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Micellization Behaviour of AOT in the Presence of Sodium Citrate

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Critical micelle concentration (cmc) values of dioctyl sulfosuccinate (AOT) in aqueous trisodium citrate (NaCit) solution were determined as functions of electrolyte concentration and temperature by using surface tension and EMF methods. Values of surface excess, counter ion binding constant (β), surface area, and standard free energies of micellization and adsorption of AOT were evaluated. Using fluorescence-quenching method, aggregation number and polarity index of AOT were also determined. A sudden increase in the value of β from almost 0.4 to 0.8, associated with a sudden increase in the aggregation number and decrease in the polarity index, was observed with a NaCit concentration of about 0.007 mol kg^{-1}, which is considered to be due to change in the micellar shape of AOT. The present study confirms the special counter ion binding behaviour of AOT as an additional special feature of AOT.

Added electrolytes are known to affect micellization and adsorption parameters of ionic surfactants. Normally, changes that occur in the values of micellization and adsorption parameters of an ionic surfactant due to the addition of electrolytes are attributed entirely to counter ion effect. A few reported studies,[1–5] however, indicate that co-ions of added electrolytes can also have influence on the micellization and adsorption parameters of ionic surfactants depending on the nature and structure of co-ion and the surfactant. Recent studies[6,7] on the micellization and adsorption behaviours of dioctyl sulfosuccinate (AOT) in aqueous medium in the presence of five electrolytes having the same counter ion (Na^+) but different co-ions, such as chloride, acetate, propionate, butyrate, and salicylate, have shown that these co-ions influence the adsorption behaviour of AOT. However, only the salicylate co-ion has been shown to effect the cmc of AOT. Moreover, the value of counter ion binding constant (β) of AOT increases when the electrolyte concentration is around 0.015 mol kg^{-1} in the case of sodium chloride (NaCl), sodium acetate (NaAc), sodium propionate (NaPr), and sodium butyrate (NaBu).[6] However, such a shift in the β value of AOT does not occur in the presence of sodium salicylate (NaSa), thereby showing the dependence of the co-ion on β of AOT.[7]

In this paper, we evaluated micellization and adsorption parameters of AOT in aqueous trisodium citrate (NaCit) solution using surface tension, electromotive force (EMF) and fluorescence emission methods. Structures of AOT and NaCit are shown in Fig. 1. An aqueous NaCit medium was chosen in this study because (i) NaCit is used as an anticoagulant in haemodialysis[8] and (ii) citrate buffer is a commonly used buffer medium for various physicochemical, biochemical, and pathological studies. Furthermore, we intend to examine how a trivalent citrate co-ion influences the cmc and β values of AOT in comparison to the univalent co-ions studied earlier.[6,7] Micellization and adsorption characteristics of AOT in the presence of unsymmetrical electrolytes, to the best of our knowledge, have not been studied yet. It is therefore considered worthwhile to investigate the aggregation and adsorption behaviours of surfactants in aqueous NaCit medium. The results of this study will be useful for designing formulations consisting of ionic surfactants and electrolytes.

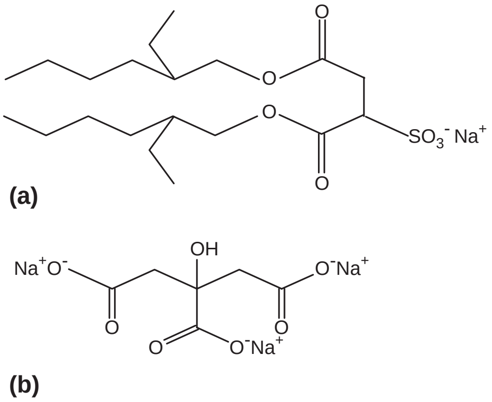

Fig. 1. Structures of (a) AOT and (b) NaCit.

Experimental

AOT (Sigma, 99%), trisodium citrate (NaCit; Qualigens, 99% assay, Excelar grade), pyrene (Fluka; as fluorescence probe), and cetylpyridinium chloride (Fluka; as quencher) were used without further purification. Surface tension measurements were made using a Krüss K11 Tensiometer. For measuring EMF of the surfactant solutions Jenway 3345 Ion Meter and Jenway 924–329 sodium selective combined electrode were used. Fluorescence emissions of pyrene (excitation wavelength = 335 nm) were recorded using Hitachi F4500 FL spectrophotometer. Details of the measurements of surface tension, EMF and fluorescence emission intensities are given in our previous paper.[6]

Results and Discussion

The values of cmc of AOT (Table 1) in aqueous NaCit solution were determined at 20, 25, and 30 °C from the measured surface tension (γ) and EMF (at 25 °C only) data. The cmc values of AOT in NaCit solutions were comparable to the reported[6] cmc values in NaCl, NaAc, NaPr, and NaBu solutions

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at 25 °C, which shows that the citrate co-ion has no effect on the cmc values of AOT, unlike salicylate co-ion.[7] The change in the values of cmc of AOT caused by the addition of NaCit was hence attributed to the effect of sodium counter ion. From Table 1, it is clear that temperature had an effect on the cmc of AOT and the cmc has a minimum at 298 K. Ionic surfactants are generally known to exhibit this type of temperature effect on cmc.[9]

The cmc values of AOT in NaCit solutions determined from the different methods were least-squares fitted to the Corrin–Harkins (CH) relation

$$\ln X_{\mathrm{cmc}} = A - \beta \ln X_{\mathrm{c}}, \tag{1}$$

where X_{cmc} and X_{c} terms in Eq. 1 refer to the cmc and counter ion concentration in mole fraction unit, respectively. The computed values of A and β at 20, 25, and 30 °C are given in Table 2. The CH plots for AOT in NaCit solution is also shown in Fig. 2. The counter ion binding feature of AOT in NaCit solution was similar to that in NaCl, NaAc, NaPr, and NaBu solutions.[6] The value of β for AOT below 0.02 mol kg^{-1} of Na$^+$ concentration ($\approx$0.007 mol kg^{-1} of NaCit) was in the range of 0.3 to 0.4, and above this concentration limit, the value of β more than two times (Table 2). The increase in the value of β for AOT was controlled by the sodium ion concentration in the solution, and the citrate co-ion, unlike salicylate co-ion,[7] did not have any effect.

Table 1. Critical Micelle Concentration ($\pm 0.05 \times 10^{-3}$ mol kg^{-1}) of AOT in Aqueous NaCit Solution Obtained by Surface Tension and EMF Methods

Surface tension				EMF	
[Na$^+$] /mol kg^{-1}	cmc × 10^3/mol kg^{-1} 293 K	298 K	303 K	[Na$^+$] /mol kg^{-1}	cmc × 10^3 /mol kg^{-1} (298 K)
0	2.69	2.66	2.75	0	2.51
0.0030	2.45	2.24	2.24	0.0159	1.38
0.0207	1.20	1.13	1.24	0.0348	1.01
0.0348	0.93	0.89	0.98	0.0447	0.75
0.0831	0.53	0.46	0.47	0.1065	0.39
0.2160	0.27	0.22	0.25	0.1968	0.22
0.2958	0.16	0.15	0.17	0.3000	0.19
0.5685	0.11	0.09	0.10	0.6009	0.10
0.9783	0.05	0.05	0.05	0.8988	0.05
1.3005	0.04	0.04	0.04		

The values of β at 25 °C in the presence of NaCit were also computed by least-squares fitting the EMF (E) data to Eqs. 2 and 3.

$$E = A_1 + B_1 \log c_{\mathrm{Na}} \quad \text{for} \quad c < c_0, \tag{2}$$

$$E = A_1 + B_1 \log[(1-\beta)c_{\mathrm{Na}} + \beta c_{\mathrm{Na0}}] \quad \text{for} \quad c > c_0, \tag{3}$$

where the terms c_0 and c_{Na} represent the cmc and concentration of sodium ion, respectively,[6] c_{Na0} is the concentration of sodium ion at the cmc, and A_1 and B_1 are empirical constants. In the absence of electrolyte, c_{Na} is equal to the concentration of the surfactant (c) and in the presence of the electrolyte $c_{\mathrm{Na}} = c + 3c_{\mathrm{e}}$, where c_{e} refers to the concentration of NaCit. The method of calculating β from EMF data using Eqs. 2 and 3 is described elsewhere,[6] and the values of β thus obtained are listed in Table 3. The values of β calculated from the EMF data show that, in the Na$^+$ ion concentration range below 0.02 mol kg^{-1}, β is equal to 0.44 (average value) and, above this concentration limit, it increased to 0.78 (average value). We ascertain that this counter ion binding behaviour

Table 2. Least-Squares-Fitted Values of the Parameters of Eq. 1 for AOT

Conc. range of added Na$^+$ /mol kg^{-1}	293 K A	293 K β	298 K A	298 K β	303 K A	303 K β
0–0.02	−13.86	0.40	−13.19	0.33	−13.10	0.32
>0.02	−17.27	0.86	−17.47	0.89	−17.28	0.87

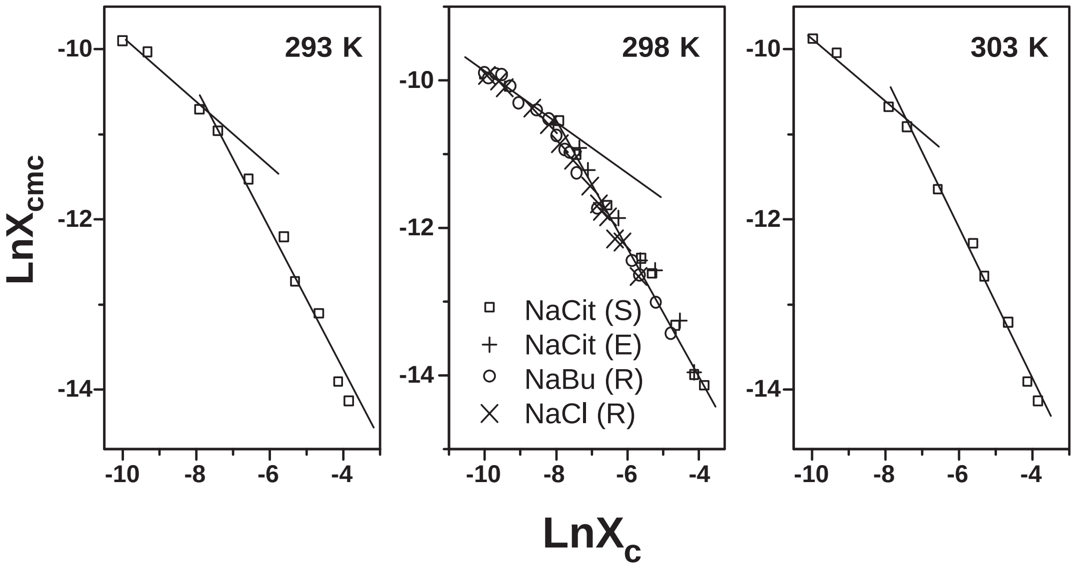

Fig. 2. Variation of $\ln X_{\mathrm{cmc}}$ with $\ln X_{\mathrm{c}}$ of AOT in NaCit solution. Letters given in the parentheses indicate that cmc is from surface tension (S), EMF (E), and reported (Ref. 6) data (R).

Table 3. Values of Intercept (A_1) and Slope (B_1) of Eq. 2 for AOT in Aqueous NaCit Solution at 25 °C

$[\mathrm{Na}^+]$ /mol kg^{-1}	A_1 /mV	B_1 /mV	$\beta \pm 0.02$
0	138.30	57.800	0.42
0.0159	140.12	65.070	0.45
0.0348	332.80	203.64	0.67
0.0447	220.86	130.20	0.63
0.1065	680.98	636.68	0.77
0.1968	3124.6	4332.5	0.80
0.3000	2528.7	4685.5	0.89
0.6009	5654.2	25161	0.92
0.8988	1865.4	38177	0.75

Table 4. Computed Values of Surface Excess (Γ_{cm}) and Surface Area per Molecule (A_0) of AOT Near CMC in Presence of NaCit

[NaCit]	($\Gamma_{\mathrm{cmc}} \pm 0.5$) × 10^6/mol m^{-2}			A_0/nm^2		
/mol kg^{-1}	293 K	298 K	303 K	293 K	298 K	303 K
0	1.80	1.63	1.63	0.92	1.02	1.02
0.0010	2.04	1.82	1.95	0.81	0.91	0.85
0.0069	2.14	2.02	2.11	0.78	0.82	0.79
0.0116	1.99	2.13	2.08	0.83	0.78	0.80
0.0277	2.04	1.94	2.25	0.81	0.86	0.74
0.0720	2.26	2.21	2.25	0.73	0.75	0.74
0.0986	2.25	2.28	2.29	0.74	0.73	0.73
0.1895	2.32	2.58	2.32	0.72	0.64	0.72
0.3261	2.52	2.51	2.41	0.66	0.66	0.69
0.4335	2.55	2.54	2.39	0.65	0.65	0.69

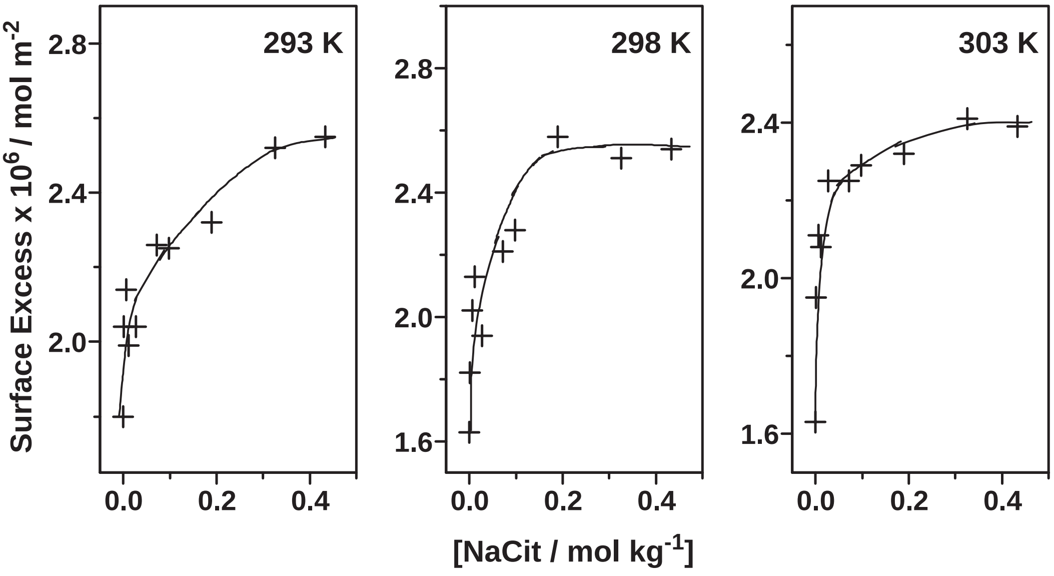

Fig. 3. Change in Γ_{cmc} of AOT at cmc with NaCit concentration.

of AOT in the presence of added sodium ions is special. In other words, this is another interesting feature of AOT.[10–13]

Surface excess (Γ_{cmc}) of AOT in the presence of NaCit was evaluated using the general expression[14]

$$\Gamma_{\mathrm{cmc}} = -\left[\frac{1}{RT}\right]\left[1 \Big/ \left(n_- + \frac{{n_+}^2 c_0}{(n_+ c_0 + n_{+\mathrm{e}} c_\mathrm{e})}\right)\right]\left[\frac{\mathrm{d}\gamma}{\mathrm{d}\ln c}\right]_{\text{at cmc}}. \tag{4}$$

In Eq. 4, n_- and n_+ are the number of moles of surfactant monomer and counter ion, respectively, produced by the dissociation of one mole of an anionic surfactant, respectively. For AOT, $n_- = 1$ and $n_+ = 1$. $n_{+\mathrm{e}}$ is the number of moles of positive ions produced by the dissociation of one mole of the added electrolyte and for NaCit, $n_{+\mathrm{e}} = 3$. R and T represent the gas constant and temperature, respectively. The values of Γ_{cmc} calculated from Eq. 4 are given in Table 4. The variation of Γ_{cmc} as a function of salt concentration is shown in Fig. 3. Γ_{cmc} of AOT increased initially upon the addition of NaCit, reached a maximum value and then remained almost constant at this maximum value. This type of surface activity behaviour of AOT in NaCit solution was similar to that of AOT in NaCl, NaAc, and NaPr solutions, but different from that in NaBu solution.[6] Thus, citrate co-ion exhibits some influence on the surface activity behaviour of AOT at higher concentrations of the added electrolyte. Salting-out effect of electrolytes is a probable reason for the influence of the co-ion on the Γ_{cmc} of surfactants, and this effect is controlled by the hydration of the ionic species of electrolytes. In Table 4, we have also included the values of the area (A_0) covered per molecule of AOT at the air–solution interface in the presence of NaCit, which were evaluated by using the relation $A_0 = (N_\mathrm{A}\Gamma_{\mathrm{cmc}})^{-1}$, where N_A is the Avogadro number.

The standard free energy of micellization per mole of monomer (ΔG^0_m) and the standard free energy of adsorption at the air–solution interface (ΔG^0_{ad}) for AOT in the presence of NaCit were estimated using the following:[9,15,16]

$$\Delta G^0_\mathrm{m} = (1 + \beta) RT \ln X_{\mathrm{cmc}}, \tag{5}$$

$$\Delta G^0_{\mathrm{ad}} = \Delta G^0_\mathrm{m} - \pi_{\mathrm{cmc}}/\Gamma_{\mathrm{cmc}}. \tag{6}$$

In Eq. 6, π_{cmc} refers to the surface pressure at cmc. For evalu-

Table 5. Values of $\Delta G^{\circ}_{\mathrm{m}}$ and $\Delta G^{0}_{\mathrm{ad}}$ of AOT in Aqueous NaCit Solution

$[\mathrm{Na}^+]$ /mol kg^{-1}	$-\Delta G^{\circ}_{\mathrm{m}} \pm 0.5$/kJ mol^{-1} 293 K	298 K	303 K	$-\Delta G^{0}_{\mathrm{ad}} \pm 0.5$/kJ mol^{-1} 293 K	298 K	303 K
0	33.88	32.78	31.88	55.83	57.93	58.24
0.0031	34.20	33.34	32.54	55.04	56.41	54.84
0.0207	36.64	34.87	34.03	57.90	57.30	56.06
0.0348	49.83	51.71	49.86	72.95	72.67	72.22
0.0831	52.65	54.90	53.41	74.95	77.69	74.07
0.2160	55.45	58.27	56.09	75.00	77.64	76.62
0.2958	57.55	59.21	57.11	77.54	78.16	77.41
0.5685	59.55	62.48	60.27	79.13	78.84	80.19
0.9783	63.15	65.27	63.44	81.36	82.37	82.73
1.3005	64.19	66.34	64.47	81.57	83.19	83.71

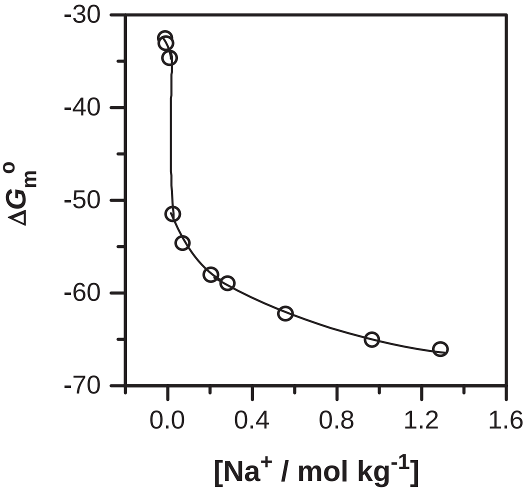

Fig. 4. Change in $\Delta G^{\circ}_{\mathrm{m}}$ of AOT at 25 °C with the concentration of added sodium ion.

ating $\Delta G^{0}_{\mathrm{m}}$, we used in Eq. 5 the values of β obtained from the CH plots (Table 2). The calculated values of $\Delta G^{0}_{\mathrm{m}}$ and $\Delta G^{0}_{\mathrm{ad}}$ are given in Table 5. The change in $\Delta G^{0}_{\mathrm{m}}$ with the concentration of added sodium ion at 25 °C is shown in Fig. 4. A sudden jump in the value of $\Delta G^{0}_{\mathrm{m}}$ for AOT above a Na^+ concentration of 0.02 mol kg^{-1} can be seen clearly from Fig. 4 and Table 5, which is due to a change in β at this concentration of added sodium ion.

The aggregation numbers (N_0) of AOT in the presence of NaCit at 25 °C were determined from the fluorescence-quenching method by using Eqs. 7 and 8:[17]

$$I_0/I_{\mathrm{q}} = \exp([\mathrm{q}]/[\mathrm{micelle}]), \tag{7}$$

$$N_0 = (c - c_0)/[\mathrm{micelle}], \tag{8}$$

where I_0 and I_{q} are the intensities of fluorescence emission of pyrene at 374 nm in the absence and presence of the quencher (cetylpyridinium chloride) of concentration [q], respectively. The values of N_0 for AOT as a function of NaCit concentration calculated using Eq. 7 are given in Table 6. From the emission spectra of pyrene in solutions of AOT in the presence of NaCit, the ratio of the intensity of the third peak at 384 nm to that of the first peak at 374 nm (I_3/I_1), which is known as polarity index,[18,19] was calculated, and its values as a function of NaCit concentration are also given in Table 6. In Fig. 5, it can be seen that N_0 and I_3/I_1 were dependent on NaCit concentration. The sudden change in N_0 for AOT between 0.007 and 0.008 mol kg^{-1} of NaCit (Table 6) is similar to the sudden change observed in the value of β of AOT. In the concentration range of NaCit, where β and N_0 have lower values, I_3/I_1 had a value greater than one. In aqueous AOT solution, in the absence of any added electrolyte, I_3/I_1 was however equal to 0.93. $I_3/I_1 > 1$ has been reported in hydrocarbon solvents, 1-pentanol and 2-propanol.[14] The value of I_3/I_1 became less than one in the NaCit concentration range (>0.007 mol kg^{-1}) where β and N_0 have higher values. The sudden change in the value of I_3/I_1 from >1 to <1 indicates that the polarity of the medium experienced by pyrene in the two concentration regions of NaCit are different. In fact, due to the sudden increase in the number of counter ions bound to AOT micelles, a change in the dielectric constant of the micelle–solution interface can be expected to take place at NaCit concentration of ≈0.007 mol kg^{-1}. The sudden increase in N_0 of AOT around 0.007 mol kg^{-1} of NaCit may also be due to the increase in the value of β, since the presence of more

Table 6. Ratio of the Intensity (I_3/I_1) of Fluorescence Emission Peak of Pyrene at 384 nm (I_3) to that at 374 nm (I_1) in Aqueous AOT + NaCit Media and Aggregation Numbers of AOT in Aqueous NaCit Solution at 25 °C

[NaCit] /mol kg^{-1}	$(c - c_0)$ /mol kg^{-1}	$N_0 \pm 5$	$\frac{I_3}{I_1} \pm 0.01$
0.001	0.005	24	1.01
0.002	0.005	28	1.03
0.004	0.005	41	1.04
0.006	0.005	38	1.03
0.007	0.002	37	1.02
0.008	0.002	71	0.97
0.010	0.004	81	0.89
0.050	0.002	75	0.88
0.100	0.002	82	0.90

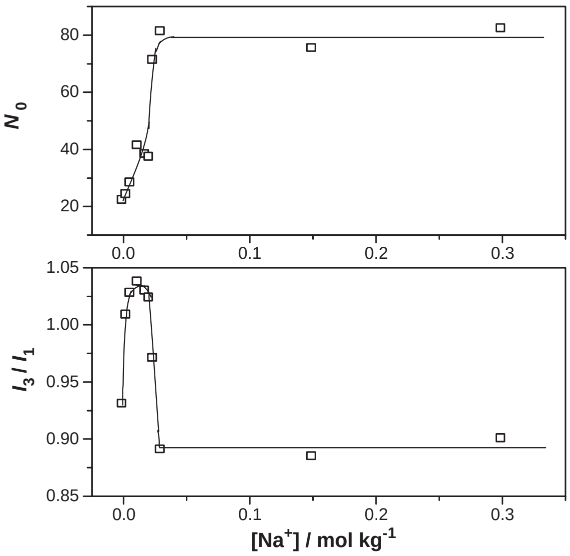

Fig. 5. Change in N_0 of AOT and I_3/I_1 ratio of pyrene in the presence of AOT as a function of added sodium ion (NaCit) concentration at 25 °C.

counter ions decreases the repulsion between the head groups, thereby facilitating the assembly of more monomers.

It has been reported recently[6,20] that a change in the shape of ionic micelle is responsible for a shift in the value of β. Fujio et al.[20] have reported that, in the cases of dodecylpyridinium bromide, dodecylpyridinium iodide, and tetradecylpyridinium bromide micelles, the value of β increases in the order of sphere-shaped < oblate ellipsoidal < rod-like micelles. In AOT, the length of the 2-ethylhexyl succinate chain and the dry volume of the double chains are equal to 12.6 Å and 546 Å^3, respectively and therefore a dry hydrophobic core of the spherical shape can accommodate the tails of only 15 AOT molecules.[21] The shape of AOT micelles having an N_0 in the range of 24 to 41 is considered to be an oblate spheroid with axial-to-polar-radius ratio varying from 1.25 to 1.63, which is supported by a SANS study made by Sheu et al.[21] Therefore, the change in the value of β of AOT at around 0.007 mol kg^{-1} of NaCit solution may be due to a change in the shape of AOT micelles from oblate spheroid to rod-like. The present and earlier studies[6,20] confirm that the amount of counter ion binding to an ionic micelle depends on the structure of the ionic surfactant and also on the shape of the micelle.

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