Stepwise Changes in Solution Properties of *N*-lauroyl-*N*-methyltaurates Having Na⁺, Mg²⁺, and Ca²⁺ as Counter Ions : Successive Micellar Reorganization in Relation to Binding of Counter Ions

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Abstract : The surface chemical properties of various *N*-lauroyl-*N*-methyltaurates (RCON(CH₃)C₂H₄SO₃Na, RCON(CH₃)C₂H₄SO₃Mg_{1/2}, RCON(CH₃)C₂H₄SO₃Ca_{1/2}; R=CH₃(CH₂)₁₀ : LMT) have been examined in terms of surface tension, electric conductivity, pNa, dynamic and static light scattering and spectral shifts of vibrational Raman lines. These parameters are found to change with surfactant concentration, depending on the particular counter ion. The micellar aggregation number in LMT-Na is much smaller than those in the other two surfactants. The Raman signal on the basis of the S-O stretching is shifted to high wavenumbers because of the formation LMT-Na micelles. LMT-Na micelles would thus appear to serve as favorable sites for Na⁺ ion capture, owing to its bulky structure formed around the hydrophilic group, compared to the Mg and Ca analogues.

Key words : *N*-lauroyl-*N*-methyltaurate, Surface tension, Conductivity, Raman scattering, Aggregation number

1 Introduction

N-acyl-*N*-methyltaurates (AMT, especially when acyl=lauroyl : LMT) have been used as a surfactant in the fabric industry since around 1930. Recently, the use of LMT has been examined in the cosmetic industry due to its improved purity. LMTs are synthetic surfactants whose structural formulas are similar to that of taurocholic acid present in bile, and they are known to possess many excellent properties; they are scarcely toxic, hard-water-proof, damage-proof for hair cuticle of a high threshold for salting out, and biodegradable^{1)~4)}. The practical use of LMT as a surfactant, especially in cosmetics and toilet articles, has been actualized by utilizing these features, and they have interestingly drawn significant attention. The characteristics of LMT solutions, however, have still remained unknown in relation to these excellent properties. Therefore, in this study, the micellar formation of LMT with various counter ions has been investigated with measurements of Krafft

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point, surface tension, critical micelle concentration (cmc), electric conductivity, pNa, light scattering, and Raman spectrum.

2 Experimental Section

2.1 Materials

Sodium *N*-lauroyl-*N*-methyltaurate; [$\text{CH}_3(\text{CH}_2)_{10}\text{CON}(\text{CH}_3)\text{C}_2\text{H}_4\text{SO}_3\text{Na}$, LMT-Na], magnesium *N*-lauroyl-*N*-methyltaurate; [$\text{CH}_3(\text{CH}_2)_{10}\text{CON}(\text{CH}_3)\text{C}_2\text{H}_4\text{SO}_3\text{Mg}_{1/2}$, LMT-Mg] and calcium *N*-lauroyl-*N*-methyltaurate; [$\text{CH}_3(\text{CH}_2)_{10}\text{CON}(\text{CH}_3)\text{C}_2\text{H}_4\text{SO}_3\text{Ca}_{1/2}$, LMT-Ca] were synthesized by Oleochemicals Research Laboratory, NOF Corporation, and were used without further purification. Injection water (produced by Otsuka Pharmaceutical Co., Ltd.) was used as the water supply (pH 5.7 : specific conductivity $1.29 \mu\text{S}/\text{cm}$; 25°C).

2.2 Krafft Points

The measurement of Krafft points was performed with a differential scanning calorimeter (DSC-8420 B type by Rigaku Co., Ltd.). A high-pressure crucible made of stainless steel (resisting pressure : 50 atm, 5 mm $\times$ 3 mm) was utilized in the measurements. The cell was sealed after water was added dropwise to make the percent moisture content reach 80 wt% using a microsyringe. Before the measurement, the temperature was increased to around 60°C to allow the sample material to mix thoroughly, and the materials were cooled down to -30°C with liquid nitrogen. The rate of temperature increase was $1^\circ\text{C}/\text{min}$. Visual observation was also done using an aqueous 1 wt% solution.

2.3 Surface Tension

The measurement of surface tension was performed at 25°C with a platinum plate and a Wilhelmy type surface tension balance (A 3 type, Kyowa Interface Science Co., Ltd.). The adsorption amount (Γ) at the air/water interface was calculated using the Gibbs adsorption equation⁵⁾:

$$\Gamma = -\frac{c}{iRT} \left(\frac{\partial \gamma}{\partial c} \right) \quad (1)$$

where R is the gas constant, T is the absolute temperature, c is the molar concentration of surface active substance, and i is the total number of anions and cations constituting a surfactant molecule. In this research, i is as follows ; $i=2$ for LMT-Na and $i=3$ for LMT-Mg and LMT-Ca. The limiting area per molecule (A) at the air/water interface was calculated using the following equation:

$$A = \frac{1}{\Gamma \times N_A} \quad (2)$$

where N_A is the Avogadro's number. The crossing point at which the decreasing curve of γ meets with its horizontal line drawn for higher concentrations indicates the critical micelle concentration (cmc_1) for each solution. The suffix 1 indicates formation of the first micelle in this report, although cmc_0 has been used in current studies.

2.4 Electric Conductivity

The measurement of specific conductivity was conducted at 25°C with an electric conductivity meter (CM-40 S, TOA Electronics Ltd.). When an inflection point appeared first on the specific conductivity curve, the point was taken as cmc_1 .

2.5 Micellar Aggregation Number and Micellar Particle Size

The measurement of the micellar aggregation number was conducted by the static light scattering method at 25°C utilizing a sub-micron particle analyzer (Malvern Instrument Co., system 4700 type) equipped with an Ar-laser with a maximum output of 5,000 mW. The same equipment was also used to measure the micelle particle size by the dynamic light scattering method at 25°C .

When the Debye equation of light scattering is applied to smaller particles compared to wavelength of light ($d \ll \lambda/20$), like micelles in a surfactant solution⁶⁾, it is expressed as equa-

tion (3):

$$\frac{K(c - \text{cmc}_1)}{R_{90} - R_{90}^0} = \frac{1}{M_m} + 2B(c - \text{cmc}_1) \quad (3)$$

where $c - \text{cmc}_1$ is the concentration of the micelle, R_{90} is the ratio of the reduced intensity of scattered light from the surfactant solution to that from pure benzene at 90° , R_{90}^0 is the ratio of the reduced intensity of scattered light from the solvent to that from benzene at 90° , B is the second virial coefficient, M_m is the micellar weight, and K is an optical constant which is expressed in the following form :

$$K = \frac{4\pi^2 \tilde{n}^2 (\partial \tilde{n} / \partial c)^2}{N_A \lambda^4} \quad (4)$$

where $\tilde{n}$ and λ are the refractive index and the wavelength, respectively, of the laser beam. For the determination of micellar aggregation number, measurements of the concentration dependence of refractive index are necessary. Then, the concentration dependence of the refractive index in Eq. (4) was measured at various surfactant concentrations and at 25°C with a differential refractometer (RM-102 type produced by Otsuka Electronics Co., Ltd.). Dust was removed from the sample solution using membrane filters (cellulose nitrate filter, pore size $0.1 \mu\text{m}$ from Advantec).

2.6 pNa

pNa was measured at 25°C using a sodium ion electrode (017 NA by Corning Co.) combined with an ionic densitometer (M-130 by Corning Co.). A saturated calomel electrode (C 002 by Iwaki Glass Co., Ltd.) was used as the reference electrode.

Counter ion activity, a , of an aqueous ionic surfactant solution above cmc_1 , is expressed by the following equation^{7)~10)}:

$$a = \gamma(\text{cmc}_1 + \alpha(c - \text{cmc}_1)) \quad (5)$$

where γ is the activity coefficient of counter ion, cmc_1 is the critical micelle concentration, c is the total surfactant concentration, and α is the degree of counter ion dissociation of micelle. Then, we have

$$\left[\frac{\partial a}{\partial c} \right]_\gamma = \gamma \left(\alpha + (c - \text{cmc}_1) \frac{d\alpha}{dc} \right) \quad (6)$$

when the degree of counter ion dissociation is independent from concentration increase, equation (6) can be reduced to equation (7).

$$\left[\frac{\partial a}{\partial c} \right]_\gamma = \gamma \cdot \alpha \quad (7)$$

According to equation (7), the activity of Na^+ ion, was plotted as a function of the concentration c . The degree of counter ion dissociation for micelle was obtained from the derivative of the curve.

2.7 Raman Spectra

The measurement of Raman spectra was carried out at 25°C with a Raman difference spectrometer¹¹⁾ (Multichannel Raman Difference Spectrometer (RDS): the sensitivity for the wavenumber shift; 0.006 cm^{-1}). This sensitivity was based on the optical mixing with a fiber array and simultaneous recording of atomic emission of Ne and Raman scattering light as well as peak read out with the band fitting¹²⁾. Even without these improvements, Multichannel RDS was found to give accurate value of band shift as accurate as FT-Raman spectrometer¹³⁾.

3 Results

3.1 Krafft Points

On the DSC curves for all of LMT-Na, LMT-Mg, and LMT-Ca, only the peak corresponding to fusion of ice is observed. No precipitation of the surfactant is visually observed. Hence, the Krafft point is found to be below 0°C for each of LMT.

3.2 Surface Tension

Fig. 1 shows the relationship between surface tension and surfactant concentration for the three surfactants.

For all of the three surfactants, the surface tension decreases with an increase in the surfactant concentration, and becomes constant above their respective cmc_1 . Their critical micelle concentrations (cmc_1), surface tensions at cmc_1 (γ_{cmc}) and limiting molecular areas are listed in Table 1.

As shown in Table 1, cmc_1 and γ_{cmc} for LMT depend on the counter ion species, and they become smaller in the following order : LMT-Na > LMT-Mg > LMT-Ca. Moreover, the limiting molecular areas at the water/air interface, which are calculated using the Gibbs adsorption equation, are in the order : LMT-Mg > LMT-Ca > LMT-Na.

Fig. 1 Relationship between the surface tension and the concentration of *N*-lauroyl-*N*-methyl-taurinate salts at 25°C.

Table 1 cmc_1 , γ_{cmc} and limiting area per molecule of LMT obtained with surface tension measurement at 25°C

	LMT-Na	LMT-Mg	LMT-Ca
$\text{cmc}_1/\text{mol}\cdot\text{l}^{-1}$	9.0×10^{-3}	1.4×10^{-3}	1.1×10^{-3}
$\gamma_{\text{cmc}}/\text{mN}\cdot\text{m}^{-1}$	43	37	34
limiting area/ $\text{\AA}^2\cdot\text{molecule}^{-1}$	81.5	99.9	90.3

3.3 Electric conductivity

Fig. 2 depicts the relationship between specific conductivity (κ) and LMT concentration.

In the case of LMT-Na (a), a bending point appears on the κ -LMT concentration curve at 9.8×10^{-3} mol/l, corresponding to cmc_1 . Above this point, κ increases linearly over a wide range of surfactant concentration. The rate of increase becomes smaller at concentrations higher than 0.4 mol/l. This suggests that Na^+ ions are rather tightly bound to the surfactant micelles at higher concentrations. In the cases of LMT-Mg and LMT-Ca, the κ -LMT concentration curves also exhibit cmc_1 (LMT-Mg ; 1.7×10^{-3} mol/l, LMT-Ca ; 1.5×10^{-3} mol/l). Although the conductivity gives a sufficiently long linear line, the rate of increase becomes larger at high concentrations. As indicated by approaching of the observed curves to the dotted lines in Fig. 2 (b), this increase starts at around 0.07 and 0.05 mol/l for LMT-Mg and LMT-Ca, respectively.

3.4 Micellar Aggregation Number and Micellar Particle Size

With the dynamic light scattering method, micellar size is obtained as 2–3 nm for LMT-

Fig. 2 Relationship between the specific conductivity and the concentration of *N*-acyl-*N*-methyltaurinate salts at 25°C.

Na at 4.5×10^{-1} mol/l, 2~3 nm for LMT-Mg at 8.5×10^{-2} mol/l and 3~4 nm for LMT-Ca at 7.5×10^{-2} mol/l. Due to the lack or interference of scattering intensity, measurements are successful only at these concentrations beyond cmc_1 . Debye plots for LMT solutions against c (concentration)- cmc_1 are shown in Fig. 3. Linearity of the plot, corresponding to micelle formation, is satisfactory until the curve gives a bending point at ~ 0.07 mol/l for LMT-Na and 0.01 mol/l for LMT-Mg and LMT-Ca. Above the bending point, the function grows linearly to indicate higher-order interaction, and another bending point is observed. This second bending points are indicated by the shadowed region in Fig. 3.

Fig. 3 Debye plot for aqueous solutions of *N*-lauroyl-*N*-methyltaurinate salts at 25°C.

In Table 2 are summarized the micellar aggregation number obtained from the Debye plot.

3.5 pNa

Fig. 4 represents the relationship of Na^+ activity in aqueous solution with the surfactant (LMT-Na) concentration.

A linear relationship is obtained above 0.05 mol/l, the slope of which gives, the degree of counter ion dissociation, α , in LMT-Na micelle. It is calculated to be 0.23, which is almost

Table 2 Micellar weight, aggregation number and particle size of LMT micelles measured by light scattering technique at 25°C

LMTs	Micellar weight	Micellar aggregation number	Particle size/nm (Concentration/mol·l ⁻¹)
LMT-Na	11100	32	2~3 (4.5×10 ⁻¹)
LMT-Mg	52600	158	2~3 (8.5×10 ⁻²)
LMT-Ca	62500	184	3~4 (7.5×10 ⁻²)

Fig. 4 Relationship between the activity of Na⁺ and the concentration of sodium *N*-lauroyl-*N*-methyltaurinate at 25°C.

the same as the value of 0.21 in SDS micelle¹⁴). However, equation (7) can not be used in the concentration range below 0.05 mol/l because linear relationship does not hold in this concentration range. It would be ascribable to variation in the degree of counter ion dissociation in the transition from the primary micelle to micelles of other kinds in this region. Therefore, some kind of structural change must be considered at these concentrations.

3.6 Raman Spectra

Raman spectrum for LMT-Na (0.98 mol/l) solution in the S-O stretching region is shown in Fig. 5.

As the Raman band assignable to symmetric SO₃⁻ stretching line ($\nu_s(\text{SO}_3)$)¹⁵) consists of several peaks, the vibrational wavenumber is examined for the strongest peak as a function of surfactant concentration. Positive shift of this band has been understood as the result of enhanced O...Na⁺ collisional interaction¹⁶). The relation between $\nu_s(\text{SO}_3)$ and surfactant concentration is shown in Fig. 6.

For each aqueous LMT solution, the vibrational wavenumber of $\nu_s(\text{SO}_3)$ shifts upward with increase in surfactant concentration. In the case of LMT-Na (a), the wavenumber keeps increasing even at higher concentrations, whereas in the cases of LMT-Mg and LMT-Ca (b), the wavenumber levels off above 6.0×10⁻² mol/l and 6.5×10⁻² mol/l, respectively. This

Fig. 5 Raman spectrum for aqueous 0.98 mol/l solution of sodium *N*-lauroyl-*N*-methyltaurate at 25°C.

Fig. 6 Concentration dependence of the wavenumber of symmetric SO_3^- stretching band of *N*-lauroyl-*N*-methyltaurate salts at 25°C.

suggests that the SO_3^- ion interacts with Na^+ strongly even at such high surfactant concentrations though the interaction of it with Mg^{2+} or Ca^{2+} becomes almost invariant above the concentration of $\sim 6.0 \times 10^{-2}$ mol/l.

4 Discussion

LMT-Na has the same alkyl chain length as that of SDS, a typical anionic surfactant, and the former also has almost the same cmc_1 and γ_{cmc} as those of the latter. However, the micellar aggregation number for LMT-Na obtained by light scattering method (32 below 7.0×10^{-2} mol/l) differs from that for SDS (62) at cmc_1 ¹⁷⁾. From the comparison with SDS, LMT-Na micelle is further smaller than the usual size. The amide group, characteristic for LMT molecule, may be responsible for the small size through complex formation with Na^+ ion. Both oxygen and nitrogen atoms in certain molecules are known to act as a ligand, as in ethylenediaminetetraacetate (EDTA^{4-}) and acetylacetonate anions. Since the oxygen atom is

negatively charged, it may provide to a better coordination to Na^+ ion under 8-membered ring formation ($\text{O}-\text{C}-\text{N}-\text{C}-\text{C}-\text{S}-\text{O}-\text{Na}^+$). Another coordination with the nitrogen ligand forms 6-membered ring ($\text{N}-\text{C}-\text{C}-\text{S}-\text{O}-\text{Na}^+$). The six- and eight-membered ring structures are postulated as bidentate ligands for a coordinated complex as shown in Fig. 7. In the figure, the sp^3 hybrid orbital lone pair of the nitrogen atom in the amide group and the sp^2 hybrid orbital lone pair of the oxygen atom bond with Na^+ , the counterion of LMT-Na.

Fig. 7 (a) Six-membered ring structure of sodium *N*-lauroyl-*N*-methyltaurate, (b) eight-membered ring structure of sodium *N*-lauroyl-*N*-methyltaurate (part of $\text{CON}(\text{CH}_3)\text{C}_2\text{H}_4\text{SO}_3\text{Na}$).

These structures inevitably provide a bulky volume to the hydrophilic group of the LMT-Na molecules. It would arise some possibility that the micellar aggregation number becomes smaller in LMT-Na than in LMT-Mg and LMT-Ca, as long as micellar volume is essentially determined geometrically by the hydrophobic and hydrophilic groups. It may be worth to exemplify one plausible case to understand how such volume-aggregation number relationship comes to appear, since large extent of sectional expansion at the hydrophilic group has not been popularly considered. One plausible case is spherical micelle. We suppose a spherical micelle with radius r , constructed geometrically by N surfactant molecules. The geometrical structure means that micellar surface is entirely covered with the hydrophilic groups of surfactant with the sectional area a and micellar interior is filled with the hydrophobic tails^{18)~20)}. In that case, a and N can be expressed as follows;

$$a = \frac{4\pi r^2 \theta}{N} \quad (8)$$

$$N = \frac{4\pi r^3}{3v} \quad (9)$$

where N is the micellar aggregation number, v is the volume of the hydrophobic group. Penetration of water inside the micelle is included in v , as long as the contribution is almost unchanged. In addition, we suppose that the micellar surface may not be entirely covered by the hydrophilic group so that we introduce coverage coefficient θ ($\theta < 1$) in eq. (8). Eliminating r from equations (8) and (9) yields the following equation:

$$N = \frac{36\pi v^2 \theta^3}{a^3} \quad (10)$$

As is evident from equation (10), the micellar aggregation number is in reciprocal proportion to the third power of the surface area of the hydrophilic group of one surfactant molecule. Moreover, v can be regarded as constant because the alkyl chain of the surfactant has enough fluidity to be packed inside the sphere. The size of the hydrophilic group of the molecule can be estimated from a molecular model. The cross sectional area of an LMT-Na molecule with the six-membered ring structure was found to be about twice the size of that with the

open structure. Correspondingly, the micellar aggregation number of LMT-Na with the six-membered ring form can reach at $\sim 1/8$ of the number of the uncoordinated structure. The surface coverage by hydrophilic group will not be established entirely in other structure such as block micelle where hydrophobic groups partially face to water. As given by eq. 9, such structure, decrease of aggregation number would also proceed at the similar power dependence on a . Therefore, it is promising that micelle size can shrink with the sectional expansion at the hydrophilic group.

In general, the micellar weight of an alkylsulfonate surfactant with Mg^{2+} counter ion is twice as large as that with Na^+ counter ion²¹⁾. However, in the case of LMT, the micellar weight of LMT-Mg is about 5 times that of LMT-Na. The smaller aggregation number of LMT-Na (32 below 7.0×10^{-2} mol/l), as $\sim 1/2$ of that of SDS (62), supports the ring structure formation in LMT-Na micelles. The amido-Na coordination seems desirable for Na^+ ion capture at the low expense of hydrating water. On the contrary, the 1 to 1 ion capture or coordination seems to be not stable enough for divalent cations, which is neutralized by two SO_3^- units. We suppose that LMT-Mg and LMT-Ca do not form such coordinated bulky structure at the micellar surface. LMT is soluble singly in a wide range of concentration or in the presence of Na^+ ions, also suggesting some kind of Na^+ ion capture. Therefore, the structural change around amido/sulfonate group suggested above for LMT-Na, seems relevant the observed micellar behavior. This scheme can be further tested in the analysis of Raman bands, where the spectral changes are bond-selective, thus expected to be directly dependent on the concentration.

On the other hand, the behavior of κ -LMT in Fig. 2 seems to suggest another critical points above cmc_1 , related with ionic association. The critical points may correspond to 0.5 mol/l for LMT-Na, 0.07 mol/l for LMT-Mg, and 0.05 mol/l for LMT-Ca. Also, the Debye plots in Fig. 3 indicate that there may be two additional transitions at ~ 0.07 mol/l and ~ 0.7 mol/l for LMT-Na, and ~ 0.01 mol/l and $0.03 \sim 0.06$ mol/l for LMT-Mg and LMT-Ca. From these two additional transitions in κ -LMT and the Debye plot, LMT solutions seem to undergo three stages of micelle formation as a whole. At certain concentrations, these micelles seem to coexist or to be converted from one to another. Therefore, a multiple micelle formation (MMF) model is necessary to distinguish different properties of each of different kind micelles and their contributions.

In the MMF model, the first kind micelles (micelle 1) and thought to be converted to the second kind ones (micelle 2) and to the third kind micelles (micelle 3), above cmc_2 and cmc_3 , respectively. As shown in Fig. 8, two types of conversion are possible: type I for which the next kind micelles are formed at the expense of the prior kind micelles and type II for which the next kind micelles are formed additionally to a fixed number of the prior kind micelles. Type of each conversion cannot be predetermined, therefore, it is judged hereafter from concentration dependence of the physicochemical properties using Raman scattering measurement.

As considered in the MMF model, the micelle structure of LMT changes according to their concentration increment. Furthermore, in the type II conversion, the wavenumber shift of the symmetric SO_3^- stretching band at Raman spectrum is expected to be given as a weighted average of the shifts from the wavenumber for each species, in which the primary species is fixed in number as shown in Fig. 8. When the specific wavenumbers of monomer, micelle 1, micelle 2, and micelle 3 species are designated by ν_0 , ν_1 , ν_2 , and ν_3 , respectively, the following relation is established. Here, C is the total surfactant concentration.

when $C < \text{cmc}_1$

$$\nu_{\text{total}} = \nu_0$$

when $\text{cmc}_1 < C < \text{cmc}_2$

(11)

Fig. 8 Concentration diagram for multiple micelle formation (MMF) with three stages.

(Type I) Higher stage of micelles are formed beyond each cmc_x ($x=0, 1..$), being accompanied with the decrease of the prior micelles.

(Type II) Formation of prior micelles are stopped at each cmc_x ($x=0, 1..$) to generate the next stage of micelles.

$$\nu_{\text{total}} = \frac{\nu_0 \text{cmc}_1 + \nu_1 (C - \text{cmc}_1)}{C} = \text{cmc}_1 (\nu_0 - \nu_1) \times \frac{1}{C} + \nu_1 \quad (12)$$

when $\text{cmc}_2 < C < \text{cmc}_3$

$$\begin{aligned} \nu_{\text{total}} &= \frac{\nu_0 \text{cmc}_1 + \nu_1 (\text{cmc}_2 - \text{cmc}_1) + \nu_2 (C - \text{cmc}_2)}{C} \\ &= \{\text{cmc}_1 (\nu_0 - \nu_1) + \text{cmc}_2 (\nu_1 - \nu_2)\} \times \frac{1}{C} + \nu_2 \end{aligned} \quad (13)$$

when $\text{cmc}_3 < C$

$$\begin{aligned} \nu_{\text{total}} &= \frac{\nu_0 \text{cmc}_1 + \nu_1 (\text{cmc}_2 - \text{cmc}_1) + \nu_2 (\text{cmc}_3 - \text{cmc}_2) + \nu_3 (C - \text{cmc}_3)}{C} \\ &= \{\text{cmc}_1 (\nu_0 - \nu_1) + \text{cmc}_2 (\nu_1 - \nu_2) + \text{cmc}_3 (\nu_2 - \nu_3)\} \times \frac{1}{C} + \nu_3 \end{aligned} \quad (14)$$

These equations would give $\nu_s(\text{SO}_3)$ a folded line as a function of the reciprocal of surfactant concentration. Zero intercept for each increment corresponds to the particular wavenumber, while the boundary points indicate the cmc values. When linearity or bending is not clear enough at an increment, such behavior must be ascribable to type I conversion. Fig. 9 represents the relation between wavenumber ($\nu_s(\text{SO}_3)$) and reciprocal LMT concentration.

From the observed profiles, type II scheme seems to be adequate except for micelle 2 formation in LMT-Na, where linearity is not sufficient and hence type I scheme can be assigned. If the counter ions are completely free, the corresponding $\nu_s(\text{SO}_3)$ would be counter ion-independent and take a smallest value, as low as that represented by the dotted, horizontal line (1046.7 cm^{-1}) in Fig. 9 (a). The crossing point of this line and the neighboring slope gives vibrationally-determined cmc_1 for each of LMT solutions, as $8.8 \times 10^{-3} \text{ mol/l}$ for LMT-Na, $1.2 \times 10^{-3} \text{ mol/l}$ for LMT-Mg, and $1.5 \times 10^{-3} \text{ mol/l}$ for LMT-Ca. Also, cmc_2 and cmc_3 are deduced from Figs. 9 as follows. In LMT-Na, Figs. 9 (a) reveals a smooth curve between $C^{-1} = 2.5$ and $161 \cdot \text{mol}^{-1}$, indicating type I transition. Therefore, $\text{cmc}_2 \sim 6 \times 10^{-2} \text{ mol} \cdot \text{l}^{-1}$ and $\text{cmc}_3 \sim 4 \times 10^{-1} \text{ mol} \cdot \text{l}^{-1}$ are determined as a point where the linear line above $C^{-1} > 101 \cdot \text{mol}^{-1}$ joins

Fig. 9 (a)

Fig. 9 (b)

Fig. 9 Shift of the wavenumber of symmetric SO_3^- stretching band of *N*-lauroyl-*N*-methylaurate salts as a function of reciprocal of concentration at 25°C.

to the curve at $C^{-1} \sim 161 \cdot \text{mol}^{-1}$ and that below $C^{-1} < 101 \cdot \text{mol}^{-1}$ joins to the curve at $C^{-1} \sim 2.51 \cdot \text{mol}^{-1}$, respectively. On the other hand, in LMT-Mg and LMT-Ca, **Figs. 9 (b)** suggests that it proceeds via type II transition. The first rising lines from cmc_1 seem to be suddenly converted to another lines at $C^{-1} = 140 \sim 150 \cdot \text{mol}^{-1}$. This would give $\text{cmc}_2 = 7 \times 10^{-3} \text{ mol} \cdot \text{l}^{-1}$. While the next converting points are not apparent enough at this scale, we can clearly determine the particular wavenumber to be 1049.37 cm^{-1} for LMT-Mg and 1049.70 cm^{-1} for LMT-Ca from the horizontal locations at the highest concentrations in **Fig. 6 (b)**. These constant values should be corresponded to horizontal lines drawn at the lowest C^{-1} in **Figs. 9 (b)**, which meet with the lines rising from cmc_3^{-1} at $C^{-1} = 14 \sim 151 \cdot \text{mol}^{-1}$. Correspondingly, combination of **Fig. 6 (b)** and **Figs. 9 (b)** suggests $\text{cmc}_3 = \sim 7 \times 10^{-2} \text{ mol/l}$ for both LMT-Mg and LMT-Ca. These results of particular wavenumbers and corresponded cmc values are summarized in **Tables 3**, in addition with cmc values obtained from conductivity measurement and the Debye plot. The cmc values obtained from Raman shift seem to be agreeable with the values obtained with other methods.

Table 3 Cmc values of LMTs obtained with various methods and characteristic wavenumber of SO_3^- vibrational signal of each micelle observed at Raman scattering method.

Methods	$\text{cmc}_n/\text{mol}\cdot\text{l}^{-1}$					
	cmc_n	Surface tension	Electric conductivity	Static light scattering	Raman scattering	
	cmc_n				cmc_n	Characteristic wavenumber (cm^{-1})
LMT-Na	cmc_1	9.0×10^{-3}	9.8×10^{-3}	—	8.8×10^{-3}	1049.1
	cmc_2	—	(continuous)	7×10^{-2}	6×10^{-2}	(continuous)
	cmc_3	—	5×10^{-1}	$(6\sim 8) \times 10^{-1}$	4×10^{-1}	1050.0
LMT-Mg	cmc_1	1.4×10^{-3}	1.7×10^{-3}	—	1.2×10^{-3}	1048.6
	cmc_2	—	(continuous)	1×10^{-2}	7×10^{-3}	1049.5
	cmc_3	—	7×10^{-2}	$(3\sim 5) \times 10^{-2}$	6×10^{-2}	1049.4
LMT-Ca	cmc_1	1.1×10^{-3}	1.5×10^{-3}	—	1.5×10^{-3}	1048.8
	cmc_2	—	(continuous)	1×10^{-2}	7×10^{-3}	1049.8
	cmc_3	—	5×10^{-2}	$(3\sim 6) \times 10^{-2}$	7×10^{-2}	1049.7

Apparently, the particular wavenumber almost unchanges after the transition from micelle 2 to micelle 3 in LMT-Mg and LMT-Ca solutions, whereas the wavenumber for micelle 2 varied continuously in LMT-Na solution as shown in the Tables. This is because the value corresponds to the zero intercept of the curve at each point between $1/\text{cmc}_1$ and $1/\text{cmc}_2$ in Fig. 6 (a), which increased continuously from the level of $\sim 1049.1 \text{ cm}^{-1}$ to $\sim 1050.0 \text{ cm}^{-1}$. Therefore, Na^+ ions are thought to be bound on the SO_3^- more tightly in the order of micelle $1 < \text{micelle } 2 < \text{micelle } 3$.

From these discussion, we can say that different types of LMT micelles coexist, provided that plots of wavenumber of SO_3^- vibrational Raman signal against C^{-1} have clear bending points given as the intersection of two linear lines. In such cases properties of micelles may be expressed as a sum of the contributions from each micelles. This would give rise to potential for the second Debye plot. The plot may be applied on the condition that simple sum rule of scattering activity from each micelles is experimentally suggested from MMF behavior. Instead of cmc_1 and R_{90}^1 in eq. (3), cmc_2 and R_{90}^2 at cmc_2 are applied as well as K value with n determined for the micellar solution. Micelle 2 has the size of 2–3 nm in diameter as observed with dynamic light scattering and hence it seems to still satisfy the condition $d \ll \lambda/20$. It is difficult to eliminate the scattering factor, $P(90^\circ)$, which is assumed to be unity in eq. (3), but is generally involved in the apparent weight of micelle 2. Scattering contributions from micelle 2 for LMT-Na is plotted against $c - \text{cmc}_2$ at concentrations above cmc_2 as shown in Fig. 10.

The plot gives a linear line due to micelle 2 and 3 formation, although deviation due to micelle 3 formation is not apparent. Thus, as long as the aggregation number is concerned, micelles 2 and 3 of LMT-Na are indistinguishable in light scattering. The second Debye plot is also applied for LMT-Mg and LMT-Ca. From the intercept, the micellar aggregation number for the micelle 2 is obtained as 7 for LMT-Na and 53 and 75 for LMT-Mg and Ca, respectively. While the numbers are small as ~ 7 in LMT-Na, the effect of $P(90^\circ)$ must be considered. The particle size is found to be 2–3 nm in LMT-Na and LMT-Mg and 3–4 nm in LMT-Ca at micelle 2 region. We therefore think that the 2–3 nm sized particles in LMT-Na solution is corresponded to micelle 1 with aggregation number ~ 32 , associating weakly to construct micelle 2 with depressed scattering activity, while the 2–3 and 3–4 nm sized

Fig. 10 The second Debye plot for LMT-Na. Original data were the same as Fig. 3.

particles in LMT-Mg and LMT-Ca solutions are related to micelle 2 with aggregation number ~ 53 and 75, respectively. Correspondingly, the numbers from the second Debye plot are fairly agreeable with the sizes obtained from dynamic light scattering. Aggregation numbers of micelle 2 for LMT-Mg (58), and Ca (65) are smaller than those for micelle 1 (158 and 184, respectively), probably due to some extent of coordination with their counter ions (Mg^{2+} , Ca^{2+}), which restricts the association of micelles.

The above association model can explain how κ -LMT grows nonlinearly. The nonlinear rise was slightly negative in LMT-Na but positive LMT-Mg and LMT-Ca and both effects are ascribed to intermicellar interaction. From the above discussion, the former can be interpreted in terms of depressed mobility due to tight binding of Na^+ ions on micelle 1 and its micellar association to micelle 2 and 3 in addition. On the contrary, the latter is ascribable to ordinary ionic association of Mg^{2+} and Ca^{2+} on micelles 2 and 3, which seems to migrate faster with the smaller aggregation number than micelle 1. Of course, smaller sized micelles are larger in number at the same surfactant concentration hence these differences are almost relative.

5 Conclusions

Several kinds of physicochemical measurements on sodium, magnesium, and calcium salts of *N*-lauroyl-*N*-methyltaurinate have independently shown that their micellar structures change successively with their concentration. The micellar aggregation number and Raman band shift suggest that the hydrophilic moiety of LMT-Na has a bulky structure at the micelle surface, where Na^+ ions easily combine. This structural flexibility seems to be responsible for the excellent interfacial properties of LMT.

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日本油化学会誌本号掲載 論文要旨

[総説]

食 用 油 脂 の 分 別

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分別は食用油脂物性の多様化のための一次加工技術として、水素添加やエステル交換技術とともに重要な役割をはたしてきた。分別は、固形状もしくは半固形状の油脂を、融点、硬さや固体脂含量の異なるいくつかのフラクションに分け、その関連製品への応用を広げる加工技術であり、工程には二つのステップがある。すなわち晶析槽での結晶化と、それに続く結晶部と液体部との分離で、工業的には3種の分別方式が知られ、結晶化、分離方法に各々特色がある。分別処理により応用が最も拡大したのがパーム油で、中融点部は製菓用油脂として、また液体部はフライ、スプレー、調理用として用途が格段に増加し、現在では大豆油に次ぐ重要な油糧資源となっている。分別は可逆的工程でロスも少なく、またトランス異性体を生成せずに高融点油脂、並びに低融点油脂が同時に得られるという、他の加工技術には見られない側面があるため、一次加工に於ける分別の重要性はますます高まるものと期待される。

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[報文]

 Na^+ , Mg^{2+} , Ca^{2+} を対イオンとして有する
N-ラウロイル-*N*-メチルタウリンの溶液物性
 —対イオンの結合によるミセルの段階的再構成—

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N-ラウロイル-*N*-メチルタウリン ($\text{RCON}(\text{CH}_3)\text{C}_2\text{H}_4\text{SO}_3\text{Na}$, $\text{RCON}(\text{CH}_3)\text{C}_2\text{H}_4\text{SO}_3\text{Mg}_{1/2}$, $\text{RCON}(\text{CH}_3)\text{C}_2\text{H}_4\text{SO}_3\text{Ca}_{1/2}$; $\text{R}=\text{CH}_3(\text{CH}_2)_{10}$: LMT) 水溶液の界面物性が電気電導度、表面張力、 pNa 、動的光散乱、ラマン分光などの測定により検討された。LMT 水溶液の物性は濃度の増加とともに変化する。また対イオンの種類にも大きく依存した。LMT- Na が形成するミセルの会合数は LMT-Mg および LMT-Ca と比べて著しく小さくなった。また、S-O 伸縮振動に由来するラマンシグナルは、LMT- Na ミセルの形成に伴い高波数側にシフトした。これらの結果から、LMT- Na ミセルでは他のイオンを有するミセルよりも親水基がかさ高い構造をとり、 Na^+ を補捉しやすくなっていることが示唆された。

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