Pergamon

0039-9140(93)E0045-F

Talanta, Vol. 41, No. 5, pp. 765–773, 1994

0039-9140/94 $7.00 + 0.00

PHYSICOCHEMICAL STUDIES OF THE CETYLTRIMETHYLAMMONIUM BROMIDE MICELLAR SYSTEM USING A BROMIDE SELECTIVE ELECTRODE

ATHANASIOS M. GERAKIS and MICHAEL A. KOUPPARIS*
Laboratory of Analytical Chemistry, Department of Chemistry, University of Athens, Panepistimiopolis, Athens 15771, Greece

(*Received* 7 *August* 1993. *Revised* 25 *November* 1993. *Accepted* 25 *November* 1993)

Summary—The use of the bromide selective electrode in physicochemical studies of the cationic micellar system of cetyltrimethylammonium bromide (CTAB) is described. Potentiometric methods and appropriate equations have been developed and used to determine the critical micellar concentration, the ionization degree, and the apparent ion-exchange constants of various anions (fluoride, chloride, hydroxide, acetate, nitrate, sulfate and borate). The interaction of the cationic micelles of CTAB with various species [the lipophilic reagent 1-fluoro-2,4-dinitrobenzene, the anionic succinate and the cationic tris-(hydroxymethyl)-aminomethane] was monitored through the measurement of the changes in the concentration of the free bromide counterions.

Micellar systems [solutions of amphiphiles (surfactants) at concentrations above their critical micellar concentration, cmc] exhibit some very interesting properties, which have found extensive use in Analytical Chemistry.[1–3] Thus, micellar systems (often referred to as organized assemblies or ordered media) can solubilize substances (reagents or analytes) with low solubility, concentrate ions and molecules on and/or within the organized assemblies (micelles), modify equilibria and acid–base or redox properties, alter reaction rates and reaction mechanisms, enhance spectroscopic properties, and influence the stereo-selectivity of chemical process (*e.g.* separation of mixtures). In all these analytical applications the knowledge of the interaction of the micellar system with the analytical chemical system (analyte, reagent, buffer species, solvent, catalyst, interferents, sample matrix, *etc.*) is essential for the optimization of the micellar analytical procedure (choice of the optimum micellar system and its concentration, choice of the optimum buffer system, prediction and explanation of the appearance of interferences, prediction of the applicability of a micellar analytical procedure to other substances, *etc.*).

The most popular micellar systems used in analytical applications are the ionic ones, *i.e.* cetyltrimethylammonium bromide (CTAB), cetyl-pyridinium chloride (CPC) and the sodium dodecylsulphate (SDS). In this paper, we propose the use of membrane electrodes, selective to the counterion of the ionic micellar system, to study the physicochemical parameters of the micellar system, *i.e.* critical micellar concentration (cmc), degree of ionization (α), and the ion-exchange constant, $K_{X/Y}$, of the counter ion Y with an ionic species X. The CTAB cationic micellar system was chosen as a model and its physicochemical study was achieved using the bromide selective electrode.

Theoretical aspects of physicochemical parameters of micellar systems

Amphiphiles or surfactants are molecules possessing both a hydrophilic (P) and a hydrophobic (R) regions on their molecule, and are often described as $R-P$. In aqueous solutions and at concentration higher, but close to their critical micellar concentration (cmc), the amphiphiles form spherical aggregates characterized by the so-called aggregation number N (the average number of monomers per micelle). In the case of cationic surfactants (like CTAB), of the general formula $R-P^+Y^-$, the cationic micelles are formed with polar headgroups P of the surfactant molecules arranged in the outer spherical shell with a certain number of anionic counterions Y (this shell is called the Stern

---

*Author to whom correspondence should be addressed.

layer), while the hydrophobic hydrocarbon tails (R) are oriented in the interior of the aggregate. The average number (m) of the ions (counter ions Y^- and any foreign ions X^-) associated with any micelle is described by the degree of ionization, α, of the micelle

$$\alpha = 1 - \left(\frac{m}{N}\right). \qquad (1)$$

The alteration of the rate of reactions carried out in micellar systems has been well known for many years. The terms micellar catalysis and micellar inhibition have been used to describe these phenomena.[4] Many attempts have been made to explain the micellar catalysis of reactions. Among the most successful models and theories for micellar catalysis are the so-called pseudophase ion-exchange model (PPIEM),[5] the transition state theory (TST)[6] and the Poisson–Boltzmann distribution (PBD).[7]

Compounds, with low aqueous solubility but high solubility in apolar solvents, can be solubilized in an aqueous micellar system (within the core and/or on the surface of micelles), resulting in an homogeneous aqueous micellar solution. This phenomenon is considered as a binding process and can be expressed by the corresponding binding constant, K_S,

$$K_S = \frac{[S]_m}{[S]_w[M]}, \qquad (2)$$

where $[S]_m$ and $[S]_w$ are the concentration of the bound to the micelles and the free in the aqueous phase of the species S, respectively. [M] is the micellar concentration, free of S molecules. The value of K_S of a series of compounds solubilized in a micellar system, ionic or nonionic, represents the selectivity for binding of these compounds. Binding constants can be determined experimentally by several techniques, such as micellar liquid chromatography,[8] micellar electro-kinetic capillary chromatography,[9] and acid–base potentiometric titrimetry in micellar systems (for acids and bases through the influence of micelles on the ionization constant).[4,10]

In the case of ionic species X, in ionic micellar systems, the electrostatic interaction is the main process involved. An ionic molecule is repelled by an ionic micelle with a charge of the same sign and attracted by oppositely charged micelles. This process is described by the pseudophase ion exchange model[5]

$$X_f + nY_b \rightleftharpoons X_b + nY_f \qquad (3)$$

and expressed by the so-called ion-exchange constant $K_{X/Y}$

$$K_{X/Y} = \frac{[X_b][Y_f]^n}{[X_f][Y_b]^n}, \qquad (4)$$

where n is the ratio of the charges ($n = Z_X/Z_Y$), and b and f refer to bound and free activities (concentrations) of the X and Y species, respectively.

Like the binding constants (equation 2), the value of the $K_{X/Y}$ expresses the selectivity for the attraction between the ionic species X and the oppositely charged micelle $R - P^{\pm}Y^{\pm}$. $K_{X/Y}$ has been utilized as a semiempirical expression by Romsted[11] and as the selectivity ratio f by Larsen and Magid.[12] Several analytical methods have been proposed to determine $K_{X/Y}$, such as the aromatic counter-ion method,[13] the reactive counter-ion method,[14] the ferrithiocyanate method,[15] ultrafiltration and fluorimetry.[16] Most of these methods utilize a third species acting as an analytical probe, which adds some more equilibria in the micellar system. Since both concentrations and activities are used for $K_{X/Y}$ calculations, their values vary with the experimental conditions and the method used. Therefore, they should be referred to as apparent ion-exchange constants, $K^{app}_{X/Y}$.

The value of an $K^{app}_{X/Y}$ depends on several factors, such as the effective micellar charge ψ^0_X and ψ^0_Y sensed by the ions X and Y, respectively, the activity coefficients in the Stern layer and consequently on the concentrations of the surfactant and the added salt of X, the temperature, and of course on the real thermodynamic $K_{X/Y}$ of equation (4). The influence of the aforementioned experimental factors increases considerably by the exponation to the ratio Z_X/Z_Y.[16]

Using the basic concepts of the PPIEM model, the extent of micellar catalysis of a reaction depends on a combination of the following factors: the surfactant concentration in the form of micelles, C_D, the binding constant, K_S, and/or the apparent ion-exchange constant, $K^{app}_{X/Y}$, between the reacting species $X^{\pm}$ and S ($X^{\pm} + S \rightarrow$ products). High values of these factors result in a remarkable concentration of the reactants in the micellar pseudophase and consequently an increase of the reaction rate. The extent of micellar catalysis is expressed by the reaction rate constant in the micellar system, $k_{\psi,m}$, which is a function of K_S, $K^{app}_{X/Y}$, C_D and of course the uncatalyzed reaction rate constant k_{ψ}.

The critical micellar concentration, cmc, is an important parameter of a micellar system, and the knowledge of its exact value very important in describing and studying a micellar system. Several methods have been described for cmc determination[17] based on the considerable changes of several physicochemical properties when micelles are formed (surface tension, interfacial tension, osmotic pressure, equivalent conductivity, solubility of a compound with low solubility in pure water *etc.*).

Ion-selective electrodes (ISEs) are chemical sensors capable to directly monitor the activity (concentration) of the free (unbound) ion of interest in a wide concentration range in the presence of the bound ion. This great advantage favoured the application of ISEs in binding studies of ionic micromolecules to macromolecules, such as cyclodextrins,[18] proteins[19] and surfactants.[20,21] In this paper we extend the use of ISEs in the physicochemical study of ionic micellar systems.

EXPERIMENTAL

Reagents and solutions

Deionized-distilled water was used throughout for the preparation of all solutions. A $0.100M$ stock solution of cetyltrimethylammonium bromide (CTAB) (Sigma 99% crystalline) was prepared and used to prepare working solutions by appropriate dilutions. Stock solutions ($0.10M$) of the various anions used in the study (bromide, hydroxide, chloride, nitrate, fluoride, acetate, benzoate, sulfate, succinate, borate and mono- and dibasic phosphate) were prepared by dissolving the appropriate mass of the corresponding sodium salt (Merck) in water. A $0.43M$ (8% w/v) stock solution of 1-fluoro-2,4-dinitrobenzene (FDNB, Sigma) in acetone (p.a. Merck) and $0.1M$ solution of tris-(hydroxymethyl)-aminomethane (TRIS) in water were also prepared and used for the study of the interactions of CTAB with a hydrophobic non-ionized molecule and the species of a cationic buffer.

Apparatus

A solid-state bromide selective electrode (ORION model 94-35) was used throughout for the potentiometric determination of the free bromide counterion of CTAB. The potential of the electrode was measured using a digital pH/mV-meter (ORION model 801, with a readability of 0.1 mV) against a double-junction Ag/AgCl reference electrode (Orion model 90-02). In experiments involving nitrate a calomel reference electrode with $1M$ KCl internal filling solution was used. When not in use, the bromide ISE was immersed in distilled water. All measurements were carried out in a double-walled 75-ml beaker thermostated at 25(±0.2)° under continuous stirring. The potentiometer was interfaced to a microcomputer (Amstrad CPC 6128).

Procedures

Response (calibration) curve of the bromide ISE. Microvolumes of $5.00 \times 10^{-3}M$ NaBr were added successively in 50 ml water, using Hamilton microsyringes, to generate a bromide concentration range from 5×10^{-4} to $5 \times 10^{-3}M$. The Nernst equation $E = E_{\mathrm{ct.}} - S\log[\mathrm{Br}^-]$ was calculated by least-squares linear regression analysis. The calibration curve was constructed every working day.

Determination of critical micellar concentration (cmc) and ionization degree (α). Microvolumes of a $0.05M$ CTAB working solution were added successively in 50 ml water using microsyringes to generate a total surfactant concentration (C_{T}) range from 5×10^{-4} to $3 \times 10^{-3}M$ and the stabilized potential was measured. The $E_{(\mathrm{i})} - C_{\mathrm{T,(i)}}$ data were used to estimate cmc and α as shown below in data analysis.

Monitoring of the free concentration of bromide during the addition of various species. Microvolumes of a mixed working solution of CTAB $5.0 \times 10^{-3}M$ and the tested species $[\mathrm{X_T}]_{(0)}M$, were added successively in 50 ml of a CTAB solution of $5 \times 10^{-3}M$ and the potential was measured after its stabilization (after a few seconds). The $E_{(\mathrm{i})}$ values were converted to $[\mathrm{Br_f^-}]_{\mathrm{i}}$, using the response curve of the electrode, and the $[\mathrm{Br_f^-}]_{\mathrm{i}} - [\mathrm{X_T}]_{\mathrm{i}}$ plots were constructed. In the case of the addition of FDNB, microvolumes of its pure acetonic stock solution were added in 50 ml of CTAB solution with practically no volume change. A previously prepared mixed FDNB–CTAB working solution was not used to prevent the micellar catalysed hydrolysis of FDNB.

Determination of the apparent ion-exchange constants between various anions and Br^- *in CTAB micellar system.* From the $E_{(\mathrm{i})} - [\mathrm{X_T}]_{(\mathrm{i})}$ data obtained during the addition of the anionic species, as described above, the value of $K^{\mathrm{app}}_{\mathrm{X/Y}}$ was estimated as shown below in data analysis. C_{T} was $5 \times 10^{-3}M$ and $[\mathrm{X_T}]_{(0)}$ $3 \times 10^{-2}M$ for the sulfate experiment and $5 \times 10^{-2}M$ in all the other experiments. In addition, for the chloride and sulfate anions a series of experiments with varying the C_T concentrations (3×10^{-3}–$8 \times 10^{-3}M$) were carried out.

Data analysis

The generalized pseudophase ion-exchange model[5] was used to describe the equilibria existing in the cationic micellar system of CTAB.

At surfactant concentrations higher than the cmc, aggregation occurs and the concentration of the free (not bound with electrostatic attraction to the Stern layer) bromide counterions, $[\mathrm{Br_f^-}]$, is given by the equation

$$[\mathrm{Br_f^-}] = \alpha C_D + \mathrm{cmc}, \tag{5}$$

where C_D is the concentration of the surfactant in micellar form ($C_D = C_T - \mathrm{cmc}$). Substitution of C_D in equation (5) results in equation (6)

$$[\mathrm{Br_f^-}] = \alpha C_T + \mathrm{cmc}(1 - \alpha). \tag{6}$$

It is clear from equation (6) that a plot of $[\mathrm{Br_f^-}]$ (calculated from the $E_{(i)} - C_{T,(i)}$ data using the calibration curve) *vs.* $C_{T,(i)}$ is a straight line with a slope equal to the ionization constant α and an intercept to the y axis equal to the product $(1 - \alpha)$cmc from which the critical micellar concentration can be calculated (linear method).

In addition to the above method, in which both α and cmc are calculated, the cmc can also be estimated directly from the $E_{(i)} - \log C_{T(i)}$ plot. This plot consists of two straight lines, one before cmc with a slope almost equal to the slope of bromide ISE (S) and one after cmc with a slope lower than S (because of the association of $\mathrm{Br^-}$ to the cationic micelles). Therefore, cmc can be found either graphically (as the C_T corresponding to the intersection of the two straight lines) or by calculation applying linear algebra to the linear equations of the two lines (computation method).

In mixed solutions of CTAB, at concentrations above its cmc containing the foreign anion X, the equilibria of equation (3) takes place, which is expressed by the $K^{\text{app}}_{X/Y}$ constant (equation 4). The following equations are valid in a such system

$$C_T = C_D + \mathrm{cmc} \tag{7}$$

$$[\mathrm{Y_T}] = C_T = [\mathrm{Y_b}] + [\mathrm{Y_f}] \tag{8}$$

$$[\mathrm{X_T}] = [\mathrm{X_f}] + [\mathrm{X_b}] \tag{9}$$

$$[\mathrm{X_b}] = \frac{[\mathrm{Y_f}] - \alpha C_D - \mathrm{cmc}}{n} \tag{10}$$

(if n counterions are replaced by one anion X, $n = Z_X/Z_Y$)

$$[\mathrm{X_f}] = [\mathrm{X_T}] - \frac{[\mathrm{Y_f}] - \alpha C_D - \mathrm{cmc}}{n}. \tag{11}$$

Substituting equations (7)–(11) in equation (4), we have

$$\boxed{K^{\text{app}}_{X/Y} = \frac{\{[\mathrm{Y_f}] - \alpha C_T - \mathrm{cmc}(1 - \alpha)\}[\mathrm{Y_f}]^n}{\{n[\mathrm{X_T}] - [\mathrm{Y_f}] + \alpha C_T + \mathrm{cmc}(1 - \alpha)\}(C_T - [\mathrm{Y_f}])^n}.} \tag{12}$$

Equation (12) can be converted to a simple form: $a = b \times K^{\text{app}}_{X/Y}$, where a is the numerator and b the denominator of equation (12). It is clear that a plot of a *vs.* b should be a straight line with a slope $K^{\text{app}}_{X/Y}$. Using the data obtained $[\mathrm{Br_f^-}]_{(i)}$- $[\mathrm{X_T}]_{(i)}$ (and the parameters C_T, cmc, n and α) a_i and b_i are calculated and $K^{\text{app}}_{X/Y}$ (the slope of the linear equation) can be estimated using linear least square fitting on the $a_i - b_i$ data.

Equation (12) is valid within the experimental range used under the following assumptions: (1) The value of the cmc and the ionization degree α are constant. (2) The value of the average number of monomers per micelle is constant (*i.e.* constant aggregation number). (3) There is no cooperative interactions between ion–ion and ion–head group of the micelles. (4) Ion–ion exchange rates are rapid relative to the lifetime of the micelle. (5) Activity coefficients approaches unity, therefore concentrations are equal to activities.

RESULTS AND DISCUSSION

Calibration (response) curve of the bromide ISE

The bromide ISE, during the 6 months period of this study, showed Nernstian response with a slope of 55.0–60.0 mV/$\mathrm{pC_{Br}}$, with a least linear concentration limit of $1 \times 10^{-5}M$. The equation of a typical calibration curve near the end of the 2 years operative life of the electrode and in a bromide concentration range of 1×10^{-5}–$3.5 \times 10^{-3}M$ was $E = -162(\pm 1) - 55.2(\pm 0.3)\log[\mathrm{Br_f^-}]$, $r = 0.9999$, $n = 15$. The stability of the electrode was excellent in both aqueous and micellar solutions. Since the total ionic strength was always less than $0.01M$, concentrations are used instead of activities.

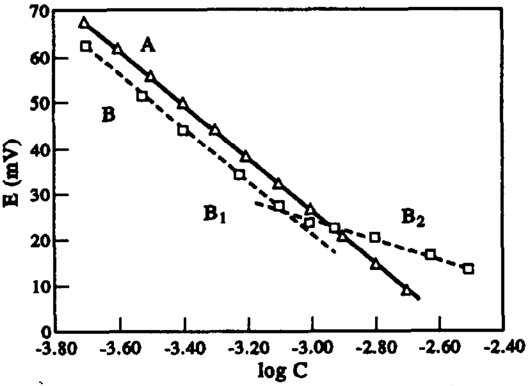

Fig. 1. Response curve of the bromide ion selective electrode in (A) aqueous solutions of NaBr (△), and (B) aqueous solutions of CTAB (□), for the determination of cmc and ionization degree.

Determination of critical micelle concentration and ionization degree of CTAB

Figure 1 shows the response of the bromide ISE in aqueous NaBr (A, calibration curve) and CTAB solutions (B). As shown, the response curve in CTAB solutions consists of two straight lines intersected at a concentration equal to $8.7 \times 10^{-4} M$ (this is the cmc of CTAB by the graphical method). The slope of the linear section B1 is almost equal to the slope of the calibration curve A, (Table 1a), showing that complete dissociation of CTAB occurs at concentrations lower than cmc. At concentrations of CTAB above its cmc (linear section B2) the slope decreases to about one third of the slope of the response curve A, revealing the association of bromide anions to the formed cationic micelles. Applying linear algebra to the equations of the two linear segments B1 and B2 (Table 1a) a value of cmc equal to that with the graphical method was found ($8.7 \times 10^{-4} M$). Finally, using equation (6) a value of $1.15(\pm 0.02) \times 10^{-3} M$ for cmc and 0.23 ± 0.02 for the ionization degree were found for CTAB (Table 1b). The high value of r found ($r > 0.999$) shows the validity of equation (6). These values are very closed to those appeared in the literature, such as the works by Larsen *et al.*[22,23] also performed with a bromide ISE.

The proposed potentiometric linear method is superior, since in a single set of experiments both the cmc and the ionization degree are obtained. The precision was very good for such studies, 1.7% RSD for cmc and 8.7% RSD for α.

The slope of section B_2 (S_{B2}) of the response curve (Fig. 1) in the presence of micelles can be predicted from the slope of curve A (S_A) and the value of ionization degree found: $S_{B2} = S_A \times \log(\alpha \times 10) = -60.4 \times \log(0.23 \times 10) = -21.8$ mV/pC [identical to that found experimentally (−22 mV/pC)].

Monitoring of the changes of the activity (concentration) of free bromide counterions during the interaction of various species with CTAB micelles

Using the bromide ISE it is possible to monitor the free bromide activity (concentration) $[Br_f^-]$, during the addition of various species (ionic or non-ionic) in solutions containing

Table 1a. Typical equations of the response curve of the bromide ISE, $E = f(\log C)$ in CTAB and NaBr solutions (25°)

	Concentration range (M)	Slope (±SD*)	Intercept (±SD*)	Correlation coefficient (r)
NaBr				
A	1.0×10^{-5}–3.5×10^{-3}	-60.4 ± 0.3	-166 ± 1	0.9998
CTAB				
B1	1.0×10^{-5}–1.0×10^{-3}	-58.2 ± 0.3	-162 ± 1	0.9999
B2	1.2×10^{-3}–3.5×10^{-3}	-22 ± 1	-40 ± 3	0.995

*Within run standard deviation.

Table 1b. Determination of the cmc and the ionization degree α of CTAB using the proposed potentiometric method

	Degree of ionization (±SD)*	cmc (M) (±SD)*
Proposed methods		
(i) Graphical method	—	$8.7(\pm 0.6) \times 10^{-4}$
(ii) Computation method	—	$8.7(\pm 0.2) \times 10^{-4}$
(iii) Linear method	0.23 ± 0.02	$1.15(\pm 0.02) \times 10^{-3}$
Range of values found in literature	0.15 – 0.25	7.0×10^{-4}–1.5×10^{-3}

*Between run standard deviation for three experiments.

CTAB micelles. We monitored the interaction of CTAB micelles with the species of the cationic buffer TRIS, some typical anions (sulfate, nitrate, succinate, fluoride, chloride, borate, benzoate, mono- and di-basic phosphate, acetate and hydroxide) and the lipophilic non-ionic reagent FDNB. The latter was chosen since its reactions with various substances (amines, phenols and thiols) are strongly catalyzed by CTAB micelles.[24-26]

The plots $[Br_f^-]$ *vs.* $[X]_T$ for some of the tested anionic species (SO_4^{2-}, NO_3^-, Cl^- and F^-) are shown in Fig. 2. Similar plots for the cationic TRIS, the non-ionic FDNB and the anionic succinate are shown in Fig. 3. It is clear that the anionic sulfate, nitrate, chloride and fluoride displace bromide counterions because of their binding to the cationic micelles and thus increase the $[Br_f^-]$ to higher values. From all tested anions, only succinate showed, unexpectedly, no displacement of bromide. This behaviour may be attributed to its structure, a chain carboxylic acid anion. The cationic TRIS, as expected, caused no displacement of bromide. The addition of FDNB molecules (surrounded by acetone molecules) caused a decrease of bromide, which may be attributed to changes of the size, the cmc or the ionization degree of the CTAB micelles, because of the solubilization of the lipophilic FDNB molecules and the acetone solvent in the micellar phase. The other anions tested (hydroxide, borate, acetate, benzoate and phosphates) also showed displacement of bromide.

Determination of apparent ion exchange constants

The monitoring of the bromide displacement during the addition of various anions in a CTAB micellar solution (Figs 3 and 4), is a qualitative depiction of the anions–cationic micelles interactions and an indication of the strength of the ion-exchange process. A quantitative measure of the interaction is the apparent ion-exchange constants $K^{app}_{X/Y}$ which can be estimated using equation (12). The tested anions were selected because they are very common in micellar catalyzed reaction systems and also their interference to the bromide ISE is negligible.

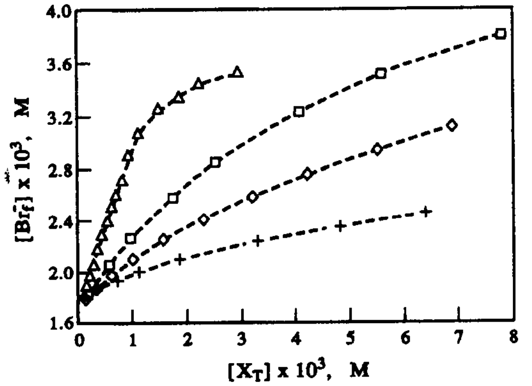

Fig. 2. Monitoring of the bromide displacement during the addition of (△) SO_4^{2-}, (□) NO_3^-, (◇) Cl^- and (+) F^-.

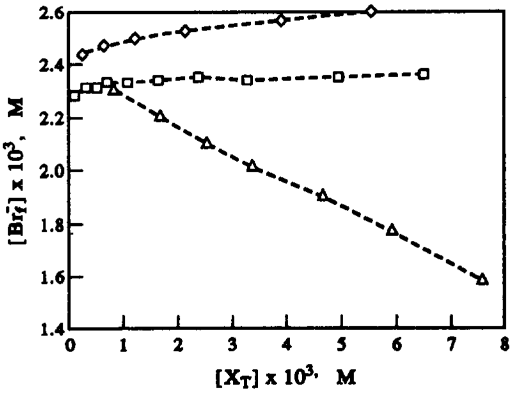

Fig. 3. Monitoring of the free bromide concentration during the addition of (◇) TRIS, (□) succinate and (△) FDNB.

Figure 4 shows typical plots for the calculation of the corresponding apparent ion exchange constants according to equation (12) for F^- and NO_3^-. The very good linearities ($r > 0.997$) and the practically zero values of intercepts at the y axis prove the validity of the model and the proposed potentiometric method as described by equation (12). This method was successful for the anions shown in Table 2. Within run precision was less than 5% RSD, while between run precision was about 10%.

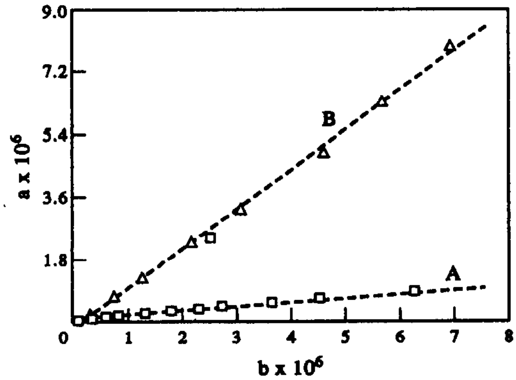

Fig. 4. Plots of a *vs.* b (see equation 12) for the determination of $K^{app}_{X/Y}$ of (A) F^- (□), (B) NO_3^- (△). Equation: (A) $a = 8.2(\pm 0.3) \times 10^{-7} + 6.33(\pm 0.09) \times 10^{-2} b$, $r = 0.9994$. (B) $a = -1.4(\pm 0.3) \times 10^{-7} + 1.08(\pm 0.02) b$, $r = 0.9998$.

Table 2. Apparent ion-exchange constants of various anions for CTAB micellar system at 25° using the proposed potentiometric method and comparison with values from the literature ([CTAB] = $5.0 \times 10^{-3}M$)

Ion X	$K^{app}_{X/Br}$ (proposed method)	$K_{X/Br}$ (found in literature)	Method
F^-	0.063	0.044	a
		0.047	b
Cl^-	0.27	0.20	a
		0.23	b
OH^-	0.099	0.048	a
		0.068	b
CH_3COO^-	0.16	0.098	a
		0.10	b
NO_3^-	1.08	1.1	a
		1.0	b
SO_4^{2-}	0.98	0.62	a
		250	c
		75	c
$H_2BO_3^-$	0.082	—	—

Method used: (a) aromatic counterion method;[13] (b) reactive counterion method;[14] (c) ultrafiltration/fluorimetry,[16] for two different concentration ratios.

As shown in Table 2 the values obtained by the proposed potentiometric method is in good agreement with those obtained by other methods and described in the literature, except in the case of sulfate. A great variety of values has been reported for this anion ranging from 0.62 to 250 (our result 0.98). This disagreement for the bivalent anion of sulfate is due to the dramatic effect of ionic strength on its apparent ion exchange constant, as well as on the approximations made on the models used for calculation.

The method failed to calculate the apparent ion-exchange constant $K^{app}_{X/Br}$ for the anions: benzoate, $H_2PO_4^-$ and HPO_4^{2-} (the plots of equation 12 were not linear). This failure of the method may be explained by the character of the anions which effects the size and the physicochemical parameters of the micelles. The lipophilic benzoate anion is bound to the micelles, not only because of electrostatic attraction (on the surface of the micelles) but also because of non-electrostatic interactions (within the micelles). Phosphate species are weak acids, the ionization degree of which is increased upon binding with the micelles. Therefore, more than one species ($H_2PO_4^- + HPO_4^{2-}$ or $HPO_4^{2-} + PO_4^{3-}$) exist in the micellar system, respectively. The ion-exchange process is very complicated and the one species model of equation (12) is not valid.

In order to examine the dependence of apparent ion exchange constants on the surfactant concentration, ion exchange experiments were carried out for chloride and sulfate at various CTAB concentrations. As shown in Table 3, the surfactant concentration (and consequently the ionic strength of the Stern layer and the total micellar charge sensed by the anions) effects more drastically the value of the bivalent sulfate anion than the monovalent chloride ion. These results reveal that the values found were apparent ones and referred to certain experimental conditions.

Effect of foreign ions on the cmc and the ionization degree of CTAB

It is well known that the cmc and the ionization degree of a micellar system may vary in the presence of a foreign ion. In order to examine this phenomenon, experiments for the calculation of cmc and α were carried out in the presence of various constant concentrations of

Table 3. Apparent ion exchange constants for chloride and sulfate in aqueous solutions of CTAB at various concentrations (C_T) of the surfactant (25°)

C_T (M)	$K^{app}_{X/Br}$
	chloride
3×10^{-3}	0.19
4×10^{-3}	0.22
5×10^{-3}	0.26
8×10^{-3}	0.30
	sulfate
5×10^{-3}	0.98
6×10^{-3}	0.68
8×10^{-3}	0.50

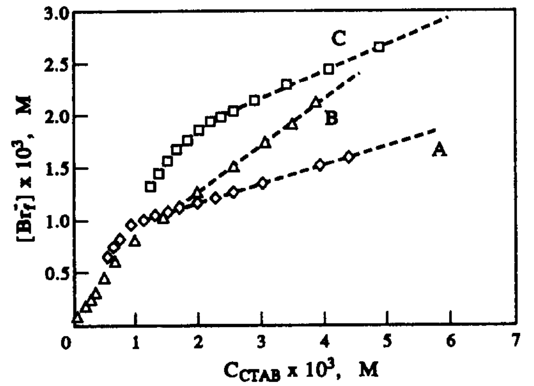

Fig. 5. Plots of $[Br_f^-]$ *vs.* C_{CTAB} for the determination of cmc and α in the absence and the presence of foreign anions. (A): In the absence of foreign anions; (B) in the presence of F^- ($3 \times 10^{-3}M$); (C) in the presence of benzoate ($2 \times 10^{-4}M$).

fluoride and benzoate (two very different anions) using the proposed linear method.

As described above the bromide ISE is capable to sense the formation of micelles in solutions containing CTAB. In the absence of any foreign anion the relationship between $[Br_f^-]$, cmc, α and C_T is given by equation (6). In the presence of a foreign anion X^{Z_X} equation (6) is not valid, since the bound foreign ion $[X_b]$ must be taken into account. In this case equation (6) is modified to:

$$[Br_f^-] = \alpha C_T + \text{cmc}(1 - \alpha) + n[X_b], \qquad (6a)$$

where $n = (Z_X/Z_Y)$. The term $n[X_b]$ can be neglected (equation 6a collapses to equation 6), when the values of total foreign ion concentration $[X_T]$, the ion-exchange constant $K^{app}_{X/Y}$ and the micellar concentration C_D are not very high.

Figure 5 shows some of obtained plots ($[Br_f^-]$ *vs.* CTAB conc.) in these experiments. As shown cmc seems to change in the presence of foreign anions. It decreases in the presence of fluoride and increases in the presence of benzoate. Table 4 shows the results of the calculated values of cmc and α at the tested concentrations of the two foreign anions. The different effect of the two anions on cmc and α, must be attributed to the size of the anions, the high lipophilicity of the benzoate and the high hydrophilicity of the fluoride.

Table 4. Determination of the apparent cmc and ionization degree (α) of CTAB, in the presence of various concentrations of sodium fluoride and sodium benzoate, using the linear method* at 25°

Salt conc. (M)	cmc (M)	α
No added salt	1.15×10^{-3}	0.23
Sodium benzoate		
2.0×10^{-4}	1.84×10^{-3}	0.25
4.0×10^{-4}	2.27×10^{-3}	0.29
8.0×10^{-4}	2.60×10^{-3}	0.33
Sodium fluoride		
2.0×10^{-3}	7.38×10^{-4}	0.41
3.0×10^{-3}	6.26×10^{-4}	0.43
5.0×10^{-3}	5.78×10^{-4}	0.45
1.0×10^{-2}	4.39×10^{-4}	0.50

*Correlation coefficients r of equation (6a) were greater than 0.99.

CONCLUSIONS

From the above results it is clear that an electrode selective to the counterion can be very useful to study the physicochemical behaviour of the corresponding micellar system: (a) determination of cmc, ionization degree and apparent ion-exchange constants; (b) study of the effect of foreign ions on apparent cmc and α; (c) study of the effect of various buffer species and reactants on the micellar ionic surface. The potentiometric study is very simple, since the free concentration of the counterion is directly available from the potential measurements. Other commercial ISEs useful for similar studies are the chloride ISE for the cetylpyridinium chloride and sodium ISE for the sodium dodecylsulfate surfactant. A limitation of the technique is the interference which may be caused by the studied ions on the ISE. For example, in this work we were unable to study the bromide displacement caused by the sulfide and thiol anions to the CTAB micelles due to their serious interference to the bromide ISE. The potentiometric method using a counterion ISE is applicable only to ionic micellar systems and is able to monitor only interactions causing ion-exchange of the counterion. It is also subject to the limitations stated for the validity of equation (12), which describes the pseudo-phase ion-exchange model.

Acknowledgements—We gratefully acknowledge support from the Ministry of Industry, Energy and Technology, General Secretariat of Research and Technology of Greece and the Greek National Drug Organization.

REFERENCES

1. L. J. Cline Love, J. G. Habarta and J. G. Dorsey, *Anal. Chem.*, 1984, **56**, 1132A.
2. E. Pelizzetti and E. Pramauro, *Anal. Chim. Acta*, 1985, **169**, 1.
3. E. Pramauro and E. Pelizzetti, *Trends Anal. Chem.*, 1988, **7**, 260.
4. I. V. Berezin, K. Martinek and A. K. Yatsimirskii, *Russ. Chem. Rev.*, 1973 (Engl. Transl.), **42**, 787.

5. F. H. Quina and H. Chaimovich, *J. Phys. Chem.*, 1979, **83,** 1844.
6. D. Hall, *J. Phys. Chem.*, 1987, **91,** 4287.
7. C. A. Bunton and J. R. Moffatt, *J. Phys. Chem.*, 1985, **89,** 4166.
8. J. Foley, *Anal. Chim. Acta*, 1990, **231,** 237.
9. A. S. Kord, J. K. Strasters and M. G. Khaledi, *Anal. Chim. Acta*, 1991, **246,** 131.
10. A. M. Gerakis, M. A. Koupparis and C. E. Efstathiou, *J. Pharm. Biomed. Anal.*, 1993, **11,** 33.
11. L. S. Romsted, in *Micellization, Solubilization and Microemulsions*, K. L. Mittal (ed.), Vol. 2, p. 509. Plenum Press, New York, 1977.
12. J. W. Larsen and L. J. Magid, *J. Am. Chem. Soc.*, 1974, **96,** 5774.
13. D. Bartet, C. Gamboa and L. Sepulveda, *J. Phys. Chem.*, 1980, **84,** 272.
14. M. Nascimento, S. Miranda and F. Nome, *J. Phys. Chem.*, 1986, **90,** 3366.
15. C. Gamboa, L. Sepulveda and R. Soto, *J. Phys. Chem.*, 1981, **85,** 1421.
16. E. A. Lissi, E. B. Abuin, L. Sepulveda and F. H. Quina, *J. Phys. Chem.*, 1985, **88,** 81.
17. P. Mukejee and K. J. Mysels, in *Critical Micelle Concentrations of Aqueous Surfactant Systems*, NSRDS-NBS 36. Superintendent of Documents, U.S. Government Printing Office, Washington, DC.
18. G. Valsami, P. Macheras and M. Koupparis, *J. Pharm. Sci.*, 1990, **79,** 1087.
19. T. Christopoulos and E. Diamandis, *Anal. Chem.*, 1990, **62,** 360.
20. K. Hayakawa and J. C. T. Kwak, *J. Phys. Chem.*, 1982, **86,** 3866.
21. K. Hayakawa and J. C. T. Kwak, *J. Phys. Chem.*, 1983, **87,** 506.
22. W. K. Mathews, J. W. Larsen and M. J. Pikal, *Tetrahedron Lett.*, 1972, **6,** 513.
23. J. W. Larsen and L. B. Terpley, *J. Coll. Interface Sci.*, 1974, **49,** 113.
24. E. Athanasiou-Malaki and M. A. Koupparis, *Anal. Chim. Acta*, 1989, **219,** 295.
25. E. Archontaki, M. A. Koupparis and C. E. Efstathiou, *Analyst*, 1989, **114,** 591.
26. A. M. Gerakis and M. A. Koupparis, *Analyst*, 1993, **118,** 1001.