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ORIGINAL CONTRIBUTION

Binding constants of calcium and/or magnesium electrolytes and aggregation numbers in oil-in-water type microemulsions formed by an amphoteric surfactant

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Abstract The effects of anti-symmetric electrolytes ($CaCl_2$, $Ca(SCN)_2$, $MgCl_2$, and/or $Mg(SCN)_2$) and pH on the phase behavior, the ζ-potential, the hydrodynamic diameter and the surface charge density of an oil-in-water type (O/W-type) microemulsion formed in solutions of an amphoteric surfactant (N^{α}, N^{α}-dimethyl-N^{ε}-lauroyllysine, DMLL)/*n*-octane/1-pentanol/brine have been examined. The formation of the microemulsion in the presence of $CaCl_2$ and/or $Ca(SCN)_2$ is of Winsor-type with an increase in the concentration of 1-pentanol. Particularly, microemulsion is not formed by the addition of $Ca(SCN)_2$ in a pH region less than 2.6. The ζ-potential and the surface charge density of the microemulsion in the presence of $CaCl_2$ decrease with an increase in pH and show slightly positive values in the isoelectric region (pH 5–7), while, in the presence of $Ca(SCN)_2$, the ζ-potential and the surface charge density show negative values in the same region at which the net charge of DMLL molecules becomes almost zero. The hydrodynamic diameters in the presence of $CaCl_2$ show a maximum value around pH 2.5, whereas, in the presence of $Ca(SCN)_2$, the minimum value is around pH 5.5. Similar tendencies are recognized in results for the ζ-potential, the hydrodynamic diameter and the surface charge density of the O/W-type microemulsion in the presence of $MgCl_2$ and $Mg(SCN)_2$. A new formula to estimate the binding constants (K) of Ca^{2+}, Mg^{2+}, Cl^-, and SCN^- to the hydrophilic groups in DMLL molecules and the adsorption density of DMLL molecules on the oil/water interface (N) in the presence of anti-symmetric electrolytes has been derived. K for Ca^{2+}, Mg^{2+}, Cl^-, and SCN^- was found to be $K_{Ca} = 0.12\ M^{-1}$, $K_{Mg} = 0.14\ M^{-1}$, $K_{Cl} = 0.0084 \pm 0.0016\ M^{-1}$, and $K_{SCN} = 0.70 \pm 0.06\ M^{-1}$, respectively. N for DMLL molecules in the presence of $CaCl_2$, $Ca(SCN)_2$, $MgCl_2$ and/or $Mg(SCN)_2$ was found to be $0.50\ nm^{-2}$, $0.38\ nm^{-2}$, $0.44\ nm^{-2}$, and $0.47\ nm^{-2}$, respectively; and the surfactant (DMLL) numbers per O/W-type microemulsion droplet change from a few hundreds to a few thousands with changing pH. The larger the hydrodynamic diameter of the O/W-type microemulsion, the greater the number of DMLL molecules adsorbed on the O/W-type microemulsion surfaces.

Key words ζ-potential – surface charge density – binding constant – aggregation number – oil-in-water type microemulsion

Introduction

Microemulsions are generally defined as clear and thermodynamically stable dispersions [1–7] of two immiscible liquids containing an appropriate amount of surfactant (and/or surfactant with cosurfactants) [8]. They differ markedly from both macro- and mini-emulsions, which depend upon intense agitation for their formation [4]. The dispersed phase consists of small droplets with diameters in the range of 10–100 nm [4].

The applications of microemulsion systems are of industrial and practical importance for enhanced oil recovery [9] and for preparation of ultramicroparticles [10–11]. In this regard, many scientists have studied the phase behavior [12] and preparation of microemulsion systems [13–16]. However, few studies have been made on the surface state and aggregation numbers of microemulsions.

In our previous paper [17], we have reported on the influence of pH on the ζ-potential of the microemulsion formed by the amphoteric surfactant (N^{α}, N^{α}-dimethyl-N^{ε}-lauroyllysine, DMLL) in the presence of NaCl. This amphoteric surfactant shows nonionic surfactant-like behavior in the isoelectric region (pH 5–7) where the net charge derived from the head groups of DMLL molecules becomes almost zero. However, the surface charge densities of the microemulsion become negative in the isoelectric region because of the preferential adsorption of Cl^- compared to Na^+. Furthermore, estimation of the range of the binding constants of Na^+ and Cl^- and the aggregation numbers of the oil-in-water (O/W) type microemulsions were made possible from the ζ-potential and particle size of the microemulsion droplets.

We also reported the effect of symmetric electrolytes on the ζ-potential of nonionic surfactant microemulsions [18]. It was suggested that the ζ-potentials and the surface charge densities of the O/W-type microemulsion show negative values only in the presence of SCN^-.

In this paper, we report on the effect of $CaCl_2$, $Ca(SCN)_2$, $MgCl_2$, and/or $Mg(SCN)_2$ on the formation of the O/W-type microemulsions with the amphoteric surfactant (DMLL), and on the preferential adsorption of Ca^{2+}, Mg^{2+}, Cl^-, and SCN^- to hydrophilic moieties of DMLL molecules. We also discuss the binding constants of Ca^{2+}, Mg^{2+}, Cl^-, and SCN^- to hydrophilic moieties of DMLL molecules and the aggregation numbers of the O/W-type microemulsions based on the results of the ζ-potential measurement.

Experimental section

Materials

N^{α}, N^{α}-dimethyl-N^{ε}-lauroyllysine (DMLL) was supplied by Central Research Laboratories of Ajinomoto Co. Inc., Tokyo, Japan. The synthesis has been described in our previous paper [19]. Pure *n*-octane, and hydrochloric acid (HCl) purchased from Wako Pure Chemical Industries, were reagent grade and were used without further purification. 1-pentanol, used as a cosurfactant, which is oriented at the oil/water interface and contributes to the decrease of the interfacial tension, purchased from Tokyo Chemical Industries and used without further purification. Calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$), and calcium thiocyanate ($Ca(SCN)_2$) purchased from Wako Pure Chemical Industries, were reagent grade and were used without further purification. Magnesium thiocyanate ($Mg(SCN)_2$) was synthesized as follows. 2 mol of NH_4SCN and 1 mol of $Mg(OH)_2$ (Kanto Chemical Co., Inc.) were added to water and the mixture was stirred. After removal of ammonia at 90 ~ 100 °C, the crystal ($Mg(SCN)_2$) was then separated by filtration. Obtained $Mg(SCN)_2$ was purified by recrystallization and dried for 24 h at 30 °C under reduced pressure. Degassed doubly distilled water was used in preparing all solutions.

Preparation of microemulsions

11.2 mM of DMLL aqueous solutions were prepared by dissolving DMLL in water whose pH was adjusted to various values by 0.1 M HCl solution. The microemulsions formed by DMLL was prepared by mixing 10 g of those aqueous solutions, 10 g oil, 0.1 M electrolytes, and various amount of 1-pentanol in Teflon-capped glassed tubes. A series of the glass tubes was well shaken and allowed to attain equilibrium in the thermostat for at least several hours.

pH measurement

The pH values were measured with a digital pH meter (M-130, Corning Co.) at 25 °C. The pH values of the O/W-type (lower microemulsion phases) or of the excess water (brine) phases were measured. They were considered to be equal to the pH values of water in the middle-phase microemulsions and in upper-phase microemulsions as would be expected from equilibrium considerations.

Measurement of electrophoretic mobilities and calculation of ζ-potentials

Electrophoretic mobilities (U) of the O/W-type microemulsions were measured in aqueous media of different pH with the System 3000 particle electrophoresis apparatus (Pen Kem, Inc., New York), equipped with a 5 mW

He–Ne laser ($\lambda = 632.8$ nm). The electrophoretic mobilities were measured at 25 °C.

The ζ-potential (ζ) is calculated numerically from the mobility (U) using Henry's equation [20]:

$$\zeta = \frac{\eta U}{\varepsilon_0 \varepsilon_r} \cdot \frac{1}{f(\varkappa a)} , \tag{1}$$

with

$$\varkappa_{2-1} = \left(\frac{6000 N_A C_0 e^2}{\varepsilon_0 \varepsilon_r k T} \right)^{1/2} , \tag{2}$$

where η is the viscosity of the medium, ε_0 is permittivity of vacuum, and ε_r is the relative permittivity of the medium, respectively. $f(\varkappa a)$ is the Henry's coefficient which depends on the radius of the particle, and $\varkappa_{2-1}$ is Debye–Hückel parameter in the presence of the anti-symmetric (2–1) electrolyte. N_A is Avogadro's number, e is the elementary electric charge, C_0 is the concentration of electrolytes, k is the Boltzmann constant, and T is the absolute temperature.

According to the numerical value of $\varkappa a$, $f(\varkappa a)$ can be expressed by the following equations [20–22]. Symbol x stands for $\varkappa a$:

[1]

$$f(x) = \frac{2}{3} \left\{ 1 + \frac{x^2}{16} - \frac{5x^3}{48} - \frac{x^4}{96} + \frac{x^5}{96} + \left(\frac{x^4}{8} - \frac{x^6}{96} \right) \exp(x) \cdot E_1(x) \right\} , \tag{3}$$

where

$$E_1(x) = \int_x^\infty \frac{\exp(-t)}{t} \, dt . \tag{4}$$

i) $0 < \varkappa a \leq 1$:

$$E_1(x) = -\ln x + C + C_1 x + C_2 x^2 + C_3 x^3 + C_4 x^4 + C_5 x^5 , \tag{5}$$

$C_0 = -0.57721566$, $C_1 = 0.99999193$,

$C_2 = -0.24991055$, $C_3 = 0.05519968$,

$C_4 = -0.00976004$, $C_5 = 0.00107857$.

ii) $1 < \varkappa a \leq 20$

$$E_1(x) = \frac{x^4 + A_1 x^3 + A_2 x^2 + A_3 x + A_4}{x^4 + B_1 x^3 + B_2 x^2 + B_3 x + B_4} \frac{1}{x \exp(x)} , \tag{6}$$

$A_1 = 8.5733287401$, $A_2 = 9.5733223454$,

$A_3 = 18.0590169730$, $A_4 = 25.6329561486$,

$B_1 = 8.6347608925$, $B_2 = 21.0996530827$,

$B_3 = 0.2677737343$, $B_4 = 3.9584969228$.

[2] $20 < \varkappa a$:

$$f(x) = 1 - \frac{3}{x} + \frac{25}{x^2} - \frac{220}{x^3} + \frac{2100}{x^4} - \frac{21840}{x^5} + \frac{246960}{x^6} - \frac{3024000}{x^7} + \frac{39916800}{x^8} . \tag{7}$$

Measurement of hydrodynamic diameters

Dynamic laser light scattering (DLLS) [23] experiments are performed to determine the mutual diffusion coefficient of the O/W-type microemulsion using a 4700-type submicron particle analyzer (Malvern Instrument, UK). The light source is an argon laser (Coherent Co., Innova 90) with a wavelength of 488 nm and a power of 5 W or less. Samples are contained in 8-mm-diameter high-precision Burchard cells, placed in a temperature-controlled vessel at a constant temperature, and then the time-dependent correlation function of the scattered light intensity is measured at a scattering angle of 90°. Data are analyzed by a Malvern 7032 correlator and the correlation functions analyzed by the method of the cumulants [24] give a z-average diffusion coefficient. The hydrodynamic diameters of the O/W-type microemulsions should be calculated from diffusion coefficients considering particle–particle interactions. Cheung et al. [25] and Qutubuddin [26] have made ζ-potential measurements in microemulsions and used ζ-potential to correct diffusion coefficients.

Results

Figure 1 represents the relationship between pH of the aqueous solution and the pH of the prepared O/W-type microemulsion (excess water phase). The pH values of the O/W-type microemulsion and excess water phase increase markedly when the pH of the aqueous solution is 3.

Figures 2(a) and (b) show the concentration range of the cosurfactant (1-pentanol) for the formation of multiphase microemulsions at various pH values in the presence of (a) 0.1 M $CaCl_2$ and (b) 0.1 M $Ca(SCN)_2$, respectively. In these figures, open and solid circles represent the concentrations at which phase transition occurs. As can be seen in these figures, with an increase in the concentration of the cosurfactant, the microemulsion moves from the lower phase, i.e., O/W-type microemulsion (Winsor-type I [27]), through the middle phase (Winsor-type III [27]),

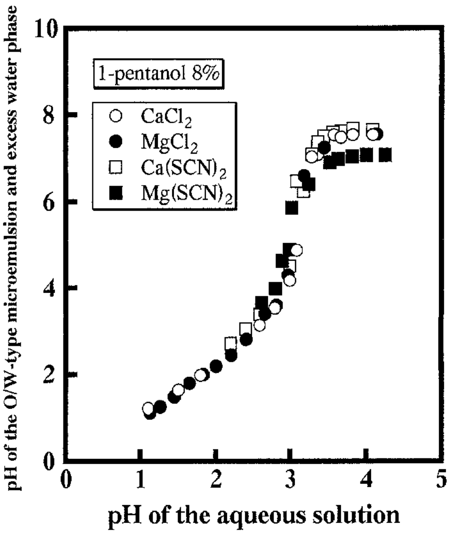
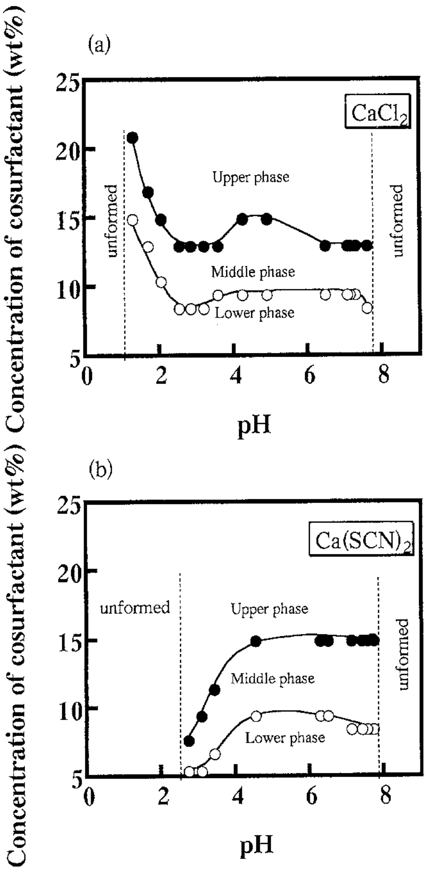


Fig. 1 Relationship between pH of the aqueous solution and the pH of the O/W-type microemulsion (excess water phase)

Fig. 2A Concentration range of cosurfactant of the multiphase microemulsion as a function of pH in the presence of 0.1 M $CaCl_2$ at 25 °C. **B** Concentration range of cosurfactant of the multiphase microemulsion as a function of pH in the presence of 0.1 M $Ca(SCN)_2$ at 25 °C

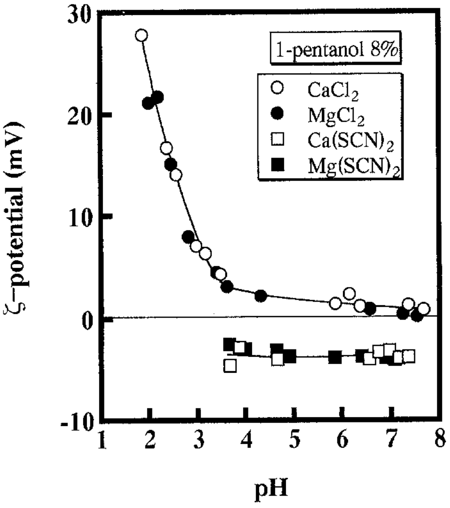


to the upper phase (W/O-type microemulsion; Winsor-type II [27]). In the presence of $CaCl_2$, the microemulsion forms in the region between pH 1 and 8 and a similar tendency was observed for the system including NaCl [17], and/or $MgCl_2$. The effect of $CaCl_2$ on the phase behavior is almost the same as that of NaCl. On the other hand, the O/W-type microemulsion in the presence of $Ca(SCN)_2$ forms in the region between pH 2.6 and pH 8, and the region for the O/W-type microemulsion formation becomes narrower as compared to that in the presence of $CaCl_2$.

Figure 3 exhibits the pH dependence of the ζ-potential of the O/W-type microemulsions in the presence of $CaCl_2$, $MgCl_2$, $Ca(SCN)_2$, or $Mg(SCN)_2$. The values of the ζ-potential in the presence of $CaCl_2$ decrease with increasing pH, and then become almost constant at 1 ~ 2 mV in the range of pH 5–8. This suggests the preferential adsorption of Ca^{2+} as compared to Cl^-, taking into accounted that ζ-potential of an O/W-type microemulsion in the presence of NaCl became slightly negative (~ − 3 mV) in the isoelectric region due to the preferential adsorption of Cl^- compared to Na^+. A similar tendency is recognized in results for the system in the presence of $MgCl_2$. While, in the presence of $Ca(SCN)_2$ or $Mg(SCN)_2$, the ζ-potential shows negative value (~ − 5 mV). This may be attributed to the preferential adsorption of SCN^- to the hydrophilic moieties of the DMLL molecules compared to Ca^{2+} or Mg^{2+}.

Figure 4 shows the hydrodynamic diameter of the O/W-type microemulsions as a function of pH in the presence of $CaCl_2$, $MgCl_2$, $Ca(SCN)_2$, or $Mg(SCN)_2$. As can be seen in Fig. 4, the hydrodynamic diameter of the

Fig. 3 ζ-potential of the O/W-type microemulsion as a function of pH in the presence of $CaCl_2$, $Ca(SCN)_2$, $MgCl_2$, or $Mg(SCN)_2$ at 25 °C. The salinity of the systems is 0.1 M



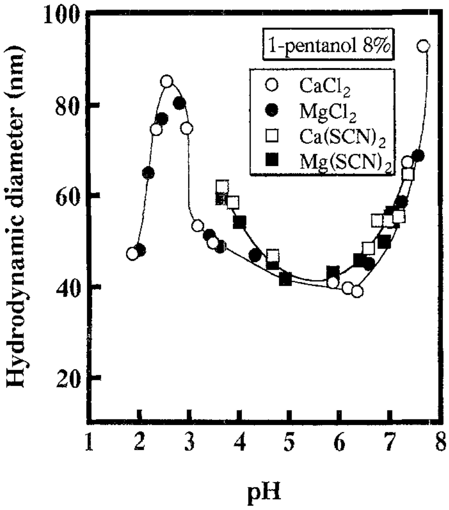


Fig. 4 Hydrodynamic diameter of the O/W-type microemulsion as a function of pH in the presence of $CaCl_2$, $Ca(SCN)_2$, $MgCl_2$, or $Mg(SCN)_2$ at 25 °C. The salinity of the systems is 0.1 M

microemulsion with $CaCl_2$ gives a maximum value around pH 2.5, whereas, in the presence of $Ca(SCN)_2$, it shows a minimum value around pH 5.5. Similar tendencies are observed when magnesium salts are used. DMLL molecules exist in two different forms around pH 3 or pH 8, i.e., cationic-type and amphoteric-type, or amphoteric-type and anionic-type [17]. These different types of the DMLL molecules may generate the attractive force (ion-dipole interaction) between them. Since the attractive force decreases the hydrophilic interactions according to Winsor's theory [27], the amount of *n*-octane in the O/W-type microemulsion droplets, i.e., the droplet size, increases.

Discussion

Surface charge density (σ) can be calculated from the values of surface potentials and particle radii on the basis of the following equations [28].

$$\sigma_{2-1} = \frac{\varepsilon_r \varepsilon_0 \varkappa_{2-1} kT}{e} pq \left\{ 1 + \frac{4}{\varkappa_{2-1} a (pq)^2} [(3-p)q - 3] + \frac{4}{(\varkappa_{2-1} a)^2 (pq)^2} \left[6 \ln\left(\frac{q+1}{2}\right) + \ln(1-p) \right] \right\}^{1/2} \quad (8)$$

where

$$p = 1 - \exp\left(-\frac{e\psi_0}{kT}\right) \quad (9)$$

and

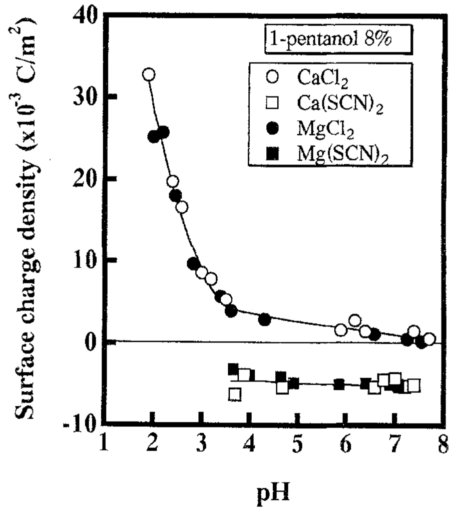
$$q = \left[\frac{2}{3}\exp\left(\frac{e\psi_0}{kT}\right) + \frac{1}{3}\right]^{1/2} . \quad (10)$$

These formulas express the relationship between surface potential (ψ_0) and surface charge density (σ_{2-1}) when an anti-symmetric electrolyte is used in the aqueous phase.

Figure 5 shows the effect of pH on the surface charge densities obtained from Eqs. (8)–(10) assuming that the ζ-potential is equal to the surface potential. Surface charge densities in the presence of $CaCl_2$ become slightly positive values, whereas, in the presence of $Ca(SCN)_2$, they show slightly negative values in the isoelectric region (pH 5–7), respectively. Similar tendencies are obtained in results for the systems in the presence $MgCl_2$ and/or $Mg(SCN)_2$.

In the range of pH 5–7, the net charge derived from the head groups of the DMLL molecule becomes almost zero. However, the surface charge densities of DMLL microemulsion in the presence of NaCl [17] become slightly negative in this isoelectric region (pH 5–7), i.e., Cl^- adsorbs preferentially onto the hydrophilic group of the DMLL molecule compared to Na^+. In the presence of $CaCl_2$ (and/or $Ca(SCN)_2$), it is suggested that the adsorption amount of Ca^{2+}(SCN^-) onto the hydrophilic groups is larger than that of Cl^-(Ca^{2+}). Similar tendencies are recognized in results for the systems including $MgCl_2$ and/or $Mg(SCN)_2$. We have tried to conduct a theoretical and quantitative analysis of the relationship between the surface charge densities of the DMLL microemulsion with DMLL and pH. The surface charge density is considered to depend upon not only the degree of the adsorption of

Fig. 5 Surface charge density of the O/W type microemulsion as a function of pH in the presence of $CaCl_2$, $Ca(SCN)_2$, $MgCl_2$, or $Mg(SCN)_2$ at 25 °C. The salinity of the systems is 0.1 M



the ions (hydrogen ions, anions or cations), i.e., binding constant (K), but also the adsorption densities of DMLL molecules on the oil/water interface (N). We have tried to derive a new equation on the surface charge densities in the presence of the 2–1 electrolytes by developing the former equation on the surface charge densities in the presence of the 1–1 electrolyte in our previous paper [17].

We assume both uniform adsorption of DMLL molecules on the surface of the O/W-type microemulsion, and Langmuir-type adsorption of hydrogen ions, anions or cations onto the head groups of DMLL molecules. Furthermore, H^+ and Ca^{2+} (Mg^{2+}) binds competitively at the carboxyl groups ($-COO^-$) having a negative charge and H^+ also binds to the dimethylammonium groups ($-N(CH_3)_2$), and then Cl^- or SCN^- will bind at these groups in the positive form ($-HN^+(CH_3)_2$).

Derivation of a new equation for the surface charge densities of DMLL microemulsion in the presence of 2–1 electrolytes

The increase in the Helmholtz free energy per unit area of the surface of the O/W-type microemulsion (F) due to anion or cation adsorption (binding) to the hydrophilic groups of DMLL can be described as follows.

$$F = \int^{\sigma} \psi_0(\sigma')d\sigma' + \mu^{\circ}_{1\mathrm{SH}}N_{1\mathrm{H}} + \mu^{\circ}_{1\mathrm{Scation}}N_{1\,\mathrm{cation}} + \mu^{\circ}_{2\mathrm{SH}}N_{2\mathrm{H}} + \mu^{\circ}_{2\mathrm{Sanion}}N_{2\,\mathrm{anion}} - TS \qquad (11)$$

with

$$\sigma = (-e)N + eN_{1\mathrm{H}} + 2eN_{1\,\mathrm{cation}} + eN_{2\mathrm{H}} \qquad (12)$$

where $\mu^{\circ}_{1\mathrm{sH}}$, $\mu^{\circ}_{1\mathrm{scation}}$, $\mu^{\circ}_{2\mathrm{sH}}$, and $\mu^{\circ}_{2\mathrm{sanion}}$ are the constant terms of $\mu_{1\mathrm{sH}}$, $\mu_{1\mathrm{scation}}$, $\mu_{2\mathrm{sH}}$ and $\mu_{2\mathrm{sanion}}$, independent of $N_{1\mathrm{H}}$, $N_{1\,\mathrm{cation}}$, $N_{2\mathrm{H}}$ and $N_{2\,\mathrm{anion}}$, respectively. $\mu_{1\mathrm{sH}}$ and $\mu_{1\mathrm{scation}}$ are the electrochemical potentials of H^+ and cations adsorbed onto the binding sites 1 (carboxyl groups; $-COO^-$), respectively. $\mu_{2\mathrm{sH}}$ and $\mu_{2\mathrm{sanion}}$ are the electrochemical potentials of H^+ and anions adsorbed onto the binding sites 2 (dimethylammonium groups; $-N(CH_3)_2$ or ($-HN^+(CH_3)_2$)), respectively. $N_{1\mathrm{H}}$, $N_{1\,\mathrm{cation}}$, $N_{2\mathrm{H}}$ and $N_{2\,\mathrm{anion}}$ are the numbers of cations or anions adsorbed on the sites 1 or 2 per unit area, respectively. S is the configurational entropy change per unit area.

$$\begin{aligned}
S &= \frac{k}{A}\ln\Bigg[\frac{(AN_{1\,\max})!}{(AN_{1\mathrm{H}})!(AN_{1\,\mathrm{cation}})!(AN_{1\,\max} - AN_{1\mathrm{H}} - AN_{1\,\mathrm{cation}})!} \\
&\quad \times \frac{(AN_{2\,\max})!}{(AN_{2\mathrm{H}} + AN_{2\,\mathrm{anion}})!\{AN_{2\,\max} - (AN_{2\mathrm{H}} + AN_{2\,\mathrm{anion}})\}!}\,\frac{(AN_{2\mathrm{H}} + AN_{2\,\mathrm{anion}})!}{AN_{2\mathrm{H}}!AN_{2\,\mathrm{anion}}!}\Bigg] \\
&= \frac{k}{A}[\ln(AN_{1\,\max})! - \ln(AN_{1\mathrm{H}})!(AN_{1\,\mathrm{cation}})! - \ln(AN_{1\,\max} - AN_{1\mathrm{H}} - AN_{1\,\mathrm{cation}})!] \\
&\quad + \frac{k}{A}[\ln(AN_{2\,\max})! - \ln(AN_{2\mathrm{H}})!(AN_{2\,\mathrm{anion}})! - \ln(AN_{2\,\max} - AN_{2\mathrm{H}} - AN_{2\,\mathrm{anion}})!]
\end{aligned} \qquad (13)$$

where $N_{1\,\max}$ and $N_{2\,\max}$ are the numbers of sites 1 and 2 per unit area, respectively. They are equal to the number of DMLL molecules per unit area (N). A is the surface area of the O/W-type microemulsion droplet. Using the Stirling formula ($\ln x! = x\ln x - x$), Eq. (13) is approximated as bellow.

$$\begin{aligned}
S \cong \frac{k}{A}[&(AN_{1\,\max})(\ln AN_{1\,\max}) - (AN_{1\mathrm{H}})(\ln AN_{1\mathrm{H}}) \\
&- (AN_{1\,\mathrm{cation}})\ln(AN_{1\,\mathrm{cation}}) \\
&- (AN_{1\,\max} - AN_{1\mathrm{H}} - AN_{1\,\mathrm{cation}}) \\
&\times \ln(AN_{1\,\max} - AN_{1\mathrm{H}} - AN_{1\,\mathrm{cation}}) \\
&+ (AN_{2\,\max})\ln(AN_{2\,\max}) - (AN_{2\mathrm{H}})\ln(AN_{2\mathrm{H}}) \\
&- (AN_{2\,\mathrm{anion}})\ln(AN_{2\,\mathrm{anion}}) \\
&- (AN_{2\,\max} - AN_{2\mathrm{H}} - AN_{2\,\mathrm{anion}}) \\
&\times \ln(AN_{2\,\max} - AN_{2\mathrm{H}} - AN_{2\,\mathrm{anion}})]\ .
\end{aligned} \qquad (14)$$

The electrochemical potentials of ions at the surface of microemulsions are, respectively, given by

$$\mu_{1\mathrm{SH}} = \left(\frac{\partial F}{\partial N_{1\mathrm{H}}}\right)_{\mathrm{T}}$$

$$= \left(\frac{\partial \sigma}{\partial N_{1\mathrm{H}}}\right)\left(\frac{\partial}{\partial \sigma}\int^{\sigma} \psi_0(\sigma')\,d\sigma'\right) + \mu^{\circ}_{1\mathrm{SH}} - T\frac{\partial S}{\partial N_{1\mathrm{H}}}$$

$$= e\psi_0 + \mu^{\circ}_{1\mathrm{SH}} + kT\ln\frac{N_{1\mathrm{H}}}{N_{1\max} - N_{1\mathrm{H}} - N_{1\,\mathrm{cation}}}\,, \quad (15)$$

$$\mu_{1\mathrm{S\,cation}} = \left(\frac{\partial F}{\partial N_{1\,\mathrm{cation}}}\right)_{\mathrm{T}}$$

$$= 2e\psi_0 + \mu^{\circ}_{1\mathrm{S\,cation}} + kT\ln\frac{N_{1\,\mathrm{cation}}}{N_{1\max} - N_{1\mathrm{H}} - N_{1\,\mathrm{cation}}}\,, \quad (16)$$

$$\mu_{2\mathrm{SH}} = \left(\frac{\partial F}{\partial N_{2\mathrm{H}}}\right)_{\mathrm{T}}$$

$$= e\psi_0 + \mu^{\circ}_{2\mathrm{SH}} + kT\ln\frac{N_{2\mathrm{H}}}{N_{2\max} - N_{2\mathrm{H}} - N_{2\,\mathrm{anion}}}\,, \quad (17)$$

$$\mu_{2\mathrm{S\,anion}} = \left(\frac{\partial F}{\partial N_{2\,\mathrm{anion}}}\right)_{\mathrm{T}}$$

$$= \mu^{\circ}_{2\mathrm{S\,anion}} + kT\ln\frac{N_{2\,\mathrm{anion}}}{N_{2\max} - N_{2\mathrm{H}} - N_{2\,\mathrm{anion}}}\,. \quad (18)$$

Here, the electrochemical potentials of cation and anion in the water phase are, respectively, given by

$$\mu_{\mathrm{WH}} = \mu^{\circ}_{\mathrm{WH}} + kT\ln\frac{n_{\mathrm{H}}}{n_0}\,, \quad (19)$$

$$\mu_{\mathrm{W\,cation}} = \mu^{\circ}_{\mathrm{W\,cation}} + kT\ln\frac{n_{\mathrm{cation}}}{n_0}\,, \quad (20)$$

$$\mu_{\mathrm{W\,anion}} = \mu^{\circ}_{\mathrm{W\,anion}} + kT\ln\frac{n_{\mathrm{anion}}}{n_0}\,, \quad (21)$$

where μ_{wH}, $\mu_{\mathrm{w\,cation}}$, and $\mu_{\mathrm{w\,anion}}$ are the electrochemical potentials of H^+, cation, and anion in the water phase, respectively. $\mu^{\circ}_{\mathrm{wH}}$, $\mu^{\circ}_{\mathrm{w\,cation}}$, and $\mu^{\circ}_{\mathrm{w\,anion}}$ are the constant terms of μ_{wH}, $\mu_{\mathrm{w\,cation}}$, and $\mu_{\mathrm{w\,anion}}$, independent of n_{H}, n_{cation}, and n_{anion}, respectively. n_{H}, n_{cation}, and n_{anion} are the numbers of H^+, cation, and anion in the unit volume of water phase, respectively. n_0 is the number of water molecules in the unit volume.

At the chemical equilibrium between the interface and the bulk of the water phase, we have

$$\mu_{1\mathrm{SH}} = \mu_{\mathrm{WH}}\,, \quad (22)$$

$$\mu_{1\mathrm{S\,cation}} = \mu_{\mathrm{W\,cation}}\,, \quad (23)$$

$$\mu_{2\mathrm{SH}} = \mu_{\mathrm{WH}}\,, \quad (24)$$

$$\mu_{2\mathrm{S\,anion}} = \mu_{2\mathrm{SH}} + \mu_{\mathrm{W\,anion}}\,. \quad (25)$$

Corresponding to Eqs. (22)–(25), we obtain

$$\frac{N_{1\mathrm{H}}}{(N_{1\max} - N_{1\mathrm{H}} - N_{1\,\mathrm{cation}})n_{\mathrm{H}}\exp\left(-\frac{e\psi_0}{kT}\right)} = \frac{1}{n_0}\exp\left(-\frac{\mu^{\circ}_{1\mathrm{SH}} - \mu^{\circ}_{\mathrm{WH}}}{kT}\right), \quad (26)$$

$$\frac{N_{1\,\mathrm{cation}}}{(N_{1\max} - N_{1\mathrm{H}} - N_{1\,\mathrm{cation}})n_{\mathrm{cation}}\exp\left(-\frac{2e\psi_0}{kT}\right)} = \frac{1}{n_0}\exp\left(-\frac{\mu^{\circ}_{1\mathrm{S\,cation}} - \mu^{\circ}_{\mathrm{W\,cation}}}{kT}\right), \quad (27)$$

$$\frac{N_{2\mathrm{H}}}{(N_{2\max} - N_{2\mathrm{H}} - N_{2\,\mathrm{anion}})n_{\mathrm{H}}\exp\left(-\frac{e\psi_0}{kT}\right)} = \frac{1}{n_0}\exp\left(-\frac{\mu^{\circ}_{2\mathrm{SH}} - \mu^{\circ}_{\mathrm{WH}}}{kT}\right), \quad (28)$$

$$\frac{N_{2\,\mathrm{anion}}}{N_{2\mathrm{H}}n_{\mathrm{anion}}\exp\left(\frac{e\psi_0}{kT}\right)} = \frac{1}{n_0}\exp\left(-\frac{\mu^{\circ}_{2\mathrm{S\,anion}} - \mu^{\circ}_{\mathrm{W\,anion}} - \mu^{\circ}_{2\mathrm{SH}}}{kT}\right). \quad (29)$$

The left-hand sides of Eqs. (26)–(29) correspond to the binding constants of anion and cation, which are defined by

$$\frac{1}{K_{\mathrm{a}1}} = \frac{1}{n_0}\exp\left(-\frac{\mu^{\circ}_{1\mathrm{SH}} - \mu^{\circ}_{\mathrm{WH}}}{kT}\right), \quad (30)$$

$$\frac{1}{K_{\mathrm{a}2}} = \frac{1}{n_0}\exp\left(-\frac{\mu^{\circ}_{2\mathrm{SH}} - \mu^{\circ}_{\mathrm{WH}}}{kT}\right), \quad (31)$$

$$K_{\mathrm{cation}} = \frac{1}{n_0}\exp\left(-\frac{\mu^{\circ}_{1\mathrm{S\,cation}} - \mu^{\circ}_{\mathrm{W\,cation}}}{kT}\right), \quad (32)$$

$$K_{\mathrm{anion}} = \frac{1}{n_0}\exp\left(-\frac{\mu^{\circ}_{2\mathrm{S\,anion}} - \mu^{\circ}_{\mathrm{W\,anion}} - \mu^{\circ}_{2\mathrm{SH}}}{kT}\right), \quad (33)$$

where $K_{\mathrm{a}1}$ and $K_{\mathrm{a}2}$ are the dissociation constants of head groups of DMLL molecules, respectively. K_{cation} and K_{anion} are the binding constants of cations (Ca^{2+} or Mg^{2+}) and anions (Cl^- or SCN^-) to the hydrophilic groups in DMLL molecules, respectively.

Equations (30)–(33) become

$$N_{1\mathrm{H}} = \frac{\dfrac{1}{K_{\mathrm{a1}}} n_{\mathrm{H}} \exp\left(-\dfrac{e\psi_0}{kT}\right)}{1 + \dfrac{1}{K_{\mathrm{a1}}} n_{\mathrm{H}} \exp\left(-\dfrac{e\psi_0}{kT}\right) + K_{\mathrm{cation}} n_{\mathrm{cation}} \exp\left(-\dfrac{2e\psi_0}{kT}\right)} N_{1\,\mathrm{max}}\,, \tag{34}$$

$$N_{1\,\mathrm{cation}} = \frac{K_{\mathrm{cation}}\, n_{\mathrm{cation}} \exp\left(-\dfrac{2e\psi_0}{kT}\right)}{1 + \dfrac{1}{K_{\mathrm{a1}}} n_{\mathrm{H}} \exp\left(-\dfrac{e\psi_0}{kT}\right) + K_{\mathrm{cation}} n_{\mathrm{cation}} \exp\left(-\dfrac{2e\psi_0}{kT}\right)} N_{1\,\mathrm{max}}\,, \tag{35}$$

$$N_{2\mathrm{H}} = \frac{\dfrac{1}{K_{\mathrm{a2}}} n_{\mathrm{H}} \exp\left(-\dfrac{e\psi_0}{kT}\right)}{1 + \dfrac{1}{K_{\mathrm{a2}}} n_{\mathrm{H}} \exp\left(-\dfrac{e\psi_0}{kT}\right)\left\{1 + K_{\mathrm{anion}} n_{\mathrm{anion}} \exp\left(\dfrac{e\psi_0}{kT}\right)\right\}} N_{2\,\mathrm{max}}\,, \tag{36}$$

with

$$10^3 N_{\mathrm{A}} C_0 = n_{\mathrm{cation}} = \frac{n_{\mathrm{anion}}}{2}\,. \tag{37}$$

Consequently, substitution of Eqs. (33)–(37) into Eq. (12) gives a new equation with K and N values for the surface charge densities of DMLL microemulsion in the presence of 2–1 electrolytes.

$$\sigma_{2-1} = \frac{K_{\mathrm{cation}} C_0 \exp\left(-\dfrac{2e\psi_0}{kT}\right) - 1}{1 + 10^{-\mathrm{pH}+\mathrm{pK_{a1}}} \exp\left(-\dfrac{e\psi_0}{kT}\right) + K_{\mathrm{cation}} C_0 \exp\left(-\dfrac{2e\psi_0}{kT}\right)} eN + \frac{1}{1 + 10^{-\mathrm{pK_{a2}}+\mathrm{pH}} \exp\left(\dfrac{e\psi_0}{kT}\right) + 2K_{\mathrm{anion}} C_0 \exp\left(\dfrac{e\psi_0}{kT}\right)} eN\,. \tag{38}$$

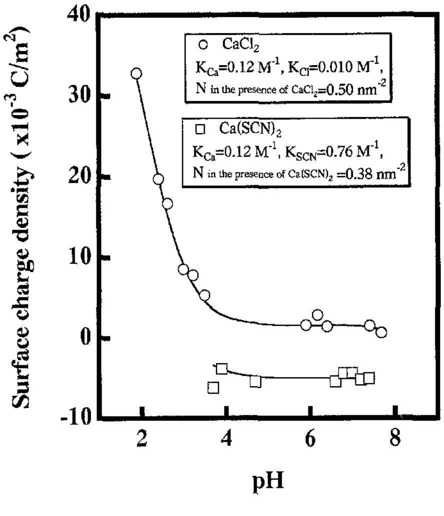
The first term on the right-hand side of Eq. (38) indicates the charge densities arising from the carboxyl group ($-\mathrm{COO}^-$) and the adsorption of cation (Ca^{2+} or Mg^{2+}) onto the carboxyl group ($-\mathrm{COO}^-$) in the DMLL molecule.

The second term indicates the charge densities arising from the dimethylammonium group ($-\mathrm{HN}^+(\mathrm{CH}_3)_2$) and the adsorption of anion (Cl^- or SCN^-) onto the $-\mathrm{HN}^+(\mathrm{CH}_3)_2$ in the DMLL molecule.

Determination of K and N, and estimation of the aggregation number of the DMLL O/W-type microemulsion in the presence of an anti-symmetric electrolyte

We have determined the values of K_{Ca}, K_{Mg}, K_{Cl}, K_{SCN} and N in the presence of CaCl_2, MgCl_2, $\mathrm{Ca(SCN)}_2$, or $\mathrm{Mg(SCN)}_2$ by the least squares methods and obtained the best fit by using the following values. The results are shown in Figs. 6 and 7. In these figures, the plots represent the experimental data of the surface charge density by Eqs.

Fig. 6 Simulational curves by Eq. (38) of the surface charge density of the O/W-type microemulsion in the presence of CaCl_2 and/or $\mathrm{Ca(SCN)}_2$ as a function of pH at 25 °C. K_{Ca}, K_{Cl}, K_{SCN}, and N in the presence of 0.1 M CaCl_2 and/or $\mathrm{Ca(SCN)}_2$ are determined by the least squares method to be 0.12 M^{-1}, 0.010 M^{-1}, 0.76 M^{-1}, 0.50 nm^{-2}, and 0.38 nm^{-2}, respectively



(8)–(10) and the curves express the simulational curves of the surface charge density by Eq. (38). In the case of $CaCl_2$,

$$K_{Ca} = 0.12\ M^{-1}\ , \tag{39}$$

$$K_{Cl} = 0.010\ M^{-1}\ , \tag{40}$$

$$N_{CaCl_2} = 0.50\ nm^{-2}\ . \tag{41}$$

In the case of $Ca(SCN)_2$,

$$K_{Ca} = 0.12\ M^{-1}\ , \tag{42}$$

$$K_{SCN} = 0.76\ M^{-1}\ , \tag{43}$$

$$N_{Ca(SCN)_2} = 0.38\ nm^{-2}\ . \tag{44}$$

In the case of $MgCl_2$,

$$K_{Mg} = 0.14\ M^{-1}\ , \tag{45}$$

$$K_{Cl} = 0.068\ M^{-1}\ , \tag{46}$$

$$N_{MgCl_2} = 0.44\ nm^{-2}\ . \tag{47}$$

In the case of $Mg(SCN)_2$,

$$K_{Mg} = 0.14\ M^{-1}\ , \tag{48}$$

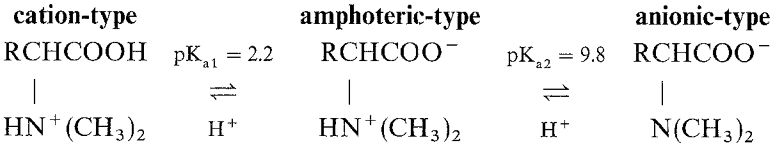
$$K_{SCN} = 0.64\ M^{-1}\ , \tag{49}$$

$$N_{Mg(SCN)_2} = 0.47\ nm^{-2}\ . \tag{50}$$

$$K_{Cl} < K_{Ca} \fallingdotseq K_{Mg} < K_{SCN}\ . \tag{51}$$

The reasons why the ζ-potential and the surface charge density in the presence of $CaCl_2$ and/or $MgCl_2$, ($Ca(SCN)_2$ and/or $Mg(SCN)_2$) become positive (negative) in the isoelectric region can be explained by the order of the intrinsic binding constants (Eq. (51)).

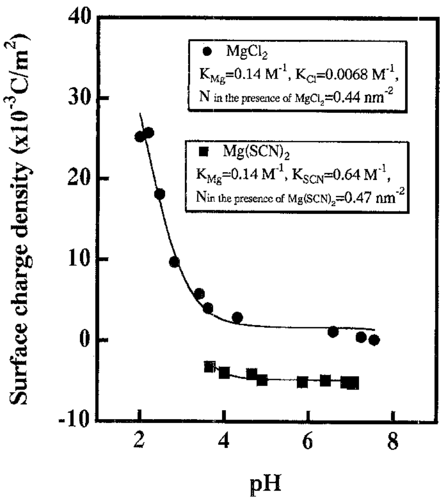
As can be seen in Figs. 2(a) and (b), the difference in the effect of $CaCl_2$ and $Ca(SCN)_2$ on the phase behavior is remarkable in a region with a pH less than 3.5. In this pH region, most of the DMLL molecules exist in the cation form as can be shown in Eq. (52).



$$\begin{array}{ccccc} \textbf{cation-type} & & \textbf{amphoteric-type} & & \textbf{anionic-type} \\ RCHCOOH & \underset{H^+}{\overset{pK_{a1}=2.2}{\rightleftharpoons}} & RCHCOO^- & \underset{H^+}{\overset{pK_{a2}=9.8}{\rightleftharpoons}} & RCHCOO^- \\ | & & | & & | \\ HN^+(CH_3)_2 & & HN^+(CH_3)_2 & & N(CH_3)_2 \end{array}$$

$$R = C_{11}H_{23}CONH(CH_2)_4\ . \tag{52}$$

Fig. 7 Simulational curves by Eq. (38) of the surface charge density of the O/W type microemulsion in the presence of $MgCl_2$ and/or $Mg(SCN)_2$ as a function of pH at 25 °C. K_{Mg}, K_{Cl}, K_{SCN}, and N in the presence of 0.1 M $MgCl_2$ and/or $Mg(SCN)_2$ are determined by the least squares method to be 0.14 M^{-1}, 0.0068 M^{-1}, 0.64 M^{-1}, 0.44 nm^{-2}, and 0.47 nm^{-2}, respectively



Cationic-type DMLL molecules which are adsorbed preferentially by the anion (Cl^- and/or SCN^-) as compared to the cation (Ca^{2+}) show nonionic surfactant-like behavior and result in a decrease in the hydrophilicity. The number of the DMLL molecules adsorbed by SCN^- with nonionic surfactant-like behavior might be larger than those adsorbed by Cl^-, because the binding constant of SCN^- is larger than that of Cl^-. Therefore, in the presence of $Ca(SCN)_2$, middle phase microemulsion forms in the region of pH 2.6–3.5 as shown in Fig. 2(b).

We can evaluate the number of the surfactant molecules per unit microemulsion, i.e., the aggregation numbers, from the value of N and the hydrodynamic diameter. The aggregation numbers (N_s) are given by the following equation.

$$N_s = 4\pi a^2 N\ . \tag{53}$$

The aggregation numbers of DMLL microemulsion in the presence of $CaCl_2$ or $Ca(SCN)_2$ are shown as a function of the hydrodynamic diameter in Fig. 8. The aggregation number changes from a few hundreds to a few thousands, and we can evaluate more precise values if we specify the

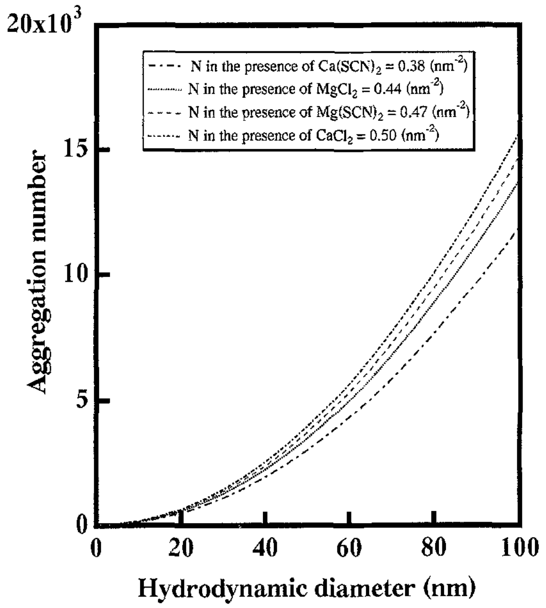


Fig. 8 Relationship between aggregation number of the O/W-type microemulsion and hydrodynamic diameter in the presence of $CaCl_2$, $Ca(SCN)_2$, $MgCl_2$, or $Mg(SCN)_2$ at 25 °C. The salinity of the systems is 0.1 M

hydrodynamic diameter of the microemulsion. For example, when the hydrodynamic diameter is about 50 nm at pH 7, *N* in the presence of $CaCl_2$, $MgCl_2$, $Ca(SCN)_2$ and/or $Mg(SCN)_2$ are 0.50, 0.44, 0.38, 0.47 nm^{-2}, respectively. Therefore, the aggregation numbers in the presence of $CaCl_2$, $MgCl_2$, $Ca(SCN)_2$ and/or $Mg(SCN)_2$ per unit particle become 3925, 3454, 2983, 3690, respectively at 25 °C.

Conclusion

The formation of the O/W-type microemulsion in the presence of $CaCl_2$ and/or $Ca(SCN)_2$ is different in an acidic region less than 3.5 when 8% 1-pentanol is used as a cosurfactant. In the isoelectric region (pH5–7), the results given by the measurements of ζ-potential and surface charge density suggest that Ca^{2+}, Mg^{2+}, Cl^- and SCN^- adsorb preferentially onto the hydrophilic groups of DMLL molecules. The new equation on the surface charge density in the presence of an anti-symmetric electrolyte is developed by modifying the equation in the presence of the symmetric electrolyte which has been derived in our previous paper [17]. By using the new equation of the surface charge density in the presence of the anti-symmetric electrolyte, the values and the order of the intrinsic binding constant (K) of Ca^{2+}, Mg^{2+}, Cl^-, and SCN^- to the hydrophilic groups of DMLL molecules are shown to be $K_{Ca} = 0.12\ M^{-1}$, $K_{Mg} = 0.14\ M^{-1}$, $K_{Cl} = 0.0084 \pm 0.0016\ M^{-1}$, and $K_{SCN} = 0.70 \pm 0.06\ M^{-1}$, $K_{Cl} < K_{Ca} \risingdotseq K_{Mg} < K_{SCN}$ respectively. The range of the aggregation numbers (the numbers of the surfactant molecules per unit microemulsion) in the presence of $CaCl_2$, $MgCl_2$, $Ca(SCN)_2$ and/or $Mg(SCN)_2$ varies from 10^2 to 10^4 orders with an increase of hydrodynamic diameter.

References

1. (1967) In: Shinoda K (ed) Solvent Properties of Surfactant Solutions. Marcel Dekker, New York, p 4
2. Danielsson I, Lindman B (1981) Colloids Surfaces 3:230
3. Friberg SE (1982) Colloid Surface 4:20
4. Rosen MJ (1989) In: Surfactant and Interfacial Phenomena. (2nd ed) Wiley Interscience, New York
5. Gillberg G, Lehtinen H, Freberg SE (1970) J Colloid Interface Sci 33:40
6. Ekwall P, Mandell L, Fontell K (1970) J Colloid Interface Sci 33:215
7. Shinoda K, Kunieda H (1973) J Colloid Interface Sci 42:382
8. Kunieda H, Sato T (1979) Yukagaku 28:627
9. Wilson LA Jr (1977) In: Shah DO, Schechter RS (eds) Improved Oil Recovery by Surfactant and Polymer Flooding. Academic Press, New York
10. Kandori K, Kon-no K, Kitahara A (1987) J Colloid Interface Sci 115:579
11. Keyima PM, Qutubuddin SJ (1989) Materials Sci Letters 8:171
12. Bennett KE, Davis HT, Scriven LE (1982) J Phys Chem 86:3917
13. (1977) In: Prince LM (ed) Microemulsions. Academic Press, New York
14. (1982) In: Robb ID (ed) Microemulsions. Prenum Press, New York
15. Bourrel M, Schechter RS (1988) In: Microemulsions and Related Systems. Marcel Dekker, New York
16. Gillberg G (1984) In: Lissant KJ (ed) Emulsions and Emulsion Technology. Pt. 3 Surfactant Science Series 6. Marcel Dekker, New York, pp 1–43
17. Abe M, Kuwabara A, Yoshihara K, Ogino K, Kim MJ, Kondo T, Ohshima H (1994) J Phys Chem 98:2991
18. Yoshihara K, Ohshima H, Momozawa N, Sakai H, Abe M (1995) Langmuir 11:2979
19. Yokota H, Sagawa K, Eguchi C, Takahashi M, Ogino K, Shibayama T (1985) J Am Oil Chem Soc 62:1716
20. Henry DC (1950) Proc R Soc London, Ser A203:514
21. Ohshima H, Healy TW, White LR (1984) J Chem Soc Faraday Trans 2 80:1643
22. (1972) In: Abramowitz M, Stegun IA (eds) Handbook of Mathematical Functions. Dover Publications, New York, p 228

23. Ogino K, Nakamae M, Abe M (1989) J Phys Chem 93:3704
24. Berne BJ, Pecora R (1976) In: Dynamic Light Scattering, Wiley Inter-science. New York, p 195
25. Cheung HM, Qutubuddin S, Edwards RV, Mann JA (1987) Langmuir 3:744
26. Qutubuddin S, Miller CA, Berry GC, Fort T Jr, Hussam A (1982) In: Mittal KL, Lindman B (eds) Surfactants in Solution Vol 3. Plenum Press, New York, p 1693
27. Winsor PA (1968) Chem Rev 68:1
28. Ohshima H, Healy TW, White LR (1983) J Colloid Interface Sci 90:17