# The use of a bromide ion selective electrode for the measurement of counter-ion activity in cationic surfactant solutions

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A bromide ion selective electrode has been used in conjunction with a saturated calomel reference electrode to measure bromide ion activity in solutions of n-decyl, n-dodecyl, n-tetradecyl and n-hexadecyl 1-trimethylammonium bromides at 30°; the critical micelle concentrations of the surfactants were measured by electrical conductance. Calibration of the electrode pair in potassium bromide solutions produced a linear response over the range 0·5 to 5·0p $Br_a^-$ with a slope of 59·1 mV for a 10-fold change in activity. Results for the surfactants were treated to give values for the degree of micellar dissociation; literature values for this quantity reveal wide variation depending on the technique used.

The degree of dissociation ($\alpha$) of ionic micelles required for an adequate description of surfactant solutions may be expressed as the ratio p/n, where p represents the number of effective charges per micelle and n the aggregation number. A variety of experimental techniques have been used for the measurement of $\alpha$. Values obtained from electrode systems employing solid ion exchange membranes (Botré, Crescenzi & Mele, 1959; Ingram & Jones, 1969) and ion selective glass electrodes (Shedlovsky, Jakob & Epstein, 1963; Lawrence & Pearson, 1967; Feinstein & Rosano, 1967) have been reported on a wide range of surfactants. Covington (1969) has reviewed the complete range of ion selective electrodes.

The behaviour of ion selective electrodes in cationic surfactant solutions has not previously been reported and the present work was undertaken to assess the feasibility of using a heterogeneous bromide ion selective electrode in conjunction with a saturated calomel reference electrode for the direct measurement of counter-ion activity in a series of quaternary ammonium surfactant solutions. Electrodes of this type have membranes consisting of finely divided insoluble silver salts dispersed in an inert binder of silicone rubber to give a composition which possesses suitable electrical and mechanical properties and have been developed largely as a result of work by Pungor (1967); further details are given by Moody, Oke & Thomas (1969).

## EXPERIMENTAL

### Apparatus and materials

The bromide ion selective electrode (Pungor-Radelkis, Type OP–Br–711; Protech Advisory Services, Rickmansworth) was used in conjunction with a calomel reference electrode employing a saturated potassium chloride salt bridge (E.I.L., Type RJ23). The output potential produced by the electrode pair was measured with an E.I.L. Vibret Model 46A pH meter and all solutions were equilibrated in a thermostat maintained at 30° $\pm$ 0·1°. This temperature was chosen since it is several degrees

higher than the Krafft point of n-hexadecyl 1-trimethylammonium bromide, the compound of greatest n-alkyl chain length in the homologous series of surfactants used. Electrical conductance measurements for the determination of critical micelle concentration (CMC) were made with a Philips Type PR9500 conductance bridge operating at 1000 Hz using Pye Type 7407 conductance cells with blackened platinum electrodes.

Quaternary ammonium surfactants used were n-decyl, n-dodecyl, n-tetradecyl and n-hexadecyl 1-trimethylammonium bromides ($C_{10,12,14,16}$ TAB's respectively). These were synthesized by direct quaternization of the purest grades of 1-bromo n-alkanes available (Fluka) using anhydrous trimethylamine (B.D.H.). Crude quaternary salts were continuously extracted with ether to remove unchanged alkyl bromide then recrystallized from diethylketone. All physical measurements were made in aqueous solution using triple distilled water.

*Calibration and procedure*

The electrode pair was calibrated by measuring the e.m.f. response in solutions of potassium bromide (AR). A graph of potential (mV) against $pBr_a^-$ ($-\log_{10}$ bromide ion activity) is linear in the region $pBr_a^-$ 0·5–5·0 with a slope of 59·1 mV for a 10-fold change in activity, in good agreement with the theoretical Nernst slope, $2·303RT/F$ of 60·16 mV at 30°. Activity coefficients used are those given by Scatchard & Prentiss (1933). Bromide ion activity of the cationic surfactants was measured by direct reference to this calibration graph which has a range of e.m.f. values from $-160$ to $+120$ mV.

Equilibration times were rapid in potassium bromide solutions, about 30 s for more concentrated solutions, several minutes for dilute solutions. In cationic surfactant solutions equilibration times were somewhat longer (*c* 1–4 min). Since long-chain surfactant ions probably adsorb on to the membrane of the ion selective electrode, frequent checks were made to confirm that the electrode pair produced a satisfactory calibration response in potassium bromide. Particularly after immersion of the electrodes in concentrated solutions of $C_{16}$ TAB response was sluggish but in all cases satisfactory reproduction of the calibration graph was observed.

Reactivity of the electrode to potassium bromide after use in cationic surfactant solutions may be achieved by pre-soaking in concentrated solutions of potassium bromide. The performance can be improved further if the electrodes are lightly wiped with tissue on passing from one solution to the next in order of increasing concentration, rather than rinsing with water which greatly increases the response time.

## RESULTS

Fig. 1 shows a plot of $pBr_a^-$ values against $pBr_c^-$ (i.e. $-\log_{10}$ surfactant concentration) for the various surfactants. For reasons of clarity the curves for the homologues are separated by an interval, and the results for potassium bromide are as for $C_{10}$ TAB including the extrapolated portion at high concentrations, shown as the broken line of the figure. Behaviour as conventional 1:1 electrolytes is apparent up to the CMC's of the surfactants (denoted by arrows), when marked positive deviation of $pBr_a^-$ is observed, an effect attributable to the strong binding of counter-ions to the micelles. Such counter-ions do not contribute therefore to the development of electrode potential and may be regarded as kinetic entities with the micelles. Since
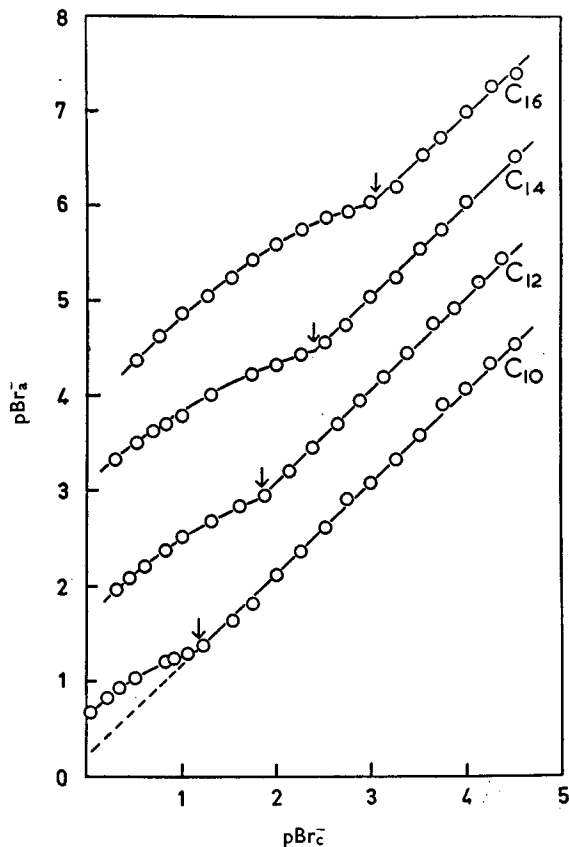
FIG. 1.  Graph of $pBr_a^-$ against $pBr_c^-$ for the $C_{10,12,14,16}$, TAB surfactants.  $pBr_a^-$ [points [for the $C_{12,14,16}$, compounds are increased by +1, +2 and +3 units respectively to prevent the curves overlapping.  Data for KBr is the same as for the pre-CMC line for $C_{10}$ TAB plus the extrapolated portion (broken line).  The arrows denote the CMC's of the surfactants which occur at $pBr_c^-$ values of 1·17, 1·84, 2·39 and 3·05 for the $C_{10,12,14,16}$, TAB's respectively.

$a_s/C = \gamma_{expt}$, where $a_s$ = activity of counter-ions, C = concentration of surfactant and $\gamma_{expt}$ = apparent experimental activity coefficient, the data shown in Fig. 1 may readily be used to give a series of values of $\gamma_{expt}$ as a function of concentration. It is necessary to assume throughout that the mean ionic activity coefficient at any given concentration is identical with the single ion activity coefficient (Guggenheim, 1930), and that with sufficient accuracy, 0° data can be used at 30°.  A further assumption is implicit, namely that the liquid junction potential between saturated KCl and surfactant solution is zero.

Using the theoretical treatments of Botré & others (1959) and Ingram & Jones (1969), the counter-ion activity may be written as:

$$a_s = C\,\gamma_{expt} = \gamma_s\,[C_o + \alpha\,(C - C_o)]$$

where $\gamma_s$ is the activity coefficient and $C_o$ the CMC.
    Therefore:

$$\gamma_{expt} = \gamma_s\,(C_o/C)\,(1 - \alpha) + \alpha\gamma_s$$

from which $\alpha$ may be found using the relation $\alpha = C_o/(S/I + C_o)$, where S and I are

the slope and intercept respectively of a plot of $\gamma_{expt}$ against $C^{-1}$ using values above the CMC (below the CMC the plot is not linear).

Values of $\alpha$ obtained in this manner are given in Table 1 together with literature values. Also shown are the CMC's of the surfactants obtained from plots of specific conductance against concentration; this method gives values which are more precise than those obtainable from the logarithmic data of Fig. 1. Slopes and intercepts involved in the calculation of $\alpha$ were computed using the method of least squares.

## DISCUSSION

Since no definitive values for $\alpha$ are available, Table 1 serves only to show the range of values observed using a variety of different techniques. The degree of dissociation of ionic micelles decreases with increasing chain length of the surfactant. This may be attributed to increased inter-chain attraction leading to closer packing of the ionic head groups in the micelle, whence more counter-ions become strongly bound to reduce the increased ionic repulsion. The degree of dissociation ($\alpha$) is also

Table 1. *Derived values of $\alpha$, and values of critical micelle concentrations obtained from plots of specific conductance against concentration*

| | | $C_{10}$ TAB | $C_{12}$ TAB | $C_{14}$ TAB | $C_{16}$ TAB |
|---|---|---|---|---|---|
| CMC (molar) | | 0·0670 | 0·0145 | 0·0041 | 0·0009 |
| $\alpha$ (this work) | | 0·27 | 0·24 | 0·13 | 0·12 |
| | Ref. 1 | 0·224 | 0·193 | 0·131 | 0·091* |
| | Ref. 2 | — | 0·256 | — | — |
| $\alpha$ | Ref. 3 | — | 0·22 | 0·15 | — |
| (lit.) | Ref. 4 (a) | — | — | 0·249 | — |
| | Ref. 4 (b) | — | — | 0·321 | — |
| | Ref. 5 | — | — | — | 0·11 |

* In the presence of 0·013 M KBr.

*Notes on references and techniques*

1. Mysels (1955). Refined calculations based on the light scattering measurements of Debye (1949).
2. Ingram & Jones (1969). Membrane potential measurements employing BDH Permaplex A-20 anion exchange membranes.
3. Padday (1967). Potentiometric method using a calomel/Ag-AgBr cell.
4. Cushman, Brady & McBain (1948). Values obtained from (a) osmotic and (b) conductance data.
5. Vold (1950). Application of the Law of Mass Action to osmotic data.

affected by the presence of additives (or impurities) which become solubilized in the surfactant micelles or by the presence of inorganic salts (Lawrence & Pearson, 1967). In the present work, measurements of potential were recorded in quiescent solutions since stirring caused the readings to drift to higher values. The high value for $C_{12}$ TAB reported by Ingram & Jones (1969) may be due to the fact that their solutions were vigorously stirred until the e.m.f. of the cell had reached a maximum. Because various techniques may respond to a different extent to the counter-ions present in the "free" or "bound" state, it is not yet possible to define the proportion of counter-ions in the electrical double layer that are responsible for the observed e.m.f. produced by the electrode pair.

The data in Fig. 1 do not provide information about the possible formation of pre-CMC aggregates which have been previously reported for certain N-alkylpyridinium

halides containing a non-ionic polar group in the pyridinium ring (Butler, Stead & Taylor, 1969) and for $C_{16}TAB$ (Bair & Krauss, 1951; McDowell & Krauss 1951). In spite of the limitations of the method we consider it of potential value in surfactant systems, in problems of solubilization and for the analysis of quaternary ammonium surfactants.

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