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Measurement of the Critical Micelle Concentration of Nonionic–Nonionic Mixed Surfactant Systems by the First Derivative Absorption Spectrum Method and the Region of Cooperative Micelles

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In nonionic–nonionic mixed surfactant systems, when two surfactants below their individual critical micelle concentrations (cmc) were mixed, the formation of mixed micelles was confirmed and the cmc values were measured by the first derivative absorption spectrum (FDAS) method, the solubilization method (with Sudan Red dye) and the surface tension method (Wilhelmy plate method). The region corresponding to mixed micelle formation was obtained from plots of the sum of the concentrations corresponding to the cmc ($=[\mathrm{OED}]_{*\mathrm{PED}}/\mathrm{cmc}_{\mathrm{OED}}+[\mathrm{PED}]_{*\mathrm{OED}}/\mathrm{cmc}_{\mathrm{PED}}$: $[\mathrm{OED}]_{*\mathrm{PED}}$ (or $[\mathrm{PED}]_{*\mathrm{OED}}$) is the concentration of OED (or PED) in the cmc for mixed micelle formation of OED–PED binary systems, and $\mathrm{cmc}_{\mathrm{OED}}$ (or $\mathrm{cmc}_{\mathrm{PED}}$) is the cmc of OED (or PED)) on the ordinate against the mole fraction normalized with respect to cmc ($=[[\mathrm{OED}]/\mathrm{cmc}_{\mathrm{OED}}]/[[\mathrm{OED}]/\mathrm{cmc}_{\mathrm{OED}}+[\mathrm{PED}]/\mathrm{cmc}_{\mathrm{PED}}]$: [OED] (or [PED]) is the concentration of OED (or PED)) on the abscissa by the FDAS method.

In the region of cooperative micelles which was a part of the region forming mixed micelles, it was found that the longer the ethylene glycol chain length of the nonionic–nonionic mixed surfactants, the wider was the region of cooperative micelles. The order of the width was 0.78 mM OED–0.43 mM PED > 0.43 mM OED–0.43 mM PED > 0.78 mM OED–0.43 mM TED = 0.43 mM PED–0.43 mM TED > 0.43 mM OED–0.43 mM TED mixed surfactant systems. In ionic–nonionic mixed surfactant systems, the cmc values of the mixed micelles were under the influence of the nonionic surfactant. But in nonionic–nonionic mixed surfactant systems, the cmc values of the mixed surfactant systems were under the influence of both nonionic surfactants. (Abbreviations used are: OED, PED and TED = octa-, penta- and triethylene glycol dodecyl ether.)

Keywords first derivative absorption spectrum; critical micelle concentration; wavelength shift; solubilization; propylparaben; triethylene glycol dodecyl ether; pentaethylene glycol dodecyl ether; octaethylene glycol dodecyl ether; mixed micelle; cooperative micelle

Introduction

Surfactants are currently used as binary or multicomponent mixed systems for their complex effects in many cases, and many reports have appeared on mixed micelle systems.[1–18] The first derivative absorption spectrum (FDAS) method which we proved and reported[19,20] showed high reproducibility in the measurement of the critical micelle concentration (cmc) of surfactant.[21,22] In a previous paper,[22] we measured the cmc values of the ionic–nonionic mixed surfactant systems by the FDAS method, the solubilization method using a water-insoluble dye (Sudan Red) and the surface tension method (Wilhelmy plate method), and the regions forming mixed micelles were shown. In the ionic–nonionic mixed surfactant systems, we were able to measure the cmc values easily, because the cmc value of ionic surfactant was much larger than that of nonionic surfactant. But in the nonionic–nonionic mixed surfactant systems, the measurement of the cmc values of the mixed surfactant systems by the solubilization method or the surface tension method is difficult since the cmc value of the one surfactant is close to that of the other.[23]

In the nonionic–nonionic mixed surfactant systems, when two surfactants were mixed at concentrations below their individual cmc values, formation of mixed micelles was confirmed by the FDAS method, the solubilization method using a water-insoluble dye (Sudan Red) and the surface tension method (Wilhelmy plate method). Further, the cmc values in mixed solution were measured by the FDAS method, and a region forming mixed micelles was shown. It was also found that the region forming cooperative micelles which was a part of that forming mixed micelles (see Results and Discussion) was influenced by the ethylene glycol chain length of the nonionic surfactant. Further, from the presence or absence of the minimum cmc values of the anionic- (or cationic-, nonionic-) nonionic mixed surfactant systems, the extent of influence of either surfactant on these values of the mixed micelle systems could be inferred.

Experimental

Materials Propyl *p*-hydroxybenzoate (propylparaben) was obtained from Nakarai Chemicals, Ltd., Sudan Red was obtained from Wako Pure Chemical Industries, Ltd., and triethylene glycol dodecyl ether (TED), pentaethylene glycol dodecyl ether (PED) and octaethylene glycol dodecyl ether (OED) were obtained from Nikko Chemicals Company, Tokyo, Japan. These chemicals were used as received. Cetyl trimethylammonium bromide (CTAB), heptaethylene glycol dodecyl ether (HED) and sodium dodecyl sulfate (SDS) were the same as those used in the previous paper.[22]

Measurement of the cmc of Nonionic–Nonionic Mixed Surfactant Solution at 30 °C by the FDAS Method A Hitachi 557 dual-wavelength double-beam spectrophotometer equipped with a Haake F2C thermostat was used. Titration was performed by adding portions (1—100 μl) of a stock solution of 0.0053—0.392 mM OED–0.0053—0.214 mM PED (or 0.0053—0.392 mM OED–0.0053—0.214 mM TED, 0.0053—0.214 mM PED–0.0053—0.214 mM TED) to 2000 μl (or 1500, 1600, 1800 μl) of 51.5—104.7 μM propylparaben solution and to 2000 μl of aqueous solution (control). We obtained the difference absorption spectra (for example, between propylparaben–OED–PED solution and OED–PED solution) from the first derivative absorption spectrum and read the wavelength of the absorption maximum. Measurement conditions were as follows: scale of expansion 20 times, scan speed 12 nm/min, derivative width ($\Delta\lambda$) 5, slit width 2 nm, scale of absorption spectra from +0.7 to −0.3 or from +0.5 to −0.5.

Measurement of the cmc of Nonionic–Nonionic Mixed Surfactant Solution by the Solubilization Method Mixed surfactant solutions (20 ml; 10—20 different concentration ratios) containing Sudan Red (water-insoluble dye) were shaken for over 30 h, and the solutions were filtered through a Millipore® filter (0.22 μm). The absorbances of the filtrates were measured at 420—560 nm using a Hitachi U-2000 dual-wavelength double-beam spectrophotometer.

Measurement of the cmc of Nonionic–Nonionic Mixed Surfactant Solution at 30 °C by the Surface Tension Method (Wilhelmy Plate Method) A Kyowa Kagaku CBVP surface tensiometer (A-1) equipped with a Tokyo Rikakikai thermostat and a glass plate was used. Each measurement was repeated at least three times, and two straight lines in the plots of absolute values (the relative values multiplied by the correction factor) were obtained by the least-squares method.

Results and Discussion

Confirmation of Mixed Micelle Formation and Determination of the cmc of Mixed Surfactant Systems by the FDAS Method The shift of the maximum absorption wavelength of a chemical agent (propylparaben in this report) in a micelle solution is utilized for the FDAS method. The lowest concentration at which the shift occurs is equal to the cmc value of the surfactant.[22] Some samples were prepared according to Table I. For example, in OED–PED binary systems, 100 ml of MIX-Q was the mixed solution of 25 ml of A (=0.78 mM OED), 50 ml of B (=0.43 mM PED) and 25 ml of H_2O, and the concentration of OED and PED were 0.20 and 0.22 mM, respectively. We used the Table I for the mixing ratios of different binary systems. In nonionic–nonionic mixed surfactant systems (OED–PED, OED–TED and PED–TED binary systems), we confirmed the occurrence of shifts similar to those described above (Fig. 1). Since the lowest concentration at which the shift occurred is lower than the cmc value of either surfactant, it is clear that mixed micelles are formed. Tables II[A], [B], III[A], [B] and IV show the cmc values for mixed micelle formation in 0.78 mM OED–0.43 mM PED, 0.43 mM OED–0.43 mM PED, 0.78 mM OED–0.43 mM TED, 0.43 mM OED–0.43 mM TED and 0.43 mM PED–0.43 mM TED binary systems, respectively. Figures 2A and B show plots of the sum of concentrations corresponding to the cmc ($=[\mathrm{OED}]_{*\mathrm{PED}}/\mathrm{cmc}_{\mathrm{OED}}+[\mathrm{PED}]_{*\mathrm{OED}}/\mathrm{cmc}_{\mathrm{PED}}$: $[\mathrm{OED}]_{*\mathrm{PED}}$ (or $[\mathrm{PED}]_{*\mathrm{OED}}$) is the concentration of OED (or PED) in the cmc of mixed micelles of OED–PED binary systems, and $\mathrm{cmc}_{\mathrm{OED}}$ (or $\mathrm{cmc}_{\mathrm{PED}}$) is the cmc of OED (or PED)) on the ordinate against the mole fraction normalized with respect to cmc ($=[[\mathrm{OED}]/\mathrm{cmc}_{\mathrm{OED}}]/[[\mathrm{OED}]/$

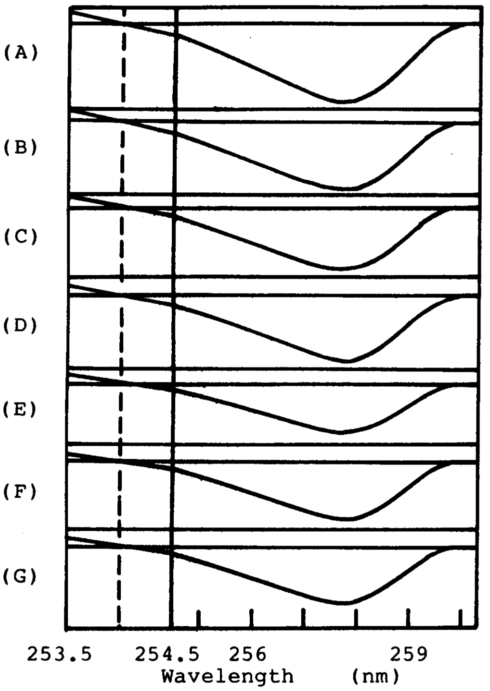

Fig. 1. First Derivative Absorption Spectra of 69.2 μM Propylparaben

(A), in H_2O; (B), in 0.051 mM OED–0.014 mM PED solution; (C), 0.072 mM OED–0.020 mM PED; (D), 0.019 mM OED–0.010 mM TED; (E), 0.10 mM OED–0.055 mM TED; (F), 0.013 mM PED–0.052 mM TED; (G), 0.014 mM PED–0.057 mM TED.

Table I. Volume Ratio of Mixed Solutions

	A	B	H_2O	Total
MIX-C	25	1	24	50
MIX-G	50	7	43	100
MIX-K	10	3	7	20
MIX-N	2	1	1	4
MIX-P	1	1	0	2
MIX-Q	1	2	1	4
MIX-T	1	4	3	8
MIX-V	1	10	9	20
MIX-Y	1	40	39	80

A, B: A–B system.

Table II. cmc of OED–PED System Determined by FDAS Method at 30 °C

		cmc $[\mathrm{OED}]_{*\mathrm{PED}}$ (mM)	cmc $[\mathrm{PED}]_{*\mathrm{OED}}$ (mM)	$[\mathrm{OED}]_{*\mathrm{PED}}/\mathrm{cmc}_{\mathrm{OED}}+[\mathrm{PED}]_{*\mathrm{OED}}/\mathrm{cmc}_{\mathrm{PED}}$	Mole fraction normalized with respect to cmc
	OED	0.138	—	1.00	—
	PED	—	0.093	1.00	—
[A]	MIX-G	0.083	0.0064	0.67	0.90
	MIX-N	0.059	0.016	0.60	0.71
	MIX-P	0.048	0.026	0.63	0.55
	MIX-Q	0.033	0.036	0.62	0.38
	MIX-T	0.020	0.044	0.62	0.24
	MIX-V	0.0099	0.054	0.65	0.11
	MIX-Y	0.0034	0.074	0.82	0.030
[B]	MIX-C	0.10	0.0040	0.77	0.94
	MIX-G	0.085	0.012	0.74	0.83
	MIX-N	0.062	0.031	0.77	0.57
	MIX-P	0.045	0.045	0.80	0.40
	MIX-Q	0.028	0.055	0.79	0.25
	MIX-T	0.016	0.064	0.80	0.14
	MIX-Y	0.0020	0.081	0.88	0.017

Concentration of source solution: [A], A=0.78 mM OED, B=0.43 mM PED; [B], A=0.43 mM OED, B=0.43 mM PED.

Table III. cmc of OED–TED System Determined by FDAS Method at 30 °C

		cmc $[\mathrm{OED}]_{*\mathrm{TED}}$ (mM)	cmc $[\mathrm{TED}]_{*\mathrm{OED}}$ (mM)	$[\mathrm{OED}]_{*\mathrm{TED}}/\mathrm{cmc}_{\mathrm{OED}}+[\mathrm{TED}]_{*\mathrm{OED}}/\mathrm{cmc}_{\mathrm{TED}}$	Mole fraction normalized with respect to cmc
	OED	0.138	—	1.00	—
	TED	—	0.080	1.00	—
[A]	MIX-C	0.12	0.0026	0.90	0.96
	MIX-G	0.10	0.0079	0.85	0.88
	MIX-K	0.090	0.015	0.84	0.78
	MIX-N	0.077	0.021	0.82	0.68
	MIX-P	0.057	0.031	0.80	0.51
	MIX-Q	0.039	0.043	0.82	0.35
	MIX-T	0.023	0.051	0.81	0.21
	MIX-V	0.012	0.066	0.83	0.096
	MIX-Y	0.0031	0.0067	0.86	0.026
[B]	MIX-C	0.11	0.0045	0.87	0.94
	MIX-G	0.098	0.014	0.88	0.80
	MIX-N	0.065	0.032	0.88	0.54
	MIX-P	0.046	0.046	0.91	0.37
	MIX-Q	0.028	0.055	0.89	0.22
	MIX-T	0.016	0.063	0.90	0.13
	MIX-Y	0.0019	0.076	0.97	0.014

Concentration of source solution: [A], A=0.78 mM OED, B=0.43 mM TED; [B], A=0.43 mM OED, B=0.43 mM TED.

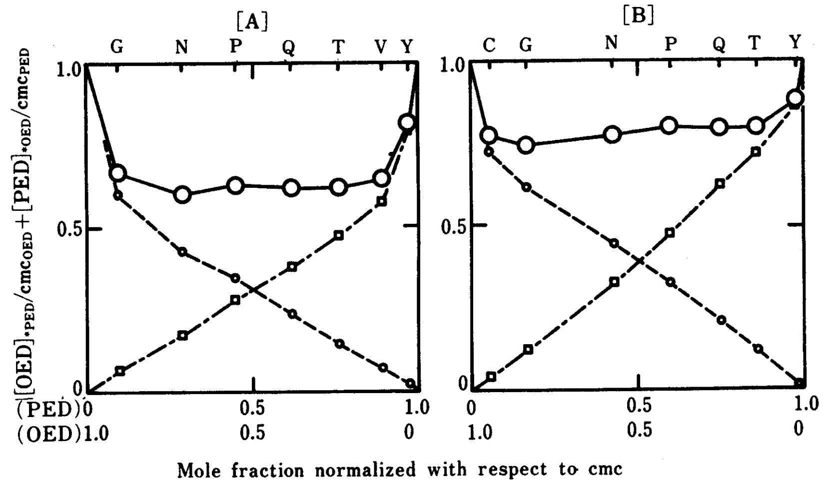

Fig. 2. Relationship between Sum of Concentrations Corresponding to cmc and Mole Fraction Normalized with Respect to cmc of OED–PED Systems Determined by the FDAS Method

○, $[OED]_{*PED}/cmc_{OED}+[PED]_{*OED}/cmc_{PED}$; o, $[OED]_{*PED}/cmc_{OED}$; □, $[PED]_{*OED}/cmc_{PED}$. Letters indicate the mixing ratio of components (see Table I).

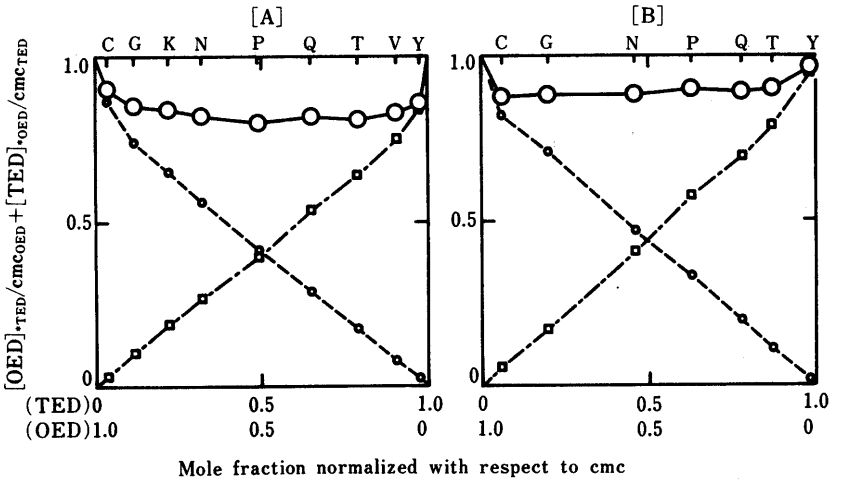

Fig. 3. Relationship between Sum of Concentrations Corresponding to cmc and Mole Fraction Normalized with Respect to cmc of OED–TED Systems Determined by the FDAS Method

○, $[OED]_{*TED}/cmc_{OED}+[TED]_{*OED}/cmc_{TED}$; o, $[OED]_{*TED}/cmc_{OED}$; □, $[TED]_{*OED}/cmc_{TED}$. Letters indicate the mixing ratio of components (see Table I).

Table IV. cmc of PED–TED System Determined by FDAS Method at 30 °C

	cmc $[PED]_{*TED}$ (mM)	cmc $[TED]_{*PED}$ (mM)	$[PED]_{*TED}/cmc_{PED}+[TED]_{*PED}/cmc_{TED}$	Mole fraction normalized with respect to cmc
PED	0.093	—	1.00	—
TED	—	0.080	1.00	—
MIX-C	0.076	0.0031	0.85	0.96
MIX-G	0.066	0.0093	0.83	0.86
MIX-N	0.048	0.024	0.81	0.63
MIX-P	0.035	0.035	0.81	0.46
MIX-Q	0.023	0.045	0.81	0.30
MIX-T	0.014	0.055	0.84	0.18
MIX-Y	0.0019	0.076	0.97	0.021

Concentration of source solution: A=0.43 mM PED, B=0.43 mM TED.

$cmc_{OED}+[PED]/cmc_{PED}$]: [OED] (or [PED]) is the concentration of OED (or PED)) on the abscissa of different equal mole concentration OED–PED binary systems, respectively. Similarly, Figs. 3A, B and 4 show plots of the values obtained with the method of calculations described

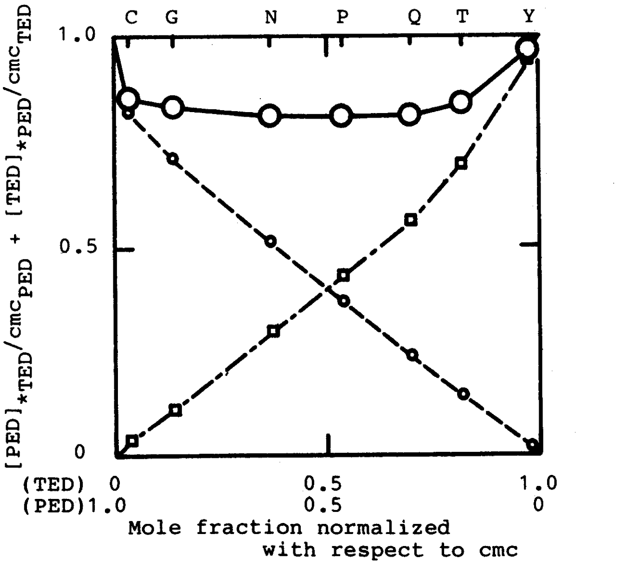

Fig. 4. Relationship between Sum of Concentrations Corresponding to cmc and Mole Fraction Normalized with Respect to cmc of PED–TED Systems Determined by the FDAS Method

○, $[PED]_{*TED}/cmc_{PED}+[TED]_{*PED}/cmc_{TED}$; ○, $[PED]_{*TED}/cmc_{PED}$; □, $[TED]_{*PED}/cmc_{TED}$. Letters indicate the mixing ratio of components (see Table I).

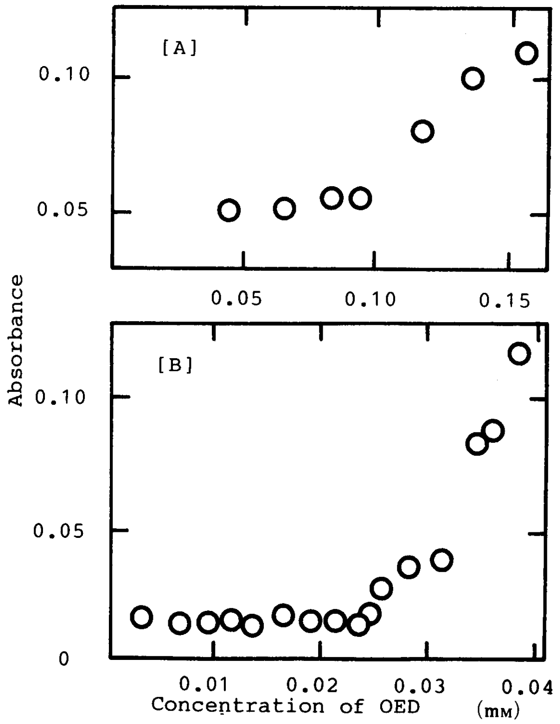

Fig. 5. Determination of cmc of OED, TED or OED–TED Solution by the Sudan Red Solubilization Method

[A], in OED solution, wavelength 450 nm; [B], in OED–TED (MIX-T) solution, wavelength 450 nm.

Table V. cmc of OED–TED System Determined by Solubilization Method

	[OED]$_{*\mathrm{TED}}$	[TED]$_{*\mathrm{OED}}$	Wavelength (nm)
MIX-N	0.078—0.087	0.021—0.024	450
MIX-P	0.057—0.078	0.032—0.042	450
MIX-Q	0.029—0.034	0.031—0.037	420
MIX-T	0.024—0.026	0.053—0.056	450
OED	0.096—0.12	—	450

Concentration of source solution: A = 0.78 mM OED, B = 0.42 mM TED.

above on different or equal mole concentration OED–TED binary systems and equal mole concentration PED–TED binary systems, respectively. These five figures also show the region corresponding to respective mixed micelle formation.

Confirmation of Mixed Micelle Formation and Determination of the cmc of Mixed Surfactant Systems by the Solubilization Method The solubilization method is one of the easiest methods for confirmation of micelle formation, and was therefore applied to the nonionic–nonionic mixed surfactant systems.

Figures 5A and B show the changes of absorbance of Sudan Red in OED solution and in OED–TED binary solution systems, respectively, determined by the solubilization method. In this method, the point of inflection (= the cmc of mixed micelles) was obtained graphically. The plot is suggestive of mixed micelle formation, because the concentration at the point of inflection of OED–TED binary systems was lower than the cmc value of either surfactant alone. The same trend was obtained with regard to the point of inflection for OED–PED and PED–TED binary systems. The cmc values for the binary systems obtained by the solubilization method are listed in Table V. These results agreed fairly well with those obtained by the FDAS method.

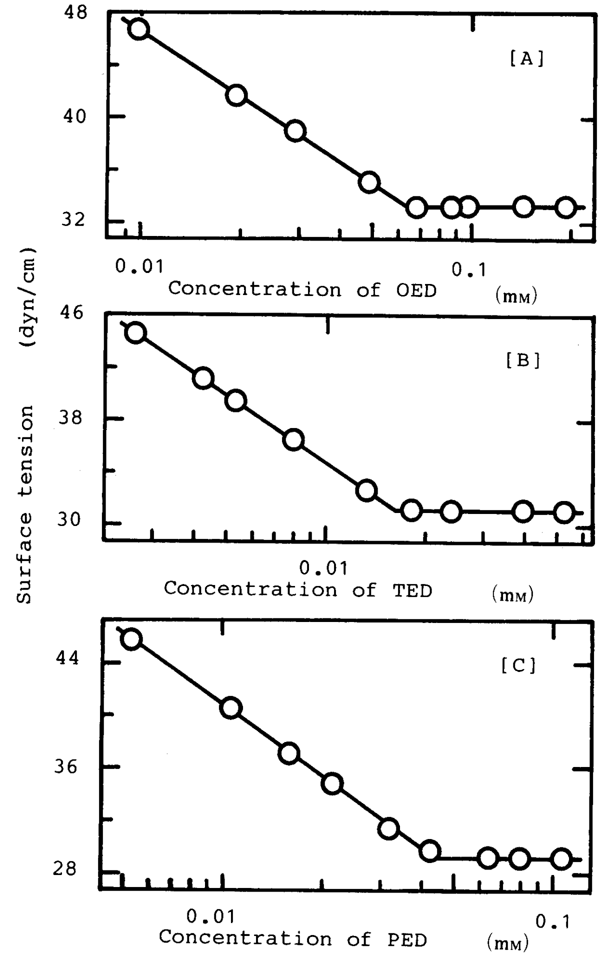

Fig. 6. Determination of cmc of OED–PED, OED–TED or PED–TED Solution by Surface Tension Measurement

[A], in OED–PED solution (MIX-N) at 30 °C; [B], in OED–TED (MIX-N) solution at 30 °C; [C], in PED–TED solution (MIX-N) at 30 °C.

Confirmation of Mixed Micelle Formation and Determination of the cmc of Mixed Surfactant Systems by the Surface Tension Method The surface tension method is appropriate for determination of the cmc values of both ionic and nonionic surfactants. It was reported earlier[22] that the surface tension values in ionic–nonionic mixed surfactant systems (SDS–HED or CTAB–OED binary systems) showed rather nonlinear patterns, while those in nonionic–nonionic mixed surfactant systems showed linear patterns.

Figures 6A, B and C show variations of the surface tension values of OED–PED binary systems, OED–TED binary systems and PED–TED binary systems, respectively. In these systems, the surface tension values become lower with increase of the concentration, and the point of inflection (= the cmc of mixed surfactant systems) is lower than the cmc value of either surfactant alone. This is added evidence of mixed micelle formation.

When two surfactants were mixed at concentrations below their individual cmc values (nonionic–nonionic binary mixed surfactant systems), formation of mixed micelles was confirmed by the three independent methods described above. The regions of mixed micelle formation were shown from the cmc values obtained by the FDAS method. The measurement of cmc values of the mixed surfactant systems by this method was shown to be easy when the cmc value of one surfactant was close to that of the other.

The mixed micelles are formed under the following conditions: 1) when there are mixed micelle systems of two surfactants over their individual cmcs, 2) when there are mixed micelle systems of two surfactants, one of whose concentrations is over and the other below the cmc, 3) when there are mixed micelle systems of two surfactants below their individual cmcs. The cmc values of the mixed surfactant systems obtained by the three methods used in this report fall under condition 3). Therefore, the mixed micelle formation depends upon the cooperativity of the two surfactants, because neither surfactant by itself can form micelles. This region was defined as the region forming cooperative micelles,[22] and is less than 1.0 of the sum of the concentrations corresponding to the cmc on the ordinate and over the cmc values of the mixed micelles in Figs. 2—4. This region of cooperative micelles was influenced by the species or the concentrations of surfactants.

The order of the width of the region of cooperative micelles was 0.78 mM OED–0.43 mM PED > 0.43 mM OED–0.43 mM PED > 0.78 mM OED–0.43 mM TED = 0.43 mM PED–0.43 mM TED > 0.43 mM OED–0.43 mM TED mixed surfactant systems at constant surfactant concentrations. Thus, the longer the ethylene glycol chain length of the nonionic–nonionic mixed surfactants (= the combination of two surfactants of large molecular weight) or the smaller the difference between the molecular weight of two surfactants, the wider was the region of cooperative micelles.

On the other hand, Figs. 7A (Table VI) and 7B (Table VII) show plots of the sum of the concentrations corresponding to the cmc on the ordinate against the mole fraction on the abscissa of anionic–nonionic (SDS–HED binary systems) and cationic–nonionic mixed surfactant systems (CTAB–OED binary systems), respectively. In these binary systems, there is a minimum of cmc values of mixed surfactant systems because of the great difference between the cmc value of ionic surfactant (= SDS or CTAB) and that of nonionic surfactant (HED or OED). These minimum values appeared in the area where SDS (or CTAB) was the component of the larger mole fraction. All cooperative micelle regions are wider where the mole fraction of ionic surfactant is dominant, because the chain length of HED molecule is longer than that of SDS

Table VI. cmc of SDS–HED System Determined by FDAS Method at 35 °C

	cmc $[SDS]_{*HED}$ (mM)	 $[HED]_{*SDS}$ (mM)	$[SDS]_{*HED}$/ cmc_{SDS} + $[HED]_{*SDS}$/ cmc_{HED}	Mole fraction
SDS	7.6	—	1.00	1.00
HED	—	0.11	1.00	0
MIX-C	6.7	0.0029	0.91	0.9995
MIX-G	5.8	0.0087	0.84	0.9985
MIX-N	4.3	0.023	0.77	0.995
MIX-P	3.3	0.035	0.75	0.989
MIX-Q	2.3	0.049	0.75	0.979
MIX-T	1.5	0.063	0.77	0.96
MIX-V	0.80	0.086	0.89	0.90
MIX-Y	0.23	0.099	0.93	0.70

Concentration of source solution: A = 64.0 mM SDS, B = 0.69 mM HED.

Table VII. cmc of CTAB–OED System Determined by FDAS Method at 30 °C

	cmc $[CTAB]_{*OED}$ (mM)	 $[OED]_{*CTAB}$ (mM)	$[CTAB]_{*OED}$/ cmc_{CTAB} + $[OED]_{*CTAB}$/ cmc_{OED}	Mole fraction
CTAB	0.80	—	1.00	—
OED	—	0.138	1.00	—
MIX-C	0.67	0.0028	0.86	0.996
MIX-G	0.61	0.0090	0.83	0.985
MIX-N	0.47	0.025	0.78	0.95
MIX-P	0.35	0.037	0.72	0.90
MIX-Q	0.25	0.053	0.72	0.83
MIX-T	0.16	0.068	0.72	0.70
MIX-V	0.086	0.082	0.74	0.49
MIX-Y	0.026	0.11	0.88	0.19

Concentration of source solution: A = 8.1 mM CTAB, B = 0.85 mM OED.

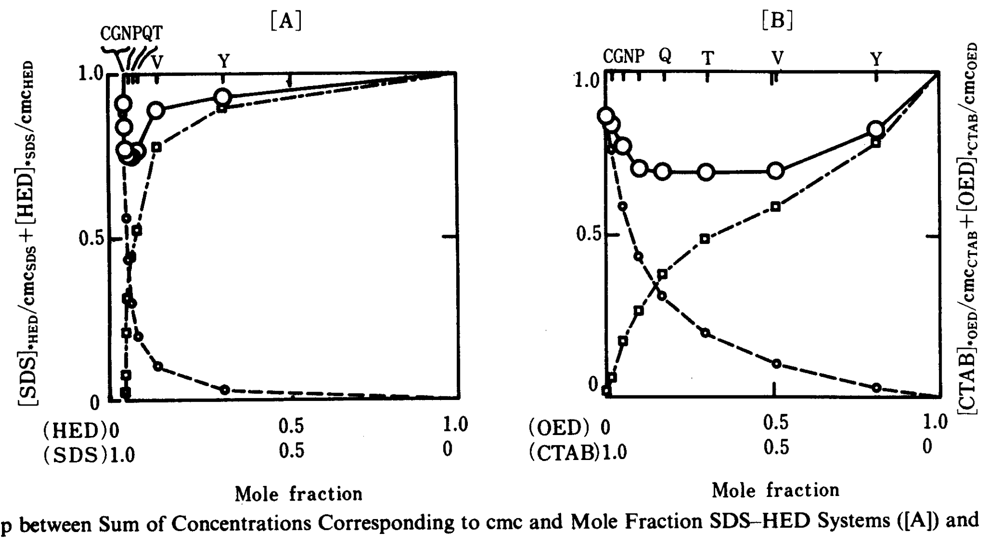

Fig. 7. Relationship between Sum of Concentrations Corresponding to cmc and Mole Fraction SDS–HED Systems ([A]) and CTAB–OED Systems ([B]) Determined by the FDAS Method

[A]: ○, $[SDS]_{*HED}/cmc_{SDS}+[HED]_{*SDS}/cmc_{HED}$; o, $[SDS]_{*HED}/cmc_{SDS}$; □, $[HED]_{*SDS}/cmc_{HED}$. [B]: ○, $[CTAB]_{*OED}/cmc_{CTAB}+[OED]_{*CTAB}/cmc_{OED}$; o, $[CTAB]_{*OED}/cmc_{CTAB}$; □, $[OED]_{*CTAB}/cmc_{OED}$. Letters indicate the mixing ratio of components (see Table I).

molecule. Therefore, the formation of mixed micelles was most strongly induced by addition of HED rather than SDS, and lower cmc values were obtained. Consequently, in the ionic–nonionic mixed surfactant systems, the nonionic surfactant has great influence on the formation of cooperative micelles. In the nonionic–nonionic mixed surfactant systems (OED–PED, OED–TED and PED–TED binary systems), however the region of cooperative micelles is influenced by both surfactants because the cmc values of each surfactant are similar.

In addition, in the combinations of two surfactants of the same property (Figs. 2A and B, or Figs. 3A and B), the region of cooperative micelles is influenced by the surfactant concentrations.

In conclusion, the findings described above can be applied to the estimation and control of the cmc value in binary mixed surfactant systems and to the utilization of mixed (or cooperative) micelles.

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