

SURFACE-ACTIVE BETAINES: N-ALKYL-*NN*-DIMETHYLGLYCINES AND THEIR CRITICAL MICELLE CONCENTRATIONS

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A series of surface-active *N*-alkyl *NN*-dimethyl glycines (alkyl betaines) and their hydrochlorides have been prepared. Some physical properties of these compounds have been investigated. The critical micelle concentrations of the betaines have been determined by a surface tension, a refractive index, a dye solubilisation and an iodine method. An explanation of the differences in critical micelle concentrations between these amphoteric surfactants and corresponding anionic and cationic surfactants is proposed.

AMPHOTERIC surfactants have not been studied so intensively as anionic, cationic or even non-ionic surfactants. Some amphoteric surfactants have been patented and a few marketed, e.g., Miranols (Mannheimer 1950), Ambiterics (Glovers Chemicals Ltd.) and Deriphats (General Mills). Incomplete details of the physical and solubilising properties have been obtained. Fundamental studies have not been possible because series of pure compounds of known chain length have not been available.

A series of pure non-ionic surfactants has recently been prepared in our laboratories (Mulley, 1960). We now report the preparation of a series of surface-active betaines which were required for detailed physical investigations.

Preparation of the Compounds

The alkyl betaines (*N*-alkyl *NN*-dimethylglycines) were prepared by treating a dimethylalkylamine with sodium chloroacetate (e.g., see Balle and Eisfeld, 1935; Tanaka, 1943). They were isolated from the sodium chloroacetate reaction mixture as their hydrochlorides (see Table II), which were then converted to the corresponding free bases by passing them through a suitable ion-exchange column. The eluate was evaporated to dryness and the residue recrystallised from ethanol:ether (1:20). The alkyl betaines (see Table III) were obtained as white amorphous solids.

Critical Micelle Concentrations

The critical micelle concentrations of the series of surfactants were determined by four independent methods; these were a surface tension, a refractive index, a dye solubilisation and an iodine method. The dye used was bromophenol blue and the iodine method was adapted from that used by Ross and Olivier (1959) for non-ionic surfactants.

EXPERIMENTAL

Synthesis

All melting points are uncorrected.

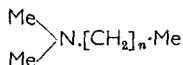
The alkyl bromides used were Eastman Kodak materials with a purity of 99 per cent.

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The primary alkylamines used were 99 per cent pure.

Alkyldimethylamines. The tertiary amines were obtained by reaction of alkyl bromides with dimethylamine or by reductive methylation of a primary alkylamine with formic acid and formaldehyde (Kirby, 1941). The bases were purified by distillation. The quaternary iodide of each tertiary base was prepared by reaction of methyl iodide with the base dissolved in acetone. The details for each tertiary amine and its quaternary iodide are given in Table I.

TABLE I
NN-DIMETHYLALKYLAMINES AND THEIR QUATERNARY IODIDES



Alkyl chain		NN-Dimethylalkylamines			NNN-Trimethyl N-alkyl ammonium iodides						
		Distillation			Equiv. weight		m.p.°C	Microanalytical data			
	<i>n</i>	Temp°	Pressure mm. Hg	Yield per cent	Calc.	Found		Carbon		Hydrogen	
							Calc.	Found	Calc.	Found	
Hexyl	5	143-4 ^a	760	77	271	272	169 ^h				
Octyl	7	79-80 ^b	16	66	299	301	142 ^h				
Decyl	9	62 ^c	0.6	72	327	326	201-2 ⁱ				
Undecyl	10	80	1.0	84	341	340	221-2	49.3	50.2	9.5	9.5
Dodecyl	11	96 ^d	1.0	88	355	356	237-7.5	50.7	50.9	9.6	9.4
Tetradecyl	13	108-9 ^e	0.5	72	383	382	238	53.3	53.6	10.0	9.7
Hexadecyl	15	142 ^f	1.0	86	411	411	248-9 ^j				

a-f. Gautier, Renault and Rabiant (1957) reported:

a. 145° at 760 mm. Hg

b. 189-190° at 760 mm. Hg

c. 106° at 9 mm. Hg

d. 133° at 8 mm. Hg

e. 103-5° at 0.5 mm. Hg

f. 159-162° at 2.5 mm. Hg

g. Kato, Morikawa and Suzuki (1952) reported 166°

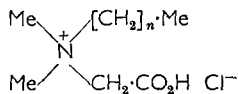
h. Kato and others (1952) reported 141°

i. Blomquist, Hallam and Josey (1959) reported 199-200°

j. Macovski (1936) reported 247°

N-Alkyl NN-dimethylglycine hydrochlorides. The alkyl-dimethylamine (1 equiv.) was refluxed in an ethanol:water mixture (1:1) with sodium chloroacetate (1 equiv.) until the system became monophasic.

TABLE II
N-ALKYL NN-DIMETHYLGLYCINE HYDROCHLORIDES



Alkyl chain		Yield per cent	Equiv. weight		m.p.°C.	Micro-analytical data					
			Calc.	Found		Carbon		Hydrogen		Nitrogen	
	<i>n</i>				Calc.	Found	Calc.	Found	Calc.	Found	
Hexyl	5	51	224	224	156-7	53.7	54.2	9.9	9.9	6.3	6.2
Octyl	7	59	252	252	170-1	57.2	57.8	10.4	10.2	5.6	5.6
Decyl	9	71	280	280	172-3	60.1	59.9	10.8	10.7	5.0	4.8
Undecyl	10	74	294	294	170-1	61.3	61.3	11.0	11.0		
Dodecyl	11	54	308	306	165-6	62.4	61.8	11.1	10.8	4.5	4.4
Tetradecyl	13	53	336	336	163-4	64.4	64.2	11.4	11.3	4.2	4.0
Hexadecyl	15	68	364	364	<i>a</i>	66.0	66.0	11.6	11.7	3.9	3.9

a. Melting point obscured by frothing of substance as it softened from 150° upwards.

The cooled reaction mixture was treated with excess concentrated hydrochloric acid. The hydrochloride crystallised and was filtered off, dried and recrystallised from ethanol:ether (2:1). In the case of the octyl and hexyl compounds, the acidified reaction mixture was evaporated to dryness and the hydrochloride was recrystallised after extracting the residue with hot ethanol. The details of these compounds are given in Table II.

N-Alkyl NN-dimethylglycines (Alkyl betaines). The *N*-alkyl *NN*-dimethylglycine hydrochloride was dissolved in water and passed through an ion-exchange column of IRA-400 (OH). The eluate was evaporated to dryness. The final drying was carried out using xylene to form an azeotropic mixture with the water. The residue was recrystallised from ethanol:ether (1:20). The undecyl, decyl, octyl and hexyl compounds were dried by heating at their melting points in a vacuum. The details of these compounds are given in Table III.

TABLE III
N-ALKYL NN-DIMETHYLGLYCINES



Alkyl chain	<i>n</i>	Yield per cent	Equiv. weight		m.p.°C.	Micro-analytical data					
			Calc.	Found		Carbon		Hydrogen		Nitrogen	
						Calc.	Found	Calc.	Found	Calc.	Found
Hexyl ^a	5	89	187	188	138-40	64.1	62.8	11.3	11.1	7.5	7.4
Octyl ^a	7	93	215	216	155-6	66.9	67.2	11.7	11.8	6.5	6.3
Decyl ^a	9	100	243	244	162	69.1	68.4	12.0	12.2	5.7	5.7
Undecyl ^a	10	97	257	256	165	70.0	70.6	12.1	12.2	5.4	5.6
Dodecyl ^b	11	71	289	278	183	66.4	66.4	12.2	12.0	4.8	4.7
Tetradecyl ^b	13	92	317	300	198-9	68.1	68.3	12.4	12.3	4.4	4.5
Hexadecyl ^b	15	66	345	331	200-1 ^c	69.5	69.1	12.5	12.5	4.1 ^d	4.2 ^d

a. Anhydrous alkyl betaine, as formula (I) above.

b. Hydrated alkyl betaine as formula (II) above.

c. Swain, Braun and Naegele (1953) reported 205-6°.

d. Swain and others (1953) reported nitrogen 3.97 per cent (calc. figure for anhydrous compound given as 4.29 per cent).

Equivalent weights of the bases were determined by titration with perchloric acid in glacial acetic acid using Oracet Blue as indicator. Mercuric acetate was added to the solution for the determinations on the hydrochlorides.

Critical Micelle Concentration Determinations

Materials. Iodine (Analar). Bromophenol Blue (Reagent Quality).

Apparatus. A Cambridge Du Nouy Tensiometer was used in the surface tension experiments.

The Hilger-Rayleigh Interferometer M.154 fitted with constant temperature water jacket was used for the refractive index measurements. A tungsten lamp and 1 cm. (or 10 cm. cells as indicated) were used.

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A Hilger and Watts Uvispek Spectrophotometer was used to measure optical densities. 1 cm. silica cuvettes with water as reference solvent were used unless otherwise stated.

Surface tension method. The ring detachment method was used to determine the surface tension of the solutions and the Harkins and Jordan (1930) corrections were applied to the results. Measurements were made at $23 \pm 1^\circ$. The results were plotted as surface tension against log surfactant concentration (e.g. see Fig. 1).

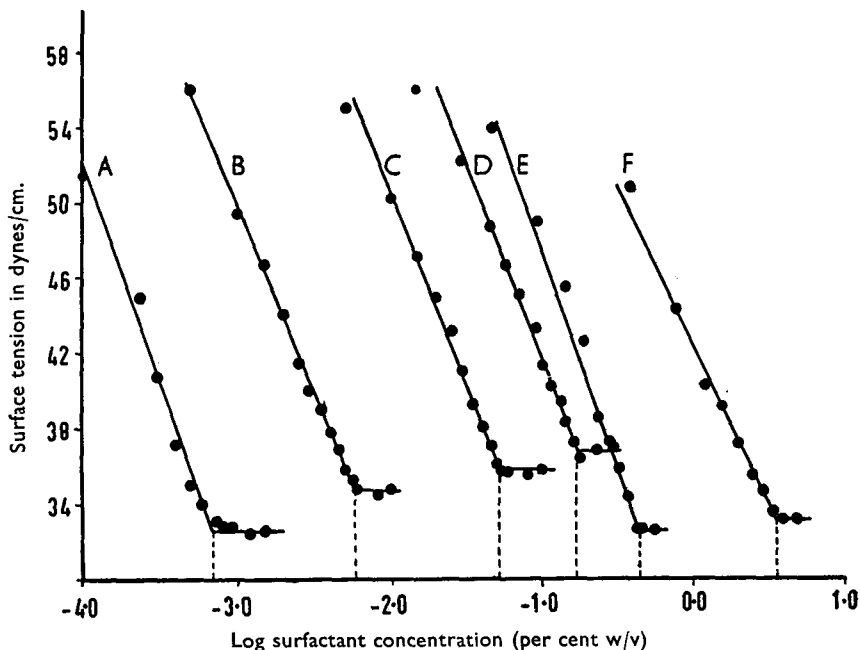


FIG. 1. Graphs of surface tension against log surfactant concentration used to determine the CMC of some alkyl betaines. A, Hexadecyl betaine. B, Tetradecyl betaine. C, Dodecyl betaine. D, Undecyl betaine. E, Decyl betaine. F, Octyl betaine.

*Refractive index method.** Measurements were made at $20.2 \pm 0.1^\circ$. The first reading was made with the starting concentration in the two cells, and each solution of betaine was then used as reference solution for the next higher concentration of betaine; the differential refractive indices were summated. The results were plotted as changes in refractive index against molar concentration; the single breaks in the curves were taken as the critical micellar concentrations (CMC) (see Fig. 2).

Bromophenol Blue solubilisation method. A series of surfactant solutions in the CMC region were prepared in 1:250,000 aqueous Bromophenol Blue. The extinction of each solution was determined at $605 \text{ m}\mu$. Measurements were made at $23 \pm 1^\circ$. The results were plotted as extinction against surfactant concentration (e.g., see Fig. 3). The CMC values

* We thank N. Choulis for carrying out these measurements.

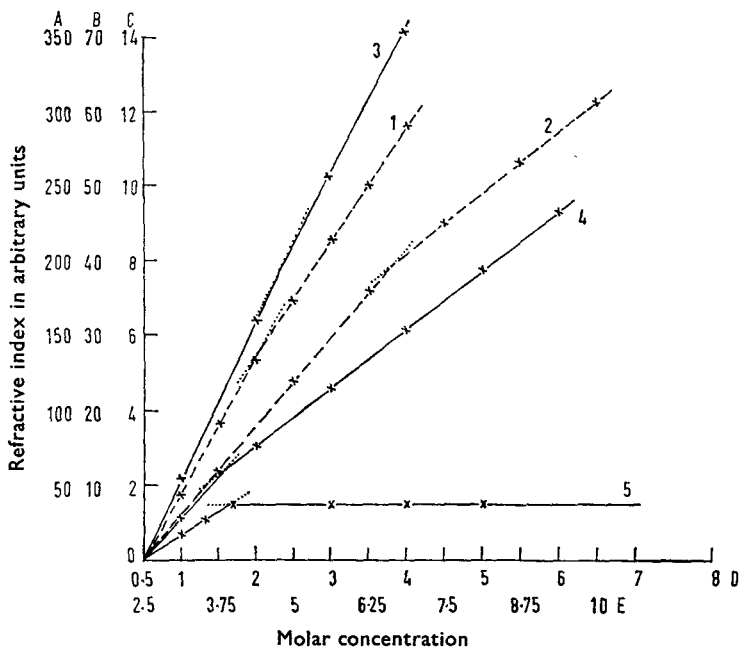


FIG. 2. Graphs of changes in refractive index against molar concentration in some betaines of structure $\text{Me} \cdot [\text{CH}_2]_n \cdot \text{N}^+ \text{Me}_2 \cdot \text{CH}_2 \text{COO}^-$ using a 1 cm. (—) or 10 cm. (---) cell. 1, decyl A/D scale (10^{-2}M); 2, undecyl B/E scale (10^{-3}M); 3, dodecyl A/D scale (10^{-3}M); 4, tetradecyl B/D scale (10^{-4}M); 5, hexadecyl C/D scale (10^{-5}M).

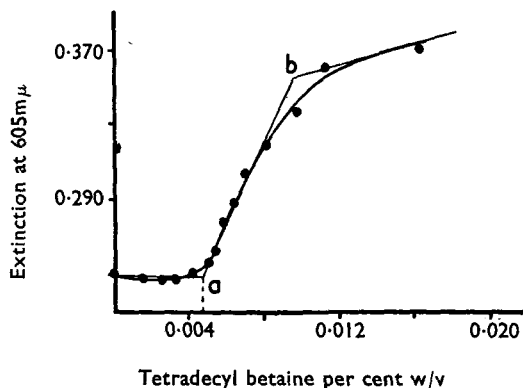


FIG. 3. Graph of optical density at $605\text{m}\mu$ against tetradecyl betaine concentration per cent w/v plotted in determining the CMC by the solubilisation of bromophenol blue method. a, $\text{CMC} = 0.0048$ per cent w/v. b, Stable micelle point (Colichman 1951) where all dye is in the solubilised state.

of the decyl and octyl betaine were determined by titration of a solution of the surfactant, at a concentration above its CMC in aqueous Bromophenol Blue (1:250,000), with dye solution (1:250,000). The CMC was

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calculated from the volume of the solution when the colour changed from blue to violet.

Iodine method. A solution of surfactant about 2–4 times the concentration of the CMC was prepared in aqueous iodine (15 mg./litre approx.). The solution was stored in the dark at $23 \pm 1^\circ$ for a week. It was diluted with water to give a series of solutions in the CMC region. The extinction of each solution was determined at $365 m\mu$. The results were plotted as extinction against surfactant concentration (e.g. see Fig. 4).

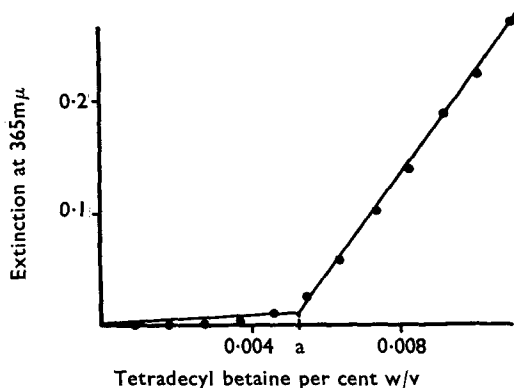


FIG. 4. Graph of observed optical density at $365 m\mu$ against tetradecyl betaine concentration plotted to determine the CMC by the iodine method. $a = \text{CMC} = 0.0054$ per cent.

RESULTS AND DISCUSSION

The *N*-alkyl *NN*-dimethylglycines with an alkyl chain greater than undecyl were obtained with a molecule of water of crystallisation. Betaines with an alkyl chain from hexyl to undecyl were obtained anhydrous provided they were subjected to severe drying conditions. The lower members of the series (hexyl and octyl betaines) were very deliquescent but this became less marked as the alkyl chain length was increased. The anhydrous compounds have sharp melting-points and end-points on titration as bases in non-aqueous media, but the hydrated compounds have indefinite values for these properties. The alkyl betaine hydrochlorides are white crystalline solids with sharp melting-points.

High purity of the present series of *N*-alkyl *NN*-dimethylglycines was indicated from the microanalytical data and the linear graphical relationship of alkyl chain length to log molar CMC. Microanalytical and physical data on the *N*-alkyl *NN*-dimethylglycine hydrochlorides indicated that these intermediates were pure.

Attempts to prepare the betaines from their hydrochlorides using inorganic bases gave products with appreciable inorganic impurity.

In the region of the CMC sharp changes occur in many of the properties of a surfactant solution. In the present work, methods for CMC determination other than those used successfully were tried. The zwitterion nature of the betaines was thought responsible for the unsuccessful

application of a conductivity method and complex polyphasic systems were obtained when attempting an octanol solubilisation method.

The results of the surface tension method for each alkyl betaine gave a graph on which the CMC was interpreted from the intercept of two straight lines (see Fig. 1). Below this value, the surface tension decreased linearly with increase in log surfactant concentration. Above it, the surface tension was almost constant. The results of the refractive index method gave graphs on which the CMC values were interpreted from the intercept of two straight lines (Fig. 2).

The results from the Bromophenol Blue solubilisation method gave a sigmoidal curve for each compound (e.g. see Fig. 3). This kind of curve has been obtained previously using the dye solubilisation methods (Mukerjee and Mysels, 1955; Colichman, 1951; Zutrauen, 1956). The CMC is usually interpreted from the lower surfactant concentration inflection (see Fig. 3).

The iodine method was adapted from that used by Ross and Olivier (1959) for determining the CMC of non-ionic surfactants. The results for each determination gave two straight lines which intersected at the CMC (see Fig. 4). Extinction measurements at the absorption peak (365 $m\mu$) on fresh aqueous surfactant with iodine systems were not reproducible hence, before use, the solutions were stored for a week in the dark. The variation in intensity at the absorption peak was attributed to chemical interactions.

TABLE IV
RESULTS OF THE CRITICAL MICELLE CONCENTRATION DETERMINATION ON A SERIES OF
N-ALKYL *NN*-DIMETHYLGLYCINES



Alkyl chain		Critical micelle concentration in moles/litre			
	<i>n</i>	Surface tension method	Dye solubilisation method	Iodine method	Refractive index method
Hexyl ^a	5	—	—	—	—
Octyl ^a	7	1.7×10^{-1}	1.7×10^{-1}	—	—
Decyl ^a	9	1.8×10^{-2}	1.8×10^{-2}	2.0×10^{-2}	2.1×10^{-2}
Undecyl ^a	10	6.6×10^{-3}	6.0×10^{-3}	6.4×10^{-3}	6.4×10^{-3}
Dodecyl ^b	11	1.8×10^{-3}	1.6×10^{-3}	1.8×10^{-3}	2.1×10^{-3}
Tetradecyl ^b	13	1.8×10^{-4}	1.5×10^{-4}	1.5×10^{-4}	1.7×10^{-4}
Hexadecyl ^b	15	2.0×10^{-5}	1.8×10^{-5}	1.8×10^{-5}	1.6×10^{-5}

a. Anhydrous alkyl betaine as formula (I) above.

b. Hydrated alkyl betaine as formula (II) above.

The critical micelle concentrations in moles/litre by the surface tension method of some compounds closely related to the alkyl betaines were found to be: dodecyl betaine HCl 1.98×10^{-2} ; tetradecyl betaine HCl 1.96×10^{-4} ; *NNN*-trimethyl *N*-dodecyl ammonium iodide 5.21×10^{-2} .

The four methods of determining the CMC of the alkyl betaines yielded similar results (see Table IV). This general agreement involving the binary systems (surfactant and water) using the surface tension and the refractive index method and those from the two types of ternary systems,

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indicated that the addition of the stated amounts of either Bromophenol Blue or iodine did not appreciably affect the CMC.

The alkyl betaine surfactants are reported to be cationic (Moore, 1960) but behave differently from the quaternary ammonium surfactants. Moore (1960) suggested that the alkyl betaine surfactants should be classified as 'Intronium Surfactants' because they were not amphoteric. However, all quaternary amphoteric surfactants will fall into this class and it is probably less confusing if the amphoteric surfactants are divided under two headings i.e., the quaternary and the non-quaternary.

In the present work, the predominantly cationic nature of the alkyl betaines was indicated by the successful application of Bromophenol Blue, an anionic dye, for the CMC determinations. Attempted use of a cationic dye (Pinacyanol bromide) was unsuccessful. Corrin and Harkins (1947) found that a dye of opposite charge to the surfactant was essential in determining the CMC by a dye solubilisation method. The successful application of an iodine method indicated that the micelles of the alkyl betaines were not wholly negative or positive, since Ross and Olivier (1959) stated that iodine precipitated with positive micelles and did not interact with negative ones.

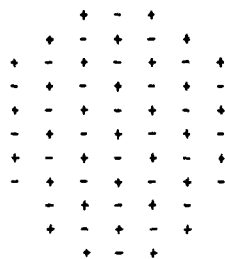


FIG. 5. Proposed arrangement of positive and negative charges on the surface of a micelle of an alkyl betaine

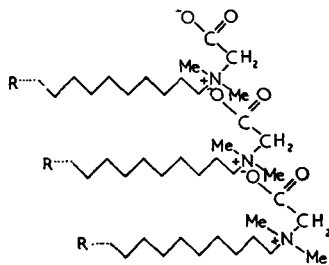
The surface of the amphoteric micelle is envisaged as covered with a net-work of positive and negative charges (see Fig. 5). The interior of the micelle in aqueous solution is assumed to be paraffinic in nature. In the present investigation, the alkyl betaines were dissolved in water and no foreign electrolytes were added. Thus, the balance between the charges on the micellar surface was dependent solely on the amphoteric character of the betaine molecule. The CMC depends on the lipophilic : hydrophilic balance in a surfactant molecule. Klevens (1953) proposed expression (I) for calculation of the CMC :

$$\log \text{CMC} = A - BN \quad \dots \quad \dots \quad \dots \quad (1)$$

in which A is a constant depending on the homologous series of the surfactant, B is a constant which for most surfactants is equal to $\log 2$ and N is the alkyl chain length. In anionic and cationic surfactants, A is the only function in (1) which is said to be dependent on the molecular structure and the term BN should be constant for all such surfactants with a straight

alkyl chain. Provided A is not the same for two series of such surfactants then the CMC values of corresponding members will be different but the change in CMC per carbon atom in the alkyl chain will be the same for both series.

The CMC values for a series of amphoteric surfactants have not been reported hitherto but these surfactants were said to have lower CMC values than corresponding anionic and cationic surfactants (Schmitz and Harris, 1958). This difference between such surfactants has been attributed to the desaturation of charges between the polar heads of amphoteric molecules, illustrated in the diagram III, leading to increased molecular



III

aggregation (McCutcheon, 1954). In the present series of alkyl betaines, not only was the position of the CMC different from corresponding anionic and cationic surfactants (related to A in expression 1), but so was the change in CMC with alkyl chain length (related to B in expression 1). The value for B in the series of alkyl betaines was found to be log 3 which indicated that changes in alkyl chain length had a greater effect on the CMC of these compounds than anionic or cationic surfactants. The polar heads of anionic or cationic surfactants repel one another but those of amphoteric agents have mutual attraction. Increase in alkyl chain length therefore has a greater effect on molecular aggregation when there is attraction rather than repulsion at the polar heads. Thus, the desaturation of charges (see III) is probably responsible for the lower CMC values and the greater effect of alkyl chain length on the CMC of the betaines than on corresponding anionic and cationic surfactants.

The alkyl betaine hydrochlorides showed similar CMC values and changes in CMC with alkyl chain length (see Table IV) to the free betaines. Thus the salts may be regarded as completely hydrolysed in aqueous solution.

The envisaged surface of the alkyl betaine micelle in aqueous solution (see Fig. 5) will provide a polarising surface for susceptible molecules.

Acknowledgement. R.J.W. gratefully acknowledges a Research Studentship from D.S.I.R.

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