and in ($-T\Delta S$), the entropy of micelle formation (Pethica, 1958).

On the other hand, Goddard and others (1953) have suggested that in aqueous solutions of double long-chain electrolytes, the organic cations also enter the micelles to form a palisade structure with the organic anions. This penetration would lead to van der Waals' interaction between the organic sections of cation and anion, similar to that observed on addition of long-chain alcohols to aqueous solutions of ordinary colloidal electro-

lytes. Such interaction would increase with increasing cation chain length and would enhance the usual interaction between the organic sections of the anions (Ooshika, 1954).

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