THE EFFECT OF POTASSIUM BROMIDE ON CRITICAL MICELLE CONCENTRATIONS OF A CATIONIC SURFACTANT IN BUFFER AND NONBUFFER SYSTEMS*

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The effect of KBr on critical micelle concentrations (CMC's) of a cationic surfactant, cetyltrimethyl ammonium bromide (CTAB) in the absence of buffer at pHs between 8.0 − 10.0 using a pH-stat technique was investigated. A study was also carried out in the presence of buffer at pH 9.2 and the results are compared. The CMCs were found to be independent of pH over the region studied. The addition of carbonate−bicarbonate buffer and KBr both reduced the CMC. The results give strong support to the fact that only the counterions of added salt make a contribution to the shift of the CMC.

INTRODUCTION

The CMC of surfactants has been defined as the concentration above which any added surfactant molecules appear with high probability as micellar aggregates [1]. The formation of micelles leads to an abrupt change in such physical properties as surface tension, electric conductance, pH, refractive index, solubility, viscosity and optical properties of surfactant solutions. These changes in physical properties result in discontinuities in the slopes of the curves obtained when the value of a given physical property is plotted as some function of surfactant concentration. Such plots are routinely utilized in the determination of CMCs. Other methods which have been recently employed in the determination of CMC include optical rotatory dispersion, gel filtration, fluorimetry and counterion magnetic resonance [2].

The CMC for a particular surfactant solution thus represents a physical quantity of no less significance than a melting point, boiling point, or refractive index, for example, of a pure substance. The literature from 1926 up to and including 1966 has been critically surveyed by Mukerjee and Mysels [3] who have published a collection of CMC values for over 700 compounds with about 5,000 entries, based on 333 references; this shows some 70 methods have been used for CMC determination.

It is now known that surfactant monomers interact to some extent below the CMC and build aggregates that are much smaller than micelles, known as premicellar aggre-

gates. A review of the work in this field up to 1967 has been presented by Mukerjee [4]. The actual size, structure and stability of these premicellar aggregates are, however, still a matter for discussion [5−7]. Examination of the literature also shows that the concentration of monomers present in solutions increases after the CMC and there is also the possibility of a second marked aggregation known as the second CMC [2,8−12]. However, this aspect of the physical chemistry of micelles is, as yet an incompletely developed area.

Effect of Electrolytes. Extensive work has been done on the effect of electrolytes and nonelectrolytes on the CMC's of ionic and nonionic surfactants [13−18]. In general, the addition of electrolytes to ionic surfactants results in a lowering of the CMC. The decrease in CMC is presumably due to the screening action of the electrolytes which lowers the repulsive forces between the polar head groups, and thus reduces the electrical work required for micelle formation. Recently Parades and his coworkers [19] have shown that there is a large decrease in CMC's of CTAB and sodium dodecyl sulphate in the presence of $0.1M$ NaCl but no significant change in CMC value of Triton X-100, which is a nonionic surfactant, was found in the presence of the same concentration of NaCl.

The CMC of ionic surfactants in the presence of added univalent salts was shown by Corrin and Harkins [20] to follow a log relationship between the CMC and the counterion concentration:

$$\ln CMC = A - B \ln C \qquad (1)$$

where C represents the total molar concentration of counterions and is equal to $(C_s + CMC)$ in the presence of uni-

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valent counterions of molar concentration C_s. A and B are negative constants. The values of A and B were first estimated to be about -0.5 and -3.0 by the use of Debye—Hückel theory [21]. Later studies, however, revealed that the values of A differ from electrolyte to electrolyte and these differences were attributed to differences in binding affinities of the counterions to the micelle as a result of differences in hydration of the ions [2]. Measurements of the salt effect on the CMC of three ionic surfactants agree quite well with the equation (1) [21].

Tartar [22] in 1962, applying the data of Corrin and Harkins, noticed that the CMC was a linear function of the 'thickness of ionic atmosphere', t:

$$CMC = A_1 t + B_1 \qquad (2)$$

where A_1 and B_1 are constants, and t is given by the Debye—Hückel relationship based on ionic strength terms:

$$t = \frac{DT}{\Sigma mi\ z_i^2} \times \frac{1000\ k}{4\ \pi\ Ne^2} \qquad (3)$$

where D is the dielectric constant of the medium, T is the absolute temperature, N is the Avogadro constant, K is the Boltzmann constant and m_i and z_i refer to the molality and valency of ion species 'i'.

Relationship (3) provides another equation relating CMC and C_s. Since at constant temperature DT is constant, and CMC is a linear function of the reciprocal of the square root of ionic strength. To evaluate 't', Tartar has taken into account every ionic species present in solution.

Equation (2) can be transferred into an eqivalent equation by using equation (3). For a 1:1 salt the result will be:

$$CMC = A_2 (CMC + C_s)^{-1/2} + B_2 \qquad (4)$$

For a 1:n salt to describe the effects of polyvalent salts on the CMC of cationic surfactant with concentration C_s (in molarity), equation (4) is modified to:

$$CMC = [\ A_3\ \frac{n\ (n+1)}{2}\ C_s + CMC\ ]^{-1/2} + B_3 \qquad (5)$$

and plots of CMC against $(CMC + C_s)^{-1/2}$ and $[\frac{n\ (n+1)}{2} C_s + CMC]^{-1/2}$ for the electrolytes in surfactant solutions should be linear with slopes of the lines defined by the counterion which illustrates the fact that only the counterions of added salts make a contribution to the shift of the CMC.

MATERIALS AND METHODS

Surfactant. This was cetyltrimethylammonium bromide (CTAB). The reagent grade sample of CTAB (BDH) was subjected to the purification process described by Mukerjee and Mysels [23], Duynstee and Grunwald [24]. Following this procedure the purity was checked by surface tension, melting point, NMR and mass spectrometry. No minimum was observed in the surface tension log concentration curves that were obtained indicating the absence of long chain contaminants. NMR studies showed the absence of branching in the hydrocarbon chain and the mass spectrometry indicated more than 99% purity of the sample. The melting point of the substance was 231.5^O (lit. $230-4^O$) [25].

Buffer Salts and Analytical Reagents were all of Analar quality.

Water. Freshly distilled water from an all-glass still was used which has a specific conductivity $< 10^{-7}$ Ohm^{-1} cm^{-1} and surface tension of 72.05 mNm^{-1} at 25°.

Buffer Solution: Delory and King's carbonate—bicarbonate buffer at pH 9.20 was prepared according to Documenta Geigy (1962).

pH Measurements. These were made using a radiometer digital pH meter type PHM 64 research pH meter, 5 digit display fitted with a radiometer GK 2401C combined glass-calomel electrode. The meter and electrode system were standardized prior to each pH determination using sodium tetraborate buffer pH 9.139 at 30° and phosphate buffer pH 6.853 at 30° prepared according to Bates [26].

pH-Stat Assembly. This consisted of radiometer titrator (type TT 11), Radiometer Auto Burette Unit (type ABU12), Overhead Stirring Motor (type M11) and pH meter (type Radiometer PHM 26). The complete unit was supplied by Electronic Measuring Instruments, Copenhagen, Denmark. Radiometer PHM 26). The complete unit was supplied by Electronic Measuring Instruments, Copenhagen, Denmark.

Bromide Ion Specific Electrode. This was Radiometer Bromide Selectrode (type F1022 Br solid state membrane) used for direct determination of the activity or concentration of bromide ions in CTAB solutions.

Light Scattering Photometer. This was Brice—Phoenix model OM-2000 with 436 and 546 nm wave-lengths obtained via mercury lamp and filters and fitted with a constant temperature circular heating jacket according to Trementozzi [27].

Ageing of Glassware. Due to its substantial negative charge density, glass surfaces have a strong affinity for cationic surface active agents [28, 29]. Therefore, all the

glassware used in the work was aged wih the appropriate concentrations of CTAB. Experience showed that measurements of surface tension and bromide ion concentration were not stable if experiments were performed in unaged glassware, whereas stable reproducible results were obtained when the glassware was treated to the ageing process [30].

Estimation of the Critical Micelle Concentration

Surface Tension. Surface tension measurements have been used by numerous authors to determine CMC's. The method has a great advantage in that it can be applied to ionic and nonionic surfactants, and can be used down to very low concentrations. Various techniques are available to measure surface tension [31] of which the Wilhelmy slide method, in which the force required to detach a thin microscope slide of known thickness and width from the surface of a liquid is measured, has been used here.

The detailed operating procedure is given by Harkins and Alexander [31].

The surface tension was then calculated using equation (6):

$$\gamma = \frac{W_g}{2(L+t)} \tag{6}$$

where γ, surface tension in mNm^{-1}; W weight in grams, necessary to detach the slide from the surface; g acceleration of gravity, taken as 981 cm sec^{-2}; L width of the slide in cm; and t thickness of the plate in cm.

Validity of the Method. The validity of the method and the accuracy of the instrument used were established prior to determination of the CMC. This was done by checking the surface tension of some standard liquids of known surface tension. Determination were carried out in replicate and Table 1 shows these values and the literature values of the surface tension of three liquids.

It can be seen from the Table that the values are well in agreement with the reported values and thus confirm the validity of the method.

For the determination of CMC of CTAB, a series of concentrations of CTAB solution were prepared in water and buffer—salt solutions. These solutions were then kept in specially designed containers previously aged and held in the water bath for approximately 3 hr to allow for surface ageing and temperature equilibration. Surface tension was then plotted against log concentration of CTAB and the CMC determined from the intersection of the 2 linear parts. A typical plot is shown in Fig. 1. Other CMC values determined by this technique are given in Table 2.

Measurement of Ion Activity. Specific ion electrodes measure the activity of ions other than H^+ in solution. At the CMC, counterion binding by micelles will result in a change in the slope of the bromide activity concentration plot. The bromide slectrode — type Radiometer TMF 1022 Br was used in conjunction with a calomel electrode Radiometer type K 701 using saturated KNO_3 in the second salt bridge. The output potential produced by the electrode pair was measured with PHM 64 Research pH meter in its millivolt mode. In the present work this method of CMC

Table 1. Surface tension of water, benzene and ethanol as determined by Wilhelmy slide method together with literature values.

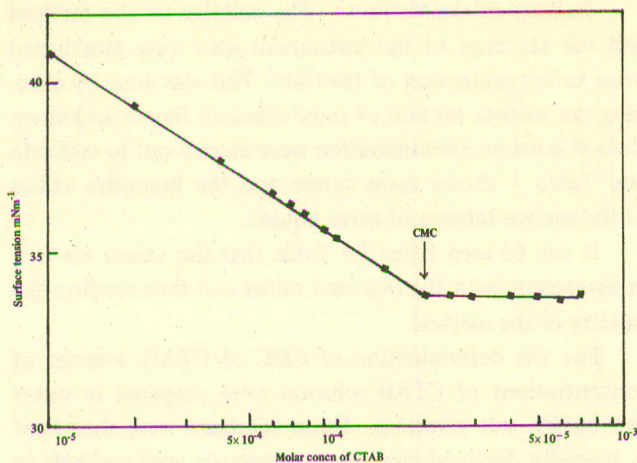| Liquid	Temp (°C)	Observed surface tension mNm^{-1}				Reported value mNm^{-1}	Ref
		I	II	III	Mean		
						72.02	31
Double distilled	25	72.05	72.03	72.05	72.04	71.96	17
water	30	71.17	71.19	71.16	71.17	71.98	17
						72—73	17
						71.18	32
Benzene (spectroscopic grade)	30	27.50	27.52	27.52	27.51	27.56	32
Ethanol (absolute A.R. grade)	30	21.72	21.85	21.86	21.81	21.89	32

Fig. 1. Surface tension vs. log concn of CTAB in carbonate–bicarbonate buffer at pH 9.2 and 30°

measurement was used for those systems in the absence of salt, where the pH was maintained by the pH-stat assembly. The use of surface tension was not suitable for nonbuffered systems, because of the absorption of atmospheric carbon dioxide by the large surface area exposed.

Solutions of appropriate concentrations were placed into the appropriate previously aged five-neck flask and were equilibrated in a water-bath at 30° ± 0.05°. When the solution reached the desired pH, the output potential (mV) was recorded from the pH meter (PHM 64). Meter readings in mV at four different pH's, (8.0, 8.6, 9.2 and 10.0) were noted for all concentrations of CTAB. The readings for the four different pHs were taken on single samples of each CTAB concentration by increasing the pH from 8.0 to 8.6, 8.6 to 9.2 and then to 10.0. Full details of the experimental techniques are available [30]. Bromide ion concentration of CTAB was then determined from the corresponding measured potential values (mV) by direct reference to the calibration curve given elsewhere [30] which has a range of emf values from around −150 to +150 mV. p-Br^-_a (i.e. $-\log_{10}$ bromide ion activity) was plotted against pBr^-_{CTAB} ($-\log_{10}$ CTAB concentration). pBr^-_a and pBr^-_{CTAB} were seen to be in equal ratio (1:1) up to the CMC region when a marked deviation of pBr^-_a was observed (Fig. 2). Above this break point, the plot was nonlinear. A similar finding was reported by Pearson and Humphreys [33] with a bromide ion selectrode on four cationic surfactants, i.e. C10, 12, 14, 16-trimethylammonium bromide. When the concentration of bromide ions were plotted against CTAB concentration on a linear scale (Fig. 3) a sharp break was observed and the plot being linear both above and below the break. The CMC's were obtained from the intersection of the linear plots and are given in Table 2.

Table 2. CMC values of CTAB measured under various sets of conditions at 30°

| pH | Systme | | Method | CMC |
	Buffer	KBr		(molar)
Water	–	–	ST	1.00×10^{-3}
alone	–	–	Br	1.00×10^{-3}
8.0	–	–	Br	1.00×10^{-3}
8.6	–	–	Br	1.00×10^{-3}
9.2	–	–	Br	9.95×10^{-4}
9.2	+	–	ST	2.00×10^{-4}
9.2	+	$10^{-4}M$	LS	2.00×10^{-4}
	+		ST	2.00×10^{-4}
9.2	+	$10^{-3}M$	LS	1.00×10^{-4}
			ST	1.00×10^{-4}
9.2	+	$0.1M$	LS	9.00×10^{-5}
9.2	+	$0.5M$	LS	6.00×10^{-5}
8.0	–	$10^{-4}M$	LS	9.00×10^{-4}
8.0	–	$10^{-3}M$	LS	7.00×10^{-4}
8.0	–	$5 \times 10^{-3}M$	LS	3.90×10^{-4}
8.0	–	$10^{-2}M$	LS	3.40×10^{-4}
8.0	–	$0.1M$	LS	2.00×10^{-4}
8.0	–	$0.5M$	LS	7.00×10^{-5}
8.6	–	$10^{-4}M$	LS	9.00×10^{-4}
8.6	–	$10^{-3}M$	LS	7.00×10^{-4}
8.6	–	$5 \times 10^{-3}M$	LS	3.95×10^{-4}
8.6	–	$10^{-2}M$	LS	3.50×10^{-4}
8.6	–	$0.1M$	LS	2.00×10^{-4}
8.6	–	$0.5M$	LS	7.00×10^{-5}
9.2	–	$10^{-4}M$	LS	9.00×10^{-4}
9.2	–	$10^{-3}M$	LS	7.00×10^{-4}
9.2	–	$5 \times 10^{-3}M$	LS	3.90×10^{-4}
9.2	–	$10^{-2}M$	LS	3.40×10^{-4}
9.2	–	$0.1M$	LS	1.95×10^{-4}
9.2	–	$0.5M$	LS	6.90×10^{-5}
10.0	–	$10^{-4}M$	LS	9.00×10^{-4}
10.0	–	$10^{-3}M$	LS	7.00×10^{-4}
10.0	–	$5 \times 10^{-3}M$	LS	3.95×10^{-4}
10.0	–	$10^{-2}M$	LS	3.45×10^{-4}
10.0	–	$0.1M$	LS	1.95×10^{-4}
10.0	–	$0.5M$	LS	6.90×10^{-5}

ST surface tension; Br, bromide ion selectrode; LS light scattering, + present; – absent; buffer, carbonate–bicarbonate

Light Scattering. CTAB solutions of various concentrations were filtered directly into the aged light scattering cell under a dust screen. The cell was covered and housed within the light scattering photometer in a circular cell heating jacket designed according to Trementozzi [27] and recommended by Smart [34]. After equilibration to 30° ± 0.05, scattering measurements were made at ∠90°, using the perspex block as standard. Full details of the
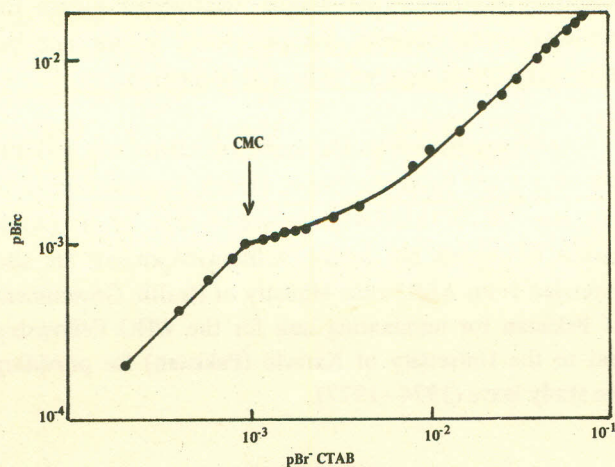
Fig. 2. $\log_{10}$ bromide ion concn vs. $\log_{10}$ CTAB concn at pH 9.2 in nonbuffer system and 30°.
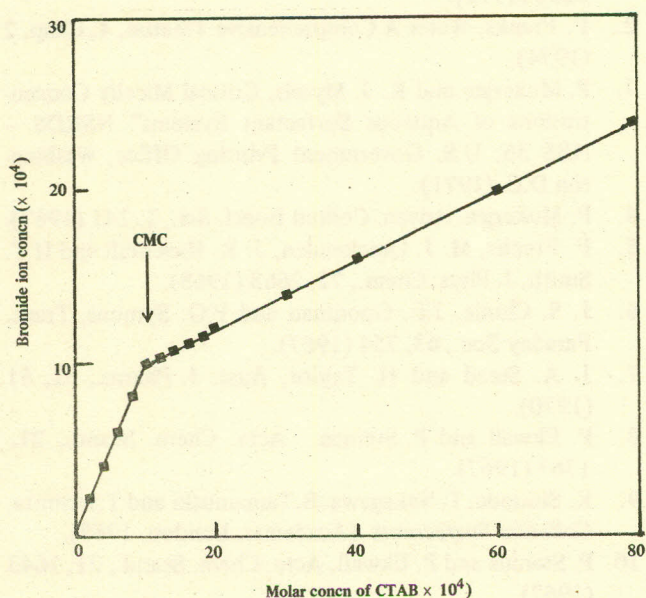

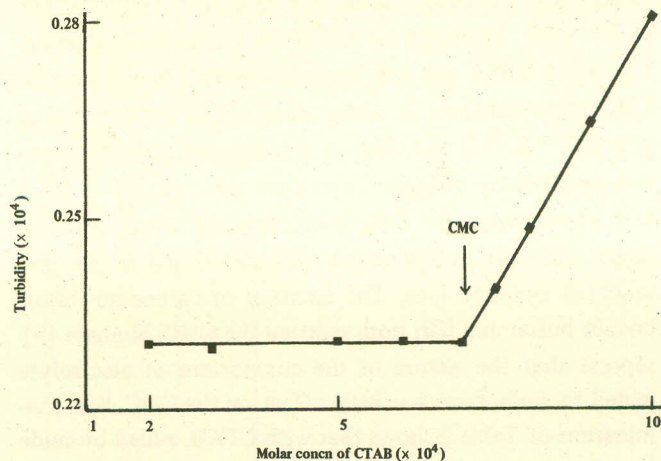Fig. 3. Bromide ion concn vs. CTAB concn in water (nonbuffer system) at pH 9.2 and 30°.

Fig. 4. Turbidity vs, CTAB concn with $10^{-3}M$ KBr in non buffer systems at pH 9.2 and 30°.
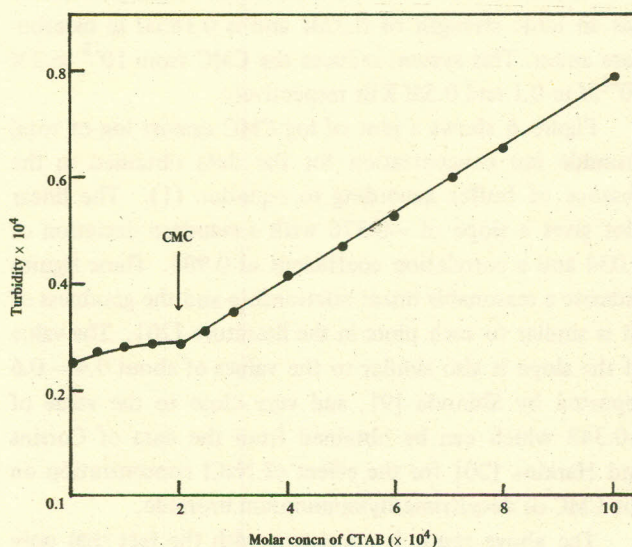
Fig. 5. Turbidity vs. molar concn of CTAB with $0.1M$ KBr in non-buffer system at pH 9.2 and 30°.

operating techniques, and mathematical derivation involved in this procedure are available [30].

The turbidities of solutions of various concentrations of CTAB were then determined using the method described elsewhere [30] at 546 nm. The turbidity was plotted against molar concentration of CTAB and the CMC obtained from the sharp break in the curve. Typical plots are shown in Figs 4 and 5 and the CMC values are given in Table 2.

RESULTS AND DISCUSSION

CMC of cetyltrimethylammonium bromide (CTAB) in the presence and absence of buffer at 30° was measured by surface tension, light scattering and bromide ion activity methods. The effect of pH in the region $8.0 - 10.0$ and added bromide ions of various concentrations on the CMC of CTAB has been investigated. The results are summarized in Table 2. 30° was adopted because this temperature is sufficiently above the Krafft point of CTAB ($23-24^\circ$) [35] to avoid solubility problems without creating gross effects on micellar structure. This is also an easy temperature to maintain in the laboratory. Experimentally the temperature was maintained by using a double-walled LTE viscometric bath; the temperature fluctuation which were recorded at 30° were $\pm 0.05^\circ$.

For any particular condition the CMC's obtained were reproducible and independent of the method used. The CMC value obtained in water at 30° of $1.0 \times 10^{-3}M$ agrees

closely with published values of $8.23 \times 10^{-4} - 1.0 \times 10^{-3} M$ at 30° [36]. However, no values are available for comparison in the buffer and KBr systems. Table 2 shows that the CMC value obtained in water alone above pH 5.5 and at pHs 8.0, 8.6, 9.2 and 10.0 in the absence of buffer were not significantly different from each other ($0.995-1.00 \times 10^{-3} M$) indicating the CMC is independent of pH over this range. This pH independence was maintained in the presence of bromide ions. The addition of carbonate—bicarbonate buffer and KBr both reduced the CMC. Shinoda [9] reports that the nature of the counterions of electrolyte added to surfactants has little effect on the CMC, but examination of Table 2 shows that with CTAB, added bromide ions have a greater effect than the carbonate—bicarbonate buffer system.

At pH 9.2 and 30° $0.2M$ bicarbonate—carbonate buffer has an ionic strength of $0.23M$ and is $0.185M$ in bicarbonate anion. This system reduces the CMC from 10^{-3} to $2 \times 10^{-4} M$ in 0.1 and $0.5M$ KBr respectively.

Figure 6 shows a plot of log CMC against log of total bromide ion concentration for the data obtained in the absence of buffer according to equation (1). The linear plot gives a slope of −0.376 with a standard deviation of 0.034 and a correlation coefficient of 0.984. These figures indicate a reasonable linear relationship and the goodness of fit is similar to such plots in the literature [20]. The value of the slope is also similar to the values of about $0.4 - 0.6$ reported by Shinoda [9], and very close to the value of −0.348 which can be obtained from the data of Corrins and Harkins [20] for the effect of NaCl concentration on the CMC of decyltrimethylammonium bromide.

The above result is consistent with the fact that only the counterions of added salt make a contribution to the shift of the CMC, and that the addition of salts decreases the CMC of ionized surfactants, presumably because the
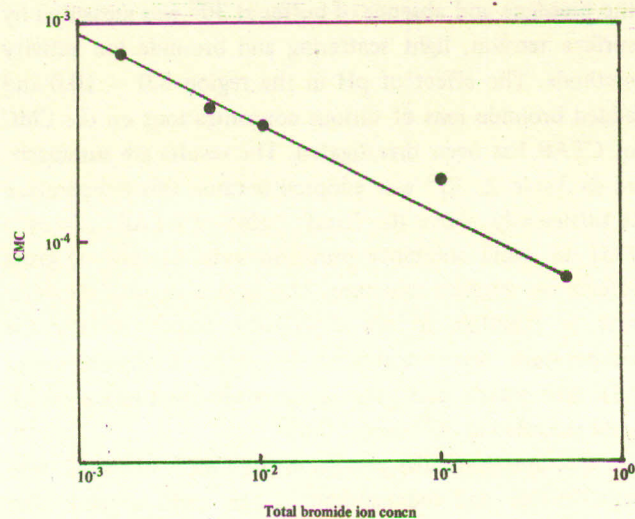

Total bromide ion concn

Fig. 6. log CMC against log total bromide ion conce (C_{Br^-} + CMC).

screening action of the simple electrolytes lowers the repulsive forces between the polar head groups, and less electrical work is required in micelle formation.

REFERENCES

1. E. Ruckenstein and R. Nagarajan, J. Phys. Chem., **79**, 2622 (1975).
2. F. Franks, Water A Comprehensive Treatise, **4**, Chap. 2 (1974).
3. P. Mukerjee and K. J. Mysels, Critical Micelle Concentrations of Aqueous Surfactant Systems" NSRDS — NBS 36, U.S. Government Printing Office, Washington D.C. (1971).
4. P. Mukerjee, Advan. Colloid Interf. Sci., **1**, 241 (1967).
5. F. Franks, M. J. Quickenden, J. R. Ravenhill and H.T. Smith, J. Phys. Chem., **72**, 2668 (1968).
6. J. S. Clunie, J.F. Goodman and P.G. Symons, Trans. Faraday Soc., **63**, 754 (1967).
7. J. A. Stead and H. Taylor, Aust. J. Pharm., **51**, 51 (1970).
8. P. Ekwall and P. Stenius, Acta. Chem. Scand., **21**, 1767 (1967).
9. K. Shinoda, T. Nakagawa, B. Tamamuski and T. Isemura, *Colloidal Surfactants* (Academic, London, 1963).
10. P. Stenius and P. Ekwall, Acta. Chem. Scand., 21, 1643 (1967).
11. P. Ekwall, L. Mandell and P. Solyom, **J. Colloid** Interf. Sci., **35**, 519 (1971).
12. P. Ekwall, I. Danielsson and L. Mandell, Kolloid-Z., **169**, 113 (1960).
13. E. W. Anacker, J. Phys. Chem., **62**, 41 (1958).
14. E. E. Goddard, O. Harva and T. G. Jones, Trans. Faraday Soc., **49**, 980 (1953).
15. I. Cohen and T. Vassiliades, J. Phys. Chem., **65**, 1774 (1961).
16. E. K. Mysels and K.J. Mysels, J. Colloid Sci., 20, 315 (1965).
17. M.J. Schick, J. Phys. Chem., **68**, 3585 (1964).
18. M. J. Schick and A.H. Gilbert, J. Colloid Sci., **20**, 464 (1965).
19. S. Parades, M. Tribout, J. Ferreira and J. Leonis, Colloid Polymer Sci., **254**, 637 (1976).
20. M. L. Corrin and W. D. Harkins, J. Am. Chem. Soc., **69**, 683 (1947).

21. M. E. Hobbs, J. Phys Chem., **55**, 675 (1951).

22. H. V. Tartar, J. Colloid. Sci., **17**, 243 (1962).

23. P. Mukerjee and K. J. Mysels, J. Phys. Chem., **77**, 2938 (1955).

24. E.F. J. Duynstee and E. Grunwald, J. Am. Chem. Soc., **81**, 4540, 4542 (1959).

25. E. Jungermann, *Cationic Surfactants* , Vol. 4, Surfactant Science Series, (Marcel Dekker, New York, (1970).

26. R. G. Bates, *Electrometric pH Determination,* (Chapman/Hall, London, England.1954).

27. Q. A. Trementozzi, J. Polym. Sci., **23**, 887 (1957).

28. C. Seong-Fong, Ph.D. Dissertation, Bristol University, U.K. (1974).

29. L. C. F. Blackman and R. Harrop, Nature, **208**, 777 (1965).

30. A. E. Beg, Ph.D. Thesis, University of Bath, U.K. (1977).

31. W.D. Harkins and A. E. Alexander, *Physical Methods of Organic Chemistry,* edited by Weissberger, (Interscience, New York (1960),Vol I, part I, p. 757.

32. *Handbook of Chemistry and Physics* (The Chemical Rubber Co., Cleveland, Ohio, U.S.A., 1969–70), fifteeth edition.

33. J. T. Pearson and K. J. Humphreys, J. Pharm. Pharmacol. **22**, Suppl., 1265 (1970).

34. C. Smart, J. Polymer Sci. **A3**, 3015 (1965).

35. P. H. Elworthy, A.T. Florence, and C. B. Macfarlane, *Solubilization by Surface Active Agents and its Application in Chemistry and the Biological Sciences,* (Chapman Hall London, 1968), p. 36