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著者	Asakawa Tsuyoshi, Kitano Hiroki, Ohta Akio, Miyagishi Shigeyoshi
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Convenient Estimation for Counterion Dissociation of Cationic Micelles using Chloride-Sensitive Fluorescence Probe.

Tsuyoshi Asakawa^{*}, Hiroki Kitano, Akio Ohta and Shigeyoshi Miyagishi

*Department of Chemistry and Chemical Engineering, Faculty of Engineering,
Kanazawa University, Kanazawa 920-8667, Japan*

Micellar Counterion Dissociation by Fluorescence Probe

Tsuyoshi ASAKAWA :

To whom correspondance should be addressed. E-mail: asakawa@t.kanazawa-u.ac.jp

ABSTRACT: Chloride-sensitive fluorescence probe provides a new approach to study the degree of micellar counterion dissociation (α). The fluorescence of N-ethoxycarbonylmethyl-6-methoxyquinolinium bromide (MQAE) is quenched by chloride ion with linear Stern-Volmer plots. Thus the fluorescence intensity can be used to monitor the concentration of free chloride ion in micellar solutions. The Stern-Volmer plot gave a distinct break at critical micelle concentration (CMC) due to the counterion binding to micelles. The estimated α and CMCs of cationic surfactants including fluorocarbon ones were in fair agreement with the reported experimental values. The MQAE has greater sensitivity to bromide ion of CTAB than chloride ion of CTAC. The α of 0.16 for CTAB micelles was almost constant up to 0.2 M CTAB at 35°C. The α values of CTAB micelles decreased with increasing the concentrations of CTAB and NaBr along with micellar growth.

KEY WORDS: the degree of micellar counterion dissociation, CMC of cationic surfactant, quinoline derivatives, fluorescence quenching, 1,1,2,2-tetrahydroperfluoroalkylpyridinium chloride

The critical micelle concentrations (CMCs) and the degree of micellar counterion dissociation (α) have been measured by various methods such as electromotive force (EMF), conductivity, light scattering, NMR and small angle neutron scattering (SANS) measurements (1-6). The concentration dependent properties exhibit a break point due to the micellization. The CMC of surfactant is usually determined by plotting those properties as a function of concentration. The other important property of ionic surfactant solutions is the degree of micellar counterion dissociation, which has been used to be quantified by the two-site model (7,8). From this simple model one can calculate the α by using the concentrations of “free” ions in the aqueous bulk phase and “bound” ions in micellar phase. The model has successfully described various micellar solutions as a first approximation. For example, the α values of CTAB were reported as 0.16, 0.12, 0.29, and 0.19 by EMF, light scattering, NMR and SANS measurements, respectively (1,6,9,10). The differences among the observed α values may be attributed to different solution conditions and/or to different theoretical treatments.

The development of chloride-sensitive fluorescence probe provides a direct approach for measuring chloride transport in liposome membranes (11,12). The high chloride sensitivity and selectivity of MQAE probe is effective for the systems such as live cells because the MQAE fluorescence was unaffected by pH or by bicarbonate, nitrate and sulfate anions. The MQAE emission are collisionally quenched by halogen ions such as Cl^- , Br^- and I^- . The purpose of paper is to examine the applicability of MQAE probe for micellar solutions and to present the results of estimated CMCs and α of cationic surfactants. On the basis of ion concentration-dependent fluorescence decrease, we have estimated the concentration of “free” ions in aqueous solutions. The systematic study of the Stern-Volmer plots for MQAE quenching have been performed by using alkyltrimethylammonium chloride (bromide) and alkyipyridinium chloride, etc. The quenching behavior have been examined further in micellar solutions at high concentrations of surfactant and salt.

Experimental Procedures. Materials. 1,1,2,2-Tetrahydroperfluoroalkylpyridinium chloride were prepared as reported previously (13). The other cationic surfactants were obtained from Tokyo Kasei Kogyo Co., Ltd. and recrystallized twice from acetone-ethanol mixtures. Lithium dodecylsulfate (LiDS) and lithium perfluorononanoate (LiPFN) were same samples with reference (14). N-ethoxycarbonylmethyl-6-methoxyquinolinium bromide (MQAE) was purchased from Dojindo Labo. and used without purification. The other reagents were of guaranteed grade. Distilled water was distilled again from dilute alkaline permanganate solution.

Measurements. Steady-state fluorescence spectra of MQAE were recorded with a Hitachi F-3010 spectrometer using a thermostated cell. The fluorescence intensity of 10^{-6} M MQAE was measured at 460 nm by excitation at 325 nm throughout the examined conditions.. The fluorescence intensity without quencher (I_0) was used as a standard.

Results and Discussion

The absorption spectra of N-ethoxycarbonylmethyl-6-methoxyquinolinium bromide (MQAE) in aqueous solution is characterized by a strong maximum at 325 nm with a shoulder band at 355 nm. No shift of the maximum was observed in surfactant solutions with salts. The fluorescence spectra of 10^{-6} M MQAE exhibit a high intensity with a broad band maximum at 460 nm in the solutions. When quenching occurs by the collision between MQAE fluorescence probe and halogen ion quencher, the variation of fluorescence intensity is related to the concentration of quencher [Q] by the Stern-Volmer relation (11).

$$I_0/I = 1 + K_{SV}[Q] \quad [1]$$

where I_0 and I are the fluorescence intensities in the absence and presence of quencher, respectively, and K_{SV} is the Stern-Volmer constant. The MQAE fluorescence is known to be quenched collisionally by halogen ions (11). The Stern-Volmer plots for quenching of MQAE by inorganic anions were linear as shown in Fig. 1. The MQAE fluorescence was quenched by Cl^- and Br^- , while there was almost no effect by NO_3^- . The Stern-Volmer constant (K_{SV}) for NaBr was 417 M^{-1} , which is larger than that of 269 M^{-1} for NaCl at 25°C . The K_{SV} for NaBr increased with the increase in temperature. The dynamic quenching predominates as judged by the temperature- and concentration-dependent fluorescence decrease without spectral shift. The quenching by halogen ions is much more effective than that of anionic surfactants such as LiDS and LiPFN. Almost no quenching by surfactants upon micelle formation suggests that MQAE fluorescence probe is selective and sensitive toward halogen ions in surfactant micellar solutions.

The MQAE probe was developed to study the transport of chloride ion in liposomes (11). The MQAE are highly polar and membrane impermeant, which has suitable physical properties for measurement of the concentration of free chloride ion. When the cationic MQAE is introduced to cationic surfactant solutions, the MQAE will tend to partition in aqueous bulk phase due to the low octanol-water partition coefficient in addition to the electrostatic effect. The fluorescence behavior of water-soluble MQAE can be expected to related to the chloride ion concentration in aqueous bulk phase. Fig. 2 shows the Stern-Volmer plots for quenching of MQAE fluorescence by various cationic surfactants. The fluorescence intensities of MQAE

were found to decrease in the presence of CTAC, TTAC, TDBAC and DAC. The observed quenching can be ascribed to the free chloride ion dissociated from the surfactant. All experimental data gave linear plots below their CMCs. The slopes of plots, K_{SV} , below CMC are summarized in Table 1. The K_{SV} for CTAC agreed very closely with that of NaCl. The K_{SV} for surfactant monomer tend to decrease with decreasing length of the alkyl chain. The decrease in K_{SV} values may come from the concentration effect of surfactant monomer because the examined concentrations become to high with increasing CMC. The collision between MQAE probe and chloride quencher may be slightly inhibited by the coexistence of ionic surfactant monomer.

The data in Fig. 2 show a distinct break, giving the CMCs in accordance with those from conductivity measurements. The variation of slope in the Stern-Volmer plot can be ascribed to the counterion binding of cationic micelles. If the fluorescence intensity of MQAE monitors the concentration of the free chloride ion in the micellar region, we can evaluate the degree of counterion dissociation of DAC micelles as illustrated in Fig. 2. The extrapolation of the linear line below the CMC was used as the calibration line to high concentrations above CMC. The values of α has been evaluated using the mass balance equation (1).

$$\alpha = (C_{\text{free}} - \text{CMC}) / (C_t - \text{CMC}) \quad [2]$$

where C_{free} and C_t are the concentrations of the free chloride ion and the surfactant, respectively. We estimated C_{free} at a total concentration C_t , then we calculated α value by using the equation [2]. The α values of DAC, TDBAC, TTAC, and CTAC were 0.10, 0.30, 0.27, and 0.24, respectively. The α values increased with increasing ionic head group size by comparing TTAC and TDBAC. The α of DTAC having a bulky head group was much larger than that of DAC (Table 1). The larger value of α for DTAC is due to the decrease of surface charge density as pointed out previously (1). The decrease of CMC and α with increasing length of alkyl chain are generally in agreement with those obtained by conductivity and EMF measurements for alkyltrimethylammonium chloride (1, 15).

The counterion dissociation of pyridinium-type perfluorinated surfactants was already examined by the EMF measurement (16). We can reexamine the behavior of counterion dissociation for fluorocarbon micelles by this convenient method. Fig. 3 shows the experimental

data of pyridinium-type surfactants by using MQAE quenching method. Below the CMC, the Stern-Volmer plots of fluorocarbon surfactants gave straight lines in similar K_{SV} values with hydrocarbon ones. The MQAE fluorescence was unaffected by the pyridinium and fluorocarbon groups. Since the surfactant ions are proved not to quench the MQAE emission, the observed quenching was due to the chloride ion. The distinct break points were also observed for all systems at the CMCs. The estimated CMCs were in fair agreement with 4.1, 1.0, 2.7, and 0.33 mM of TPC, CPC, HFDePC, and HFDPC by the conductivity measurement, respectively. The estimated α values of 0.24 to 0.25 were slightly small compared to 0.31, 0.25, 0.31, and 0.30 of TPC, CPC, HFDePC, and HFDPC by the EMF measurement, respectively. The differences between the experimental data are due partly to the different experimental conditions and the different theoretical treatment. The α values of the fluorocarbon surfactants were revealed to be similar to those of the hydrocarbon surfactants probably owing to the same ionic head group.

The bromide sensitivity of MQAE is known to be higher than chloride sensitivity (11). The diffusion coefficient of hydrated bromide ion is larger than that of chloride ion due to the difference in the radii of hydrated ions. Thus the MQAE fluorescence is effectively quenched bromide ion with a collisional mechanism. The MQAE probe will be advantageous for the estimation of the concentration of free bromide ion in cationic surfactants, e.g., CTAB. The CTAB monomer gave a K_{SV} value about 40% larger than that of CTAC, while the K_{SV} value of CTAB was about 10% smaller than $K_{SV} = 417 \text{ M}^{-1}$ of NaBr. The reasons for this smaller K_{SV} of CTAB compared with NaBr are not clear but the Stern-Volmer plot gave a distinct break in similar way to the CTAC system. The α of CTAB at 25°C was 0.11, which was relatively small compared to 0.24 of CTAC (Table 1). Several studies have shown that the counterion binding to micelles depend on the radii of the hydrated halogen ions (17,18). The α estimated by MQAE probe method was slightly smaller than 0.16 of the EMF measurement (1).

The CTAB micelles is known to exhibit a sphere-rod transition as the concentration is increased. Quirin and Magid reported the variation of counterion binding along with micellar growth by SANS and light scattering measurements (6). Lindman et al. mentioned that the shape transition is associated with an increase in micellar counterion binding (19). We studied the behavior of MQAE fluorescence in wide concentration ranges of CTAB system without and

with NaBr. Fig. 4 shows the Stern-Volmer plots with total bromide concentration as abscissa in CTAB micellar systems at 35°C. The data of NaBr followed a straight line up to 300 mM NaBr (not shown in Fig. 4), while the Stern-Volmer plots for CTAB was found to be linear up to 200 mM CTAB in the micellar region. The α of CTAB micelles can be estimated to be 0.16, which is large compared to the α value at 25°C. An increase of α value with temperature has been found to involving the changes in hydration of ionic groups. On the other hand, the data of CTAB beyond 200 mM deviated from the straight line. That is, the depression of fluorescence quenching may be attributed to the increase in counterion binding of CTAB micelles. This behavior at 200 mM CTAB corresponded to the decrease of α along with the sphere-rod transition of CTAB as reported by Quirin and Magid (6).

From the experimental data of Fig. 4, the α values of CTAB micelles were 0.15, 0.11, 0.09 and 0.06 in the presence of 10, 35, 40, 50 mM constant concentrations of NaBr, respectively. The α values of CTAB micelles decreased with increasing concentration of NaBr as expected. It is generally accepted that the addition of salt gives rise to an increase in counterion binding upon the micellar growth. The MQAE fluorescence quenching method prove to give quantitative information on the behavior of α along with the micellar growth. This method is effective up to high concentrations of bromide ion without experimental difficulties.

Conclusions. Both chloride and bromide are major ionic constituents of cationic surfactants. The counterion dissociation is one of the important properties, which depend on many factors such as surfactant structure, temperature, concentration of additives. The good reproducibility of MQAE fluorescence intensity enable us to carry out the simultaneous determination of CMC and α . The MQAE fluorescence quenching method is very convenient to estimate α even if the concentration of surfactant and salt are enough high. The effect of additives such as alcohol toward α will be also investigated by this method, which will give useful insight into the various difficulties encountered in other experimental methods.

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Table 1. Stern-Volmer constant of surfactant monomer, CMC and the degree of counterion dissociation determined by the quenching of MQAE fluorescence at 25°C

Surfactant		K_{SV}/M^{-1}	CMC/mM	α
$C_{12}H_{25}NH_3Cl$	(DAC)	248	14.6	0.10
$C_{12}H_{25}N(CH_3)_3Cl$	(DTAC)	221	24.4	0.47
$C_{14}H_{29}N(CH_3)_3Cl$	(TTAC)	256	5.27	0.27
$C_{16}H_{33}N(CH_3)_3Cl$	(CTAC)	264	1.31	0.24
$C_{14}H_{29}N(CH_3)_2CH_2C_6H_5Cl$	(TDBAC)	244	2.16	0.30
$C_{14}H_{29}NC_5H_5Cl$	(TPC)	254	3.88	0.25
$C_{16}H_{33}NC_5H_5Cl$	(CPC)	288	0.98	0.25
$C_8F_{17}CH_2CH_2NC_5H_5Cl$	(HFDePC)	261	2.61	0.24
$C_{10}F_{21}CH_2CH_2NC_5H_5Cl$	(HFDPC)	255	0.34	0.24
$C_{12}H_{25}N(CH_3)_3Br$	(DTAB)	362	15.4	0.18
$C_{14}H_{29}N(CH_3)_3Br$	(TTAB)	369	3.82	0.12
$C_{16}H_{33}N(CH_3)_3Br$	(CTAB)	373	1.00	0.11
$C_{16}H_{33}NC_5H_5Br$	(CPB)	373	0.72	0.14

Figure 1. Stern-Volmer plots for MQAE fluorescence quenching by various ions.

(○) NaCl, (△) NaBr, (□) NaNO₃, (●) LiDS, (▲) LiPFN.

Figure 2. Effects of cationic surfactant concentration on quenching of MQAE fluorescence.

The estimation of free chloride concentration was illustrated for dodecylammonium chloride (DAC) system.

Figure 3. Effect of concentrations of pyridinium-type surfactants on quenching of MQAE fluorescence.

(○) CPC, (△) TPC, (●) HFDPC, (▲) HFDePC.

Figure 4. Effect of NaBr addition on the counterion dissociation of CTAB micelle at 35°C.

(○) CTAB without NaBr, (△) 10 mM NaBr, (□) 35 mM NaBr,
(◇) 50 mM NaBr, (▲) NaBr without CTAB.







