SD&C Technical

Physical Chemical Properties of Solutions of Bis-Quaternary Ammonium Bromides

H.C. PARREIRA[1], Johnson & Johnson Research, New Brunswick, NJ,
E.R. LUKENBACH, and **M.K.O. LINDEMANN,** Johnson & Johnson Baby Products Company, Raritan, NJ

ABSTRACT

The physical chemical properties of a series of bis-alkyldimethyldi-ammonium polyoxyethylene bromides were studied by measuring the critical micelle concentrations as function of their molecular structure. The conductivity vs. concentration plots revealed the existence of two distinct discontinuities which were labeled CMC1 and CMC2. The CMC1 was always lower than the CMC2. The conventional surface tension vs. log concentration curve showed the classical sharp break which coincided with either the CMC1 or the CMC2, but failed to reveal the presence of both critical micelle concentrations in the same experiment. The existence of two CMC2 was attributed to the presence of the two charges localized in separated atoms. The CMC1 and CMC2 appear to follow an expression of the type CMC = A - Bn, where A and B are constants and n the number of carbon atoms present in the hydrocarbon long chain attached to the quaternary ammonium nitrogen. The CMCs appear to increase with the increasing number of oxyethylene residues up to a certain length of the polyoxyethylene chain. For most compounds there was a substantial drop in surface tension with the increasing concentration of the salt. However, some compounds containing only one oxyethylene residue showed practically no surface tension dependence on concentration although the critical micelle concentrations were apparent in the conductivity vs. concentration curve. The energy to transfer one methylene group from the aqueous to the micellar phase was found to vary from -0.57 kT to -0.84 kT. The alkylene oxylated bis-quaternary bromides studied appear to have unusual physical chemical properties.

INTRODUCTION

Surface active agents possessing difunctional groups have been known for some time (1) yet only recently has the physical chemistry of their aqueous solutions been investigated systematically. Most of the work, however, deals with dicarboxylic acid derivatives (2-5) although the properties of a series of alkyl di-ammonium chlorides have been reported recently (6). The increasing interest in difunctional surface active agents results from their unusual physical chemical properties.

There is a substantial number of publications on singly charged quaternary ammonium salts containing polyoxyethylene chains. The quaternary chlorides of alkylene diamines recently investigated by Deinega and collaborators (6) were difunctional salts of general formulae:

$[C_nH_{2n}+1\ O_2CCH_2NMe_2\ (CH_2)_mN\ Me_2CH_2CO_2C_nH_{2n+1}]^{2+}, 2\ Cl^-$ A

where (n = 6, 9, 10, 12, 14, 16) and (m = 2, 6), and

$[H(CH_2)_{12}\ NMe_2(CH_2)_m\ N\ Me_2\ (CH_2)_{12}\ H]^{2+}, 2\ Cl^-$ B

(m = 2, 4, 6, 10, 20)

These difunctional quaternary ammonium salts contain an alkylene chain bridging the two nitrogen charges.

The present report deals with the study of difunctional quaternary ammonium bromides that possess a polyoxyethylene chain bridging the two quaternary ammonium charges and a long hydrocarbon chain attached to each nitrogen atom. They have the general formula:

$[C_nH_{2n+1}\ NMe_2\text{-}C_2H_4(OC_2H_4)_m\ NMe_2C_nH_{2n+1}]^{2+}, 2Br^-$ C

(m = 1, 3, 7) and (n = 14, 16, 18, 22).

These diquaternary ammonium bromides will be denoted by Qmn and the oxyethylene units will be represented by OE. There is substantial evidence in the current literature pointing to the fact that an increase in the OE chain length decreases the CMC of singly charged surfactants (7,8). However, it has been shown recently that the effect of varying the polyoxyethylene chain in monofunctional surfactants depends not only on the length of the OE chain alone but also on its position in the molecule itself (9). The insertion of a second charged group at the end of the polyoxyethylene chain should bring about an increase in the solubility of the compound. Furthermore, an increase in the hydrocarbon chain length should render the surfactant more lipophilic, whereas an increase in the polyoxyethylene chain length would cause an increase in the CMCs of the bis-quaternary ammonium bromides.

Very little has been reported on difunctional salts. The present authors are unaware of systematic studies on oxylated bis-quaternary bromides. The presence of a polyoxyethylene chain bridging the two charges confers unusual properties to this class of surface active agents. In this report the effect of the molecular structure (obtained by changing m and n) on the critical micelle concentration of alkylenoxylated bis-quaternary compounds was studied by measuring both the conductivity and surface tension of their aqueous solutions in the absence of an indifferent electrolyte.

EXPERIMENTAL

Conditions

All experiments were carried out in a laboratory kept at constant temperature of 23 ± 0.5 C and constant humidity ca. 40%.

Materials

All reagents were A.R. grade. The bis-quaternary am-

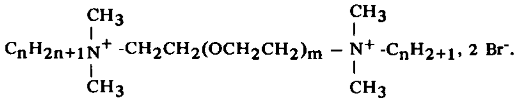
---

[1] Author to whom inquiries should be addressed.

monium bromides were prepared by reacting the proper polyethylene glycol with phosphorous tribromide. The resulting dibromide was reacted with the appropriate tertiary alkyldimethylamine to yield the bis-quaternary ammonium bromide. These steps are represented by the reaction-

$$3HO\text{-}CH_2CH_2(OCH_2CH_2)_m\text{-}OH + 2PBr_3 \rightarrow 3Br\text{-}CH_2CH_2(OCH_2CH_2)_m\text{-}Br + 2\ H_3PO_3 \text{ and}$$

$$Br\text{-}CH_2CH_2(OCH_2CH_2)_m\text{-}Br + 2C_nH_{2n+1}N(CH_3)_2 \rightarrow$$



$$C_nH_{2n+1}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}\text{-}CH_2CH_2(OCH_2CH_2)_m - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}\text{-}C_nH_{2+1}, 2\ Br^-.$$

Detailed synthesis procedures for compounds Q118 and Q-718 were:

a) N,N′-dioctadecyl-N,N,N′,N′-tetramethyl-1,5-(3-oxapentylene) diammonium dibromide (Q118). 104.2 Grams (0.35 moles) of octadecyldimethylamine was added to 39.2 g (0.175 moles) of $\beta - \beta'$-dibromoethylether dissolved in 300 ml of methanol and refluxed for 96 hr. The progress of the reaction was followed by argentometric titration. After the reaction appeared to have reached completion, one-half of the methanol volume was evaporated, followed by the addition of excess acetone. A white precipitate was isolated by filtration after the mixture was left standing at 4 C for 18 hr. The raw precipitate was crystallized a few times from the appropriate methanol/acetone mixture.

b) N,N′-dioctadecyl-N,N,N′,N′-tetramethyl-1,23-(3,6,9,-12,15,18,21)-heptaoxatricosanylene diammonium dibromide (Q-718). The synthesis of this and other bis-quaternary ammonium compounds with more than four oxyethylene groups was similar to the aforementioned procedure but complicated by the unavailability of the corresponding polyethylene glycols or dibromides. For this reason a commercially available polyethylene glycol, Carbowax 400® (The Union Carbide Co.), was brominated and the homologous dibromides separated by high vacuum distillation employing a falling film molecular distillation apparatus (Kontes Glass Co.). Gas chromatographic analysis using flame ionization detection (Varian Model 2100) was employed to monitor the progress of separation. In a typical case the dibromide mixture, $Br(CH_2CH_2O)_m CH_2CH_2Br$, obtained from Carbowax 400®, had the composition presented in Table I.

TABLE I

Composition of Carbowax 400[a]

m	Composition (%)
1	4.43
2	4.46
3	7.10
4	10.64
5	14.41
6	18.62
7	17.96
8	13.08
9	6.87
10	2.22

[a] This composition does not necessarily reflect the molecular weight distribution of the starting material as the isolation procedure tends to be more efficient for the dibromides of lower molecular weight.

To obtain the 1,23-dibromo-3,6,9,12,15,18,21-heptaoxatricosanylene needed for the synthesis of the title compound, the crude dibromide mixture was subjected to multiple distillations at various temperatures. The material considered acceptable for the synthesis of the bis-quaternary ammonium compound was analyzed to contain 97.91% 1,23-dibromo-polyethylene glycol, 1.20%, 1,20-dibromopolyethylene glycol, 0.87% 1,26-dibromopolyethylene glycol. Other bromides were isolated in a similar manner. A detailed description of the synthesis can be found elsewhere (10).

Elemental analyses (carried out by Robertson Laboratories, Florham Park, NJ) revealed that all compounds were pure. The melting points were measured with the help of the Electrothermal melting point apparatus (Electrothermal Engineering, London, England). The following were the results.

Q112: Found; C, 57.95%, H, 10.97%, N, 4.14%, Br, 24.19%. Theoretical; C, 58.36%, H, 10.64%, N, 4.26%, Br, 24.32%.m.p.,255 C.

Q114: Found; C, 60.73%, H, 10.85%, N, 3.72%, Br, 22.36%. Theoretical; C, 60.50%, H, 10.92%, N, 3.92%, Br, 21.41%, m.p., 259 C.

Q116: Found: C, 61.51%, H, 11.72%, N, 3.45%, Br, 21.07%. Theoretical; C, 62.34%, H, 11.17%, N, 3.64%, Br, 20.78%, m.p., 256 C.

Q316: Found; C, 61.28%, H, 11.14%, N, 3.03%, Br, 18.89%. Theoretical; C, 61.52%, H, 11.03%, N, 3.26%, Br, 18.60%, m.p., 87 C.

Q716: Found; C, 58.36%, H, 10.48%, N, 2.46%, Br, 15.82%. Theoretical; C, 60.41%, H, 10.55%, N, 2.71%, Br, 15.49%, m.p., 53 C. Very hygroscopic.

Q118: Found; C, 63.65%, H, 11.66%, N, 3.17%, Br, 19.41%. Theoretical; C, 63.90%, H, 11.45%, N, 3.39%, Br, 19.32%, m.p., 241 C.

Q318: Found; C, 60.19%, H, 10.80%, N, 2.85%, Br, 17.49%. Theoretical; C, 63.02%, H, 11.16%, N, 3.06%, Br, 17.51%, m.p., 212 C.

Q718: Found; C, 61.26%, H, 10.93%, N, 2.43%, Br, 14.97%. Theoretical; C, 61.63%, H, 10.90%, N, 2.51%, Br, 14.64%, m.p. 58 C. Hydroscopic.

Q122: Found: C, 66.06%, H, 11.87%, N, 2.87%, Br, 15.98%. Theoretical: C, 66.50%, H, 11.81%, N, 2.98%, Br, 17.08%, m.p., 236 C.

Q322: Found: C, 63.31%, H, 11.48%, N, 2.45%, Br, 15.58%. Theoretical: C, 65.47%, H, 11.58%, N, 2.73%, Br, 15.52%, m.p., 75 C.

Q722: Found: C, 61.52%, H, 11.47%, N, 2.20%, Br, 14.32%. Theoretical: C, 63.89%, H, 11.15%, N, 2.33%, Br, 13.31%, m.p., 61 C. Hygroscopic.

METHODS

Conductivity measurements. The conductivity of the solutions was measured with a General Radio Impedance Bridge, Model 1650 B. The bridge was energized by an external signal generator Hewlett-Packard 4204A set at 1kHz. The null point was detected with the help of an ordinary oscilloscope. All conductivity measurements were carried out at 25 ± 0.1 C. and were corrected for the solvent contribution. This correction was not used in the determination of the Krafft temperatures. The resistance of the solutions was measured in a closed conductivity cell fitted with bright platinum electrodes. The conductivity of water never exceeded 1.8×10^{-6} mho.cm^{-1} at 25 C. In most cases the stock solution was warmed to ca. 60 C to assist solubilization. Perfectly clear solutions were obtained in all cases. The stock solution was ca. 10^{-3} M/1. In all experiments reported in this paper, the pipettes were previously rinsed with the stock solution once before delivery to minimize losses due to the adsorption of the compounds on the glass surface. The molecule of the Q-122 compound has an area of ca. 350A^{o2} in the "lying flat" configuration because of the double charge. A 10^{-5}M solution prepared in a 100 ml flask will have a maximum error of 2% assuming that a close packed monolayer is formed. The error decreases for the larger Q compounds.)

Krafft temperature determination. The Krafft temperature was measured by the conductivity method (4,11). The same apparatus as described above was used. An excess of surfactant was weighed and shaken vigorously in 100 ml of distilled water contained in a stoppered cylinder. After the coarse particles settled, 25 ml of the middle portion of the fine suspension was placed in the conductivity cell. This procedure ensured the presence of excess solids in the system. The temperature inside the cell was measured with the calibrated cell thermometer and that of the water bath was followed with a Chromel-Alumel thermocouple connected to a Keithley Microvolt Ammeter, model 150B. The conductivity was measured when the cell thermometer and the thermocouple indicated the sample temperature. The conductivity increased linearly with the concentration below and above the Krafft point. The latter was taken as the temperature given by the intersection of the straight lines of the conductivity vs. temperature plots (4).

Surface tension measurements. A Cenco DuNouy tensiometer No. 70545 fitted with a platinum ring was used. The correction factors were obtained by computer solving the Zuidema and Waters expression (12). The experiments, except where indicated otherwise, were carried out at 23 ± 0.5 C. Ten readings were taken for each solution. In addition, surface tension measurements for Q118 compound were also carried out at 45 ± 0.5 C. In this case a jacketed beaker was used as the water bath. The beaker was connected to a Haake FK2 circulating bath. Forty ml of solution were placed in a 50 ml beaker which was, in turn, inserted into the jacketed beaker. This contained a certain volume of water to promote thermal equilibrium. The stage of the tensiometer was removed and a Rudolf Grauer jack (Switzerland) was used instead, to lower the solution smoothly. The beakers were preheated to ca. 48 C and the solutions were kept in the circulating water bath at ca. 47 C prior to the measurements. The surface tension of distilled water was found to be 68.2 mN/m as compared with 68.75 nM/m (13).

RESULTS

Krafft Temperature

The conductivity vs. temperature curve for compound Q118 is presented in Figure 1. The curves for the other Qmn compounds were similar. The Krafft temperature was obtained from the sharp break in the conductivity curve. The temperatures were Q116, 28.8 C; Q118, 40.5 C; Q122, 53.2 C; Q316, 12.4 C; Q318, 23.0 C; Q322, 40.6 C; Q716, < 0 C; Q718, 4.0 C; Q722, 24.8 C. The Krafft temperature was found to increase linearly with increasing n as shown in Figure 2. The slopes of the lines increase slightly in the order Q1n, Q3n, Q7n. The data of Meguro and Collaborators (4) show that a linear dependence between the Krafft temperature and n appears to be followed also by disodium di-sulfoalkyl dicarboxylates between n = 12 - 16, but not for n = 10. Sodium alkyl sulfates behave in the same manner for n = 10 - 18 (14). The slope was found to be somewhat higher for the alkyl sulfates series than for either the bis-quaternary ammonium salts or the disodium di-sulfoalkyl dicarboxylates. The Krafft temperature for Qmn compounds appears to decrease with m according to the general expression: Kt = A - Blog (m+2), where A and B are constants. The least squares plots of Kt against (m+2) are presented in Figure 3, and the correlation coefficient was very nearly 1.0. These curves allow one to predict the Krafft temperature of Qmn compounds. Q716 was estimated to have a Krafft temperature below 0 C. The data are in keeping with the increasing solubility of Qmn compounds with increasing m (n, invariant) and decreasing n (m, invariant).

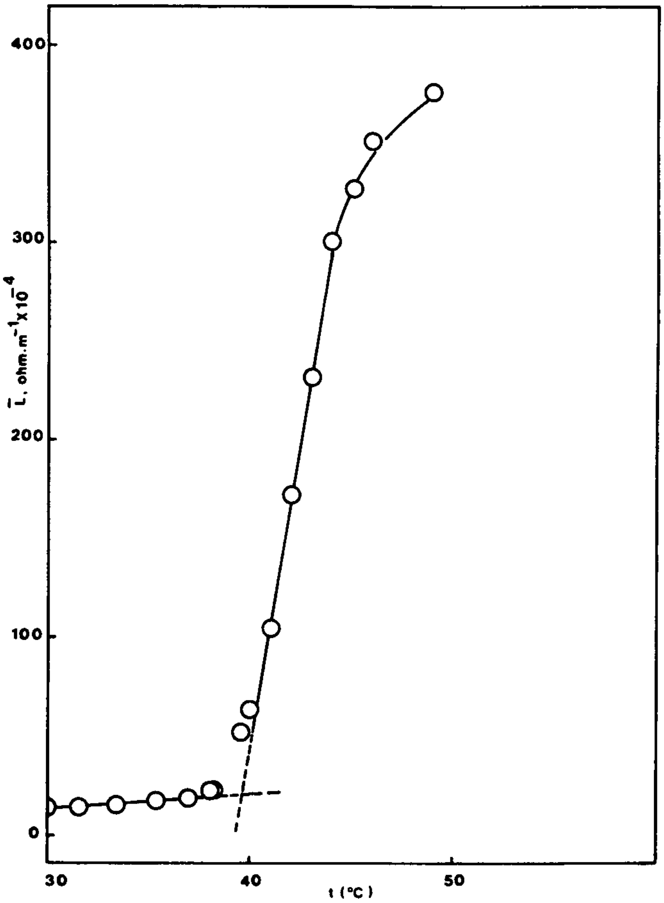


FIG. 1. Krafft Temperature of Q118.

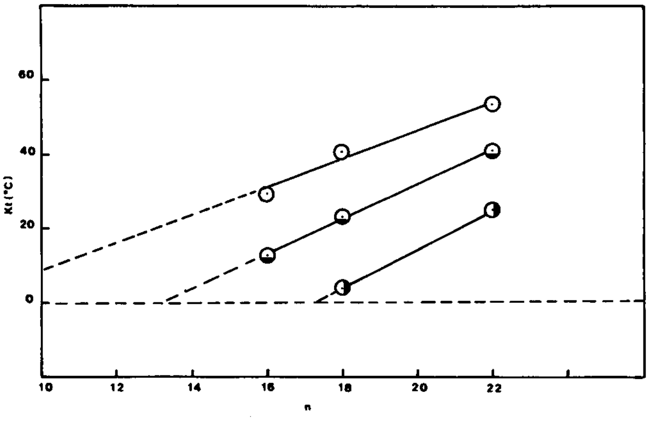


FIG. 2. Krafft Temperature vs. n. ○Q1n;◒Q3n;◑Q7n.

The conductivity vs. concentration graph for Q118 is given in Figure 4. The Qmn compounds without exception showed two distinct breaks in the conductivity curves. These were labeled CMC1 and CMC2. The CMC1 was always substantially lower than the CMC2. The breaks associated presumably with micellization were also apparent in the work of other investigators (4-6). The conductivity increased linearly with concentration below, above and between the breaks.

It is noteworthy that although the conductivity-temperature curve for compound Q-118 indicates a Krafft point of 40.5 C and its conductivity-concentration curve shows breaks which may be critical micelle concentrations at 1.2 x 10^{-5} and 8.7 x 10^{-5} mole/dm^3, solutions of concentration up to 10^{-3}M can be prepared at a temperature (23 C) below the Krafft point. The reason for this is unknown.

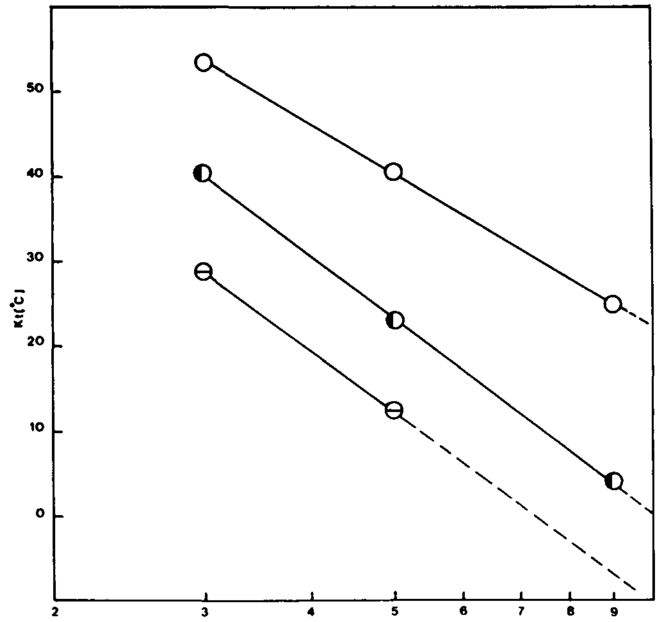


FIG. 3. Krafft temperature vs. (m + 2). ○ Qm22; ◐ Qm18; ⊖ Qm16.

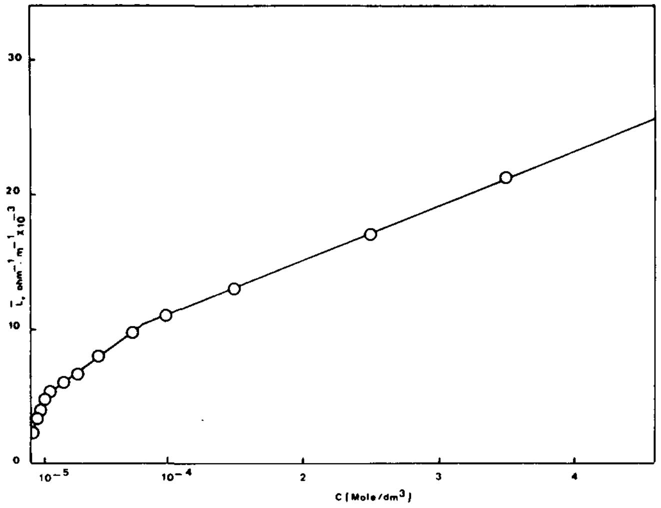


FIG. 4. Conductivity vs. Concentration for Q118 at 25± 0.1 C in distilled water.

Surface Tension

The γ-log c plots for Q118 and Q716 are given in Figure 5. The sharp discontinuity in the curve is the surface tension critical micelle concentration denoted by CMCγ. In contrast with the conductivity plots, the γ-log c curves always showed one break only. In some cases (e.g., Q118, Q122 and Q322) the γ-log c curve failed to show any discontinuity and did not permit the CMCγ to be obtained. Refer to Figure 5 where the surface tension curve for Q118 is shown to be almost parallel to the concentration axis. This behavior was also found at 45 C for the same compound. In many cases the CMC1 = CMCγ (e.g., Q116, Q716, etc.), but it was also found that CMC2 = CMCγ for Q318 and Q722. Although no explanation can be given for this behavior at the present moment, it is, however, opportune to note that agreement between CMC1 and CMCγ has been reported (5), whereas CMC2 was found to coincide with CMCγ as well (6). The dye method also appears to reveal the presence of CMC1 only (4). The critical micelle concentrations for Qmn compounds are presented in Table II.

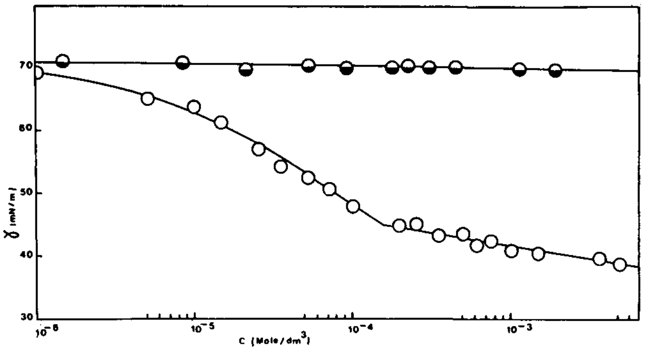


FIG. 5. γ log c. curve for Qmn compounds at 23 ± 0.5 C in distilled water. ◒Q118; ○Q716.

DISCUSSION

The relationship between the CMC and the micellar parameters of a surface active agent possessing more than one ionic group and in the absence of indifferent electrolyte was given by Shinoda (15). Maintaining most of his notation one may write:

$$\ln CMC = [1/(1 + jKg)]\ (-nw/kT + jKg\ln 2000\pi\sigma^2/DN\ kTj+K) \qquad 1.$$

where j is the number of ionic groups, Kg the fraction of counterions bound to the micelle, w the energy required to transfer one methylene group from the aqueous to the micelle phase, n the number of methylene groups in the hydrocarbon chain, D the dielectric coefficient, T the absolute temperature, σ the surface charge density of the micelle and k the Boltzmann's constant and N is the Avogadro's number.

It has also been experimentally established that the CMC decreases with the increasing chain length according to the expression:

$$\log CMC = A - Bn \qquad 2.$$

where A and B are the intercept and the slope of the log CMC vs. n curve, respectively. The energy w can be obtained with the help of the expression:

$$w = 2.303\ kT\ B\ (1 + j\ Kg) \qquad 3.$$

The transfer energy was calculated assuming that the value Kg = 0.65 for alkyltrimethylammonium bromides (16) applies to bis-quaternary ammonium bromides. The energy w was also calculated for disodium di-sulfoalkyl dicarboxylates using Kg = 0.56 (15). The values, calculated with the help of the least squares plots presented in Figures 8 and 9, are summarized in Table III.

Effect of the Oxyethylene Chain Length

The attachment of an oxyethylene chain directly to the head group of an ionic surface active agent causes the CMC to decrease with the increasing length of the oxyethylene chain (7,8). To a certain extent this is an unexpected effect since oxyethylene interacts, via hydrogen bond, with the water molecules. The hydrophilic character of the polyethylene chain was recognized by Davies, who ascribed to it a positive hydrophilic group number for the computation of HLB values (17). The introduction of a second ionic group into a singly charged surfactant increases the CMC (15). Consequently, the properties of surfactants that

TABLE II

Critical Micelle Concentrations for Qmn Compounds in Distilled Water

	Conductivity		Surface tension	
Qmn	CMC1 (Mole/dm^3)	CMC2 (Mole/dm^3)	CMCγ (Mole/dm^3)	Remarks
112[a]	---	---	4.8×10^{-4}	
114	5.0×10^{-5}	2.5×10^{-4}	---	
116	3.4×10^{-5}	1.46×10^{-4}	3.8×10^{-5}	CMC1 = CMCγ
118	1.20×10^{-5}	8.7×10^{-5}	Not apparent	
122	7.2×10^{-6}	3.4×10^{-5}	Not apparent	
316	6.0×10^{-5}	7.0×10^{-4}	6.5×10^{-5}	CMC1 = CMCγ
318	3.75×10^{-5}	3.67×10^{-4}	3.3×10^{-4}	CMC2 = CMCγ
322	1.40×10^{-5}	8.0×10^{-5}	Not apparent	
716	1.55×10^{-4}	1.40×10^{-3}	1.6×10^{-4}	CMC1 = CMCγ
718	8.2×10^{-5}	6.6×10^{-4}	8.4×10^{-5}	CMC1 = CMCγ
722	2.35×10^{-5}	2.25×10^{-4}	2.3×10^{-4}	CMC2 = CMCγ

[a] Fits well the CMC2 vs. n graph (see Fig. 9).

possess an oxyethylene chain could be tailored according to the structure of the molecule.

The plots of CMC1 and CMC2 for Q1n, Q3n and Q7n series are presented in Figures 6 and 7, respectively. It is apparent that the CMCs increase with increasing m, everything else remaining invariant. However, preliminary studies on compound Q2022 revealed that the CMC does not increase indefinitely with increasing OE chain length. For this compound CMC1 = 1.45×10^{-5} mole/dm^3 and CMC2 = 1.35×10^{-4} mole/dm^3. These values are substantially lower than those predicted for the Qm22 series. The Qmn compounds that possess very large polyoxyethylene chains (for n constant) behave as if they were singly charged, since one end of the molecule will act almost independently of the other.

Singly charged compounds containing OE residues change their properties not only with the number of residues present in the molecule, but also with the OE chain position in the molecule itself, if the hydrocarbon chain length n remains invariant (7,9,18). In the present work the results suggest that the CMCs of Qmn compounds pass through a maximum at a certain m value. This agrees with the observation of other workers on singly charged compounds (18). The maximum perhaps indicates the point of transition at which the Qmn compound (with n invariant) begins to behave like monofunctional oxylated ionic surfactants. This maximum value in m is probably different for the different Qmn series. At the present moment only the Qm22 series has been probed.

The unique effect of the polyoxyethylene chain length on the colloidal properties of bis-quaternary ammonium salts can be better appreciated if a comparison is made with the results of Deinega and collaborators (6). The comparison can only be qualitative because the nature of the halide counter ion also affects the micellar properties of surface active agents (19). The lengthening of the methylene chain between the charges decreases the CMC2 of the bis-quaternary chlorides of alkylene diamine (Refer to formula A) according to expression (2). Similar behavior was reported by Meguro and associates for their difunctional salts. (4). The insertion of methylene groups between the charges of bipolar surfactants is equivalent to the lengthening of the conventional hydrocarbon chain of the compound and to the lengthening of the polyoxyethylene chain of singly charged surface active agents. The results suggest that the polyoxyethylene chain affects the micelle through changes in the electrical parameters as well as in the aggregation number. The type of micellar unit present at the CMC1 and the CMC2 is not clearly understood yet. Perhaps the two distinct CMCs represent two different types of micelles. Furthermore, at the present moment it is difficult to state with any degree of certainty whether or not the CMC1 or the CMC2 represent the "true" CMC (5,6). More work needs to be done to clarify this point.

It is, perhaps, reasonable to assume that the charge separation alone cannot entirely explain the behavior of bipolar surface active agents, particularly those containing OE residues. It seems that the nature of the chain that separates the charges is of relevant importance. The least aquare plots for bis-quaternary chlorides of alkylene diamine obtained from the data of Deinega (6) show that the methylene chain length has practically no effect on the CMC2 = CMC$_\gamma$ of the salts for m = 2 or 6. (see formula A). Also for compounds described by formula B dlog CMC/dn = 0 for m = 2,4,6, but decreases for m for m> 6.

Inspection of Table III shows that the differences presented by the Qmn compounds are indeed significant and that their behavior is caused by the presence of the double charge and the polyoxyethylene chain that bridges them.

TABLE III

Values of A, B and w for the Qmn Series at 25 C

Series	CMC	B	w	A
Q1n	CMC1	-0.1069	-0.57 kT	-2.7852
Q1n	CMC2	-0.1079	-0.57 kT	-2.1027
Q3n	CMC1	-0.1056	-0.56 kT	-2.530
Q3n	CMC2	-0.1582	-0.84 kT	-0.609
Q7n	CMC1	-0.1364	-0.72 kT	-1.628
Q7n	CMC2	-0.1301	-0.69 kT	-0.799

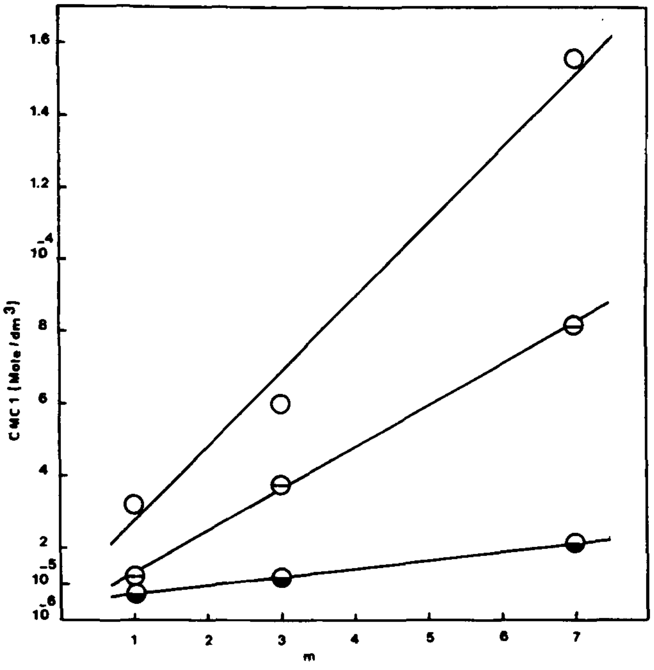


FIG. 6. CMC1 vs. m for Qmn compounds at constant n. ◒Qm22; ⊖Qm18; ○Qm16.

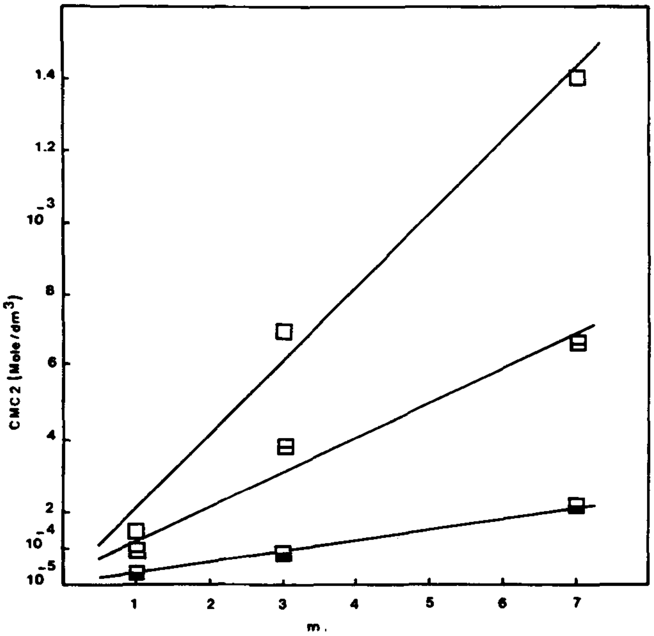


FIG. 7. CMC2 vs. m for Qmn compounds at constant n. ⬓ Qm22; ⊟Qm18; ☐Qm16.

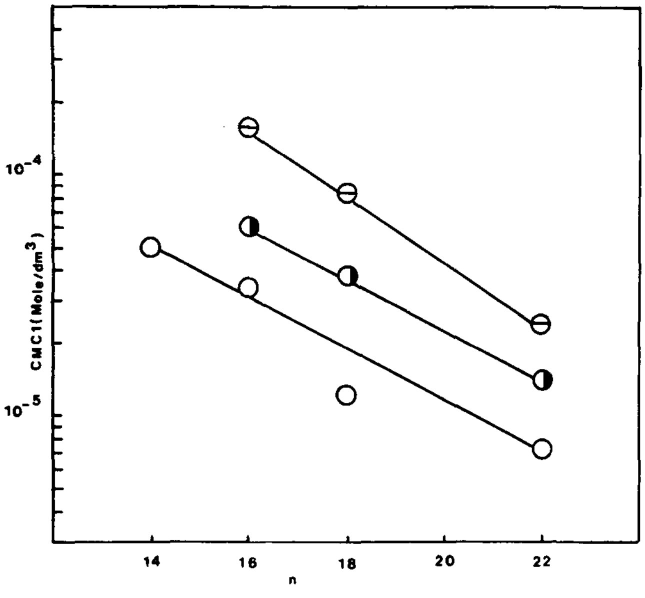


FIG. 8. CMC1 vs. n for Qmn compounds at constant m. ○Q1n; ◑ Q3n; ⊖Q7n.

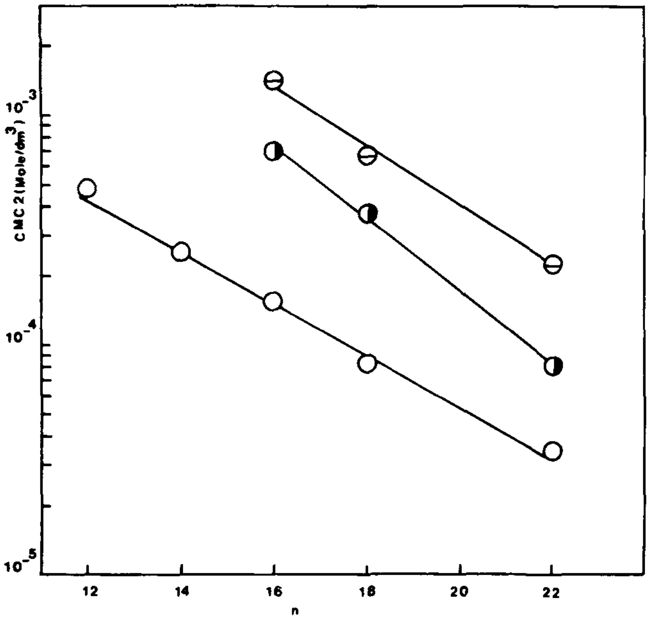


FIG. 9. CMC2 vs. n for Qmn compounds at constant m. ○Q1n; ◑ Q3n; ⊖Q7n.

Effect of the Hydrocarbon Chain Length

The effect of the hydrocarbon chain length on the micellar properties of bis-quaternary ammonium bromide can be seen in Figures 8 and 9. Both CMC1 and CMC2 appear to decrease with the hydrocarbon chain length according to expression (2). The expressions for CMC1 and CMC2 for each series were calculated by the least squares method and are represented by the solid lines in the figures.

The CMC2 = CMCγ of Deinega and collaborators (6) for compounds represented by formula A were plotted against n'. The least squares plots gave B = 0.1112. The effect of the long hydrocarbon chain on the CMC of Qmn compounds is similar to that found for the bis-quaternary chlorides of alkylene diamine. This is also, not unexpectedly, in agreement with the behavior of singly charged surfactants (15).

The energy of transfer w, calculated with the help of expression (3), varied from -0.57 kT to -0.72 kT for CMC1 and from -0.57 kT to -0.84 kT for CMC2. A value of Kg = 0.65 (16) was taken for all bis-quaternary salts. Using this same value, the energy of transfer w was found to be -0.59 kT for the bis-quaternary chlorides of alkylene diamine. The energy of transfer for the Q1n series compares very well with this value. Also, if Kg-0.56 (15) is used in conjunction with the data available for disodium disulfoalkyl dicarboxylates (4) a value of -0.69 kT is obtained for these salts. The values for w compare well with -0.61 kT to -0.69 kT found for fatty acids, alkyl sulfates, alkylammonium and trimethylammonium bromides (20). For the same series (m constant) the energy appears to be the same for micelles at the CMC1 and CMC2. Also the energy seems to increase somewhat with the OE chain length. The value of -0.84 kT for the CMC2 of the Q3n series is somewhat high. The energy does not seem to vary substantially with the nature of the "head group." The results obtained suggest that the micelle units at the CMC1 and CMC2 are different. Assuming that the counter-ion binding are comparable for micelles 1 and 2, present at the CMC1 and CMC2, respectively, then $N_1 > N_2$ (N_1 = aggregation number of micelle 1 and N_2 = aggregation number of micelle 2). Furthermore, it is likely that the aggregation numbers for the same kind of micelle varies for the different series. This is apparent from the plots in Figures 8 and 9.

The low values of w can be explained if a micelle model similar to that proposed by Tanford (21) is adopted. In the Qmn micelles the quaternary group and the polyoxyethylene chain form a hydrophilic mantle that is permeated by water molecules. The transfer energy will therefore be lower than that required to transfer an alkyltrimethylammonium bromide pair from the aqueous phase to the hydrocarbon/solution interphase (this requires ca. -1.4 kT [22]), since water molecules are already entrained in the polar mantle.

By force, most questions concerning the behavior of bis-quaternary ammonium salts remain unresolved. The determination of the light scattering micellear weight and the measurement of the temperature coefficient of micellization should provide sufficient data for the computation of the proper thermodynamic quantities that will help shed more light onto the difficult problem of micellization of difunctional ionic salts.

ACKNOWLEDGMENT

The authors express gratitude to Johnson & Johnson for permission to publish this paper, particularly to the Baby Products Company for its encouragement and support, to A.M. Schwartz for the interesting discussions, R. Kennedy for his untiring help in the synthesis of the compounds, and V. Vit for his diligent assistance in the physical chemical measurements reported in this work.

REFERENCES

1. Wysocki, A.J., and D. Taber, "Cationic Surfactants," Vol. 4, Edited by E. Jungermann, Marcel Dekker, New York, 1970, p. 71.
2. Danielson, I., Acta Acad. Abo. Ser. B 20:7(1956).
3. Elworthy, P.H., J. Pharm. Pharmacol. 11:557 (1959).
4. Ueno, M., T. Hikota, T. Mitama, and K. Meguro, JAOCS 49:250 (1972).
5. Mino, J., E. Matijevic, and L. Meites, J. Colloid Interface Sci. 60:148 (1977).
6. Deinega, Yu F., Z. R. Ul'Berg, L.G. Marochko, V.P. Rudi, and V.P. Denisenko, Kolloidn. Zh. 36 (4):649 (1974).
7. Mandru, I., J. Colloid Interface Sci. 41:430 (1972).
8. Barry, B.W., and R.J. Wilson, Pharm. Pharmacol. 26, Suppl. 125P, (1974).
9. Lin, I.J., and L. Marszall, J. Colloid Interface Sci. 57:85 (1975).
10. R. Kennedy, R. Verdicchio, and M.K.O. Lindemann, U.S. Pat. No. 4,110,263.
11. Nakayama, H., K. Shinoda, and E. Hutchinson, J. Phys. Chem. 70:3502 (1966).
12. Zuidema, H.H., and G.W. Waters, Ind. Eng. Chem. 13:312 (1941).
14. Raison, M., Proc. 2nd Int. Conf. Surface Activity, Butterworths, (London), 1:374 (1957).
15. Shinoda, K., T. Nakagawa, B. Tamamushi, and T. Isemura, "Colloidal Surfactants," Academic Press, New York, 1963, p. 46.
16. Barry, B.W., J.C. Morrison, and G.F. Russell, J. Colloid Interface Sci. 33:554 (1970).
17. Davies, J.T. Proc. 2nd Int. Conf. Surface Activity, Butterworths, London, 1:426 (1957).
18. Lin, I.J., Colloid and Interface Science, 2:431 (1976), 50th National Colloid Symposium, Puerto Rico.
19. Ford, W.P.J., R.H. Ottewill, H.C. Parreira, J. Colloid Interface Sci. 21:522 (1966).
20. Lin, I.J., and P. Somasundaran, J. Colloid Interface Sci. 37:731 (1971).
21. Tanford, C., Y. Nozaki, and M.F. Rohde, J. Phys. Chem. 81:1555 (1977).
22. Haydon, D.A., and F.H. Taylor, Phil. Trans. 252A:225 (1960).

[Received December 12, 1978]