REVIEW

Macro- and Microemulsions

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Abstract: In this review, the distinction between macro- and microemulsion, properties and structure of macro- and microemulsion, the stability and breakdown of macroemulsion, the preparation (physical and/or chemical techniques) of macroemulsion, selection of emulsifier, the preparation of multi-phase microemulsions, the interfacial electric phenomena in some O/W type microemulsion are discussed.

Key words: macroemulsion, microemulsion, stability, winsor type phase behavior, interfacial electric phenomena, aggregation number

1 Introduction

The term "emulsion" is defined as a heterogeneous liquid system, consisting of one immiscible liquid intimately dispersed in another in the form of droplets (whose diameters are less than 0.1 mm). Such systems possess a minimal stability on the whole. An operation and/or technique to produce the emulsion above-mentioned is called an emulsification. An emulsion is widely applied in many fields such as cosmetics, foods, paints and etc, because its volume fraction (or weight fraction) of two immiscible liquids can be easily changed by giving a suitable means, and then can create a high value-added products, which is never produced by single surfactant micellar systems.

If we are faced with the requirement of producing a homogeneous formulation from a group of mutually insoluble ingredients, the utilization of emulsification may be the most acceptable procedure.

The essence of an emulsification should be that an emulsifier (mainly, a surfactant, but in some cases a high molecular weight compound as well) adsorbs on the interface between oil and water to form fine droplets surrounding by the emulsifier molecules, and then the adsorbed films (in other words, liquid films) formed on the droplet surfaces will prevent an increase in particle sizes with time.

In this review, the distinction between macro- and microemulsion, properties and structure of macro- and microemulsion, the stability of macroemulsion, the preparation (chemical and/or physical techniques) of macroemulsion, the preparation of microemulsion, the interfacial electric phenomena of microemulsion are discussed.

2 Definition

The IUPAC definition is that an emulsion (a macroemulsion) is a dispersion of droplets of one liquid in another one with which it is incompletely miscible; emulsion of droplets of an organic liquid (an "oil") in an aqueous solution are indicated by the symbol O/W and emulsions of aqueous droplets in an organic liquid as W/O; in emulsions the droplets often exceed the usual limits for colloids in size.

A microemulsion is completely different from a macroemulsion. Microemulsions are ho-
homogeneous mixtures of hydrocarbons and water with large amounts of surfactants, and are thermodynamically stable isotropic dispersions\(^2\). Looking at a microemulsion in a new light would be thought of as being like a swollen micelle, that is apparently similar to a solubilized solutions. There exists an energy gap when a macroemulsion turns to be a microemulsion\(^3\). In order to understand easily, physical properties of macroemulsion and microemulsion together with solubilized solution are shown in Table 1.

However, these distinctions are only available when the conditions in the Table is satisfied simultaneously.

Recently, there have been reports on a thermodynamically unstable microemulsion\(^4\),\(^5\). This interpretation would be caused by ambiguity in the microemulsion terminology by Schulman\(^6\).

### Table 1

<table>
<thead>
<tr>
<th>Emulsion</th>
<th>particle size (Å)</th>
<th>Appearance</th>
<th>Tyndall effect</th>
<th>Thermodynamic Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10,000–100,000</td>
<td>Opaque like milk</td>
<td>no</td>
<td>Unstable</td>
</tr>
<tr>
<td></td>
<td>1,000–10,000</td>
<td>Bluish white</td>
<td>Weak Blue</td>
<td></td>
</tr>
<tr>
<td>Microemulsion</td>
<td>500–1,000</td>
<td>Translucency (or Opalescency)</td>
<td>Blue</td>
<td>Stable</td>
</tr>
<tr>
<td></td>
<td>200–500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solubilized Solution</td>
<td>100–200</td>
<td>Tranceperency</td>
<td>no</td>
<td></td>
</tr>
<tr>
<td>Micellar Solution</td>
<td>50–150</td>
<td></td>
<td>no</td>
<td></td>
</tr>
</tbody>
</table>

3 Properties and structure

Macroemulsions consist of two immiscible phases (e.g., oil and water), which are separated by an adsorbed film of emulsifier molecules. The phase which is present in the form of finely divided droplets is called a dispersed phase (dispersoid); the phase which forms the matrix in which these droplets are suspended is called a dispersing medium and/or continuous phase. Taking the typical case of a macroemulsion of oil and water, a macroemulsion containing oil as the dispersed phase in the form of globules in aqueous phase is termed as oil-in-water (O/W) macroemulsion, whereas the macroemulsion formed by the dispersion of water droplets in the oil phase (continuous phase) is termed as water-in-oil (W/O) macroemulsion. Moreover, there may exist double or multiple macroemulsions, which are formed by two or more than two immiscible phases separating by at least two emulsifier adsorbed films. Multiple macroemulsions can also be subdivided as single macroemulsions into two categories (O/W/O, which means the immiscible water phase separates the two oil phases) and (W/O/W, which means the immiscible oil phase separates the two aqueous phases) macroemulsions. There also exists P.O.O. (Polymeric Oil in Oil) macroemulsion\(^7\).

The most effective factor to determine the type of macroemulsions is the types and concentrations of emulsifier.

Let us consider the solubility of a surfactant in solvents. The Bancroft rule\(^8\) states that the phase in which the emulsifier is more soluble will be the continuous phase when an emulsion is formed, e.g., the emulsifier possessing a good water-solubility forms O/W emulsions. Harusawa et al.\(^9\) have studied the partition behavior of homogeneous nonionic surfactants in the oil-water system in connection with the type of macroemulsion produced. They have stated that the phase in which micelles are formed will preferably become the continuous
phase in the formation of emulsions. For the polyoxyethylenated nonylphenols (NPE$_6$ and NPE$_8$, subscripts denote the ethylene oxide chain lengths) which are far more soluble in the cyclohexane than in the water phase, however, at the concentration above each critical micelle concentration (cmc), NPE$_8$ produces O/W macroemulsion at 25°C (incidentally, NPE$_6$ does W/O macroemulsion$^{10}$). This may imply that the partition coefficient of the surfactant changes before and after the cmc of surfactant. They$^9$ have also studied that the relationship between the partition coefficients (K$_i$) of a homogeneous series of polyoxyethanated p, t-octylphenols (OPEs) for the isooctane-water system at the concentrations below the cmc and the type of macroemulsion formed at 25°C as shown in Table 2.

Here, C$_o$ and C$_w$ are the molar concentrations of the surfactant in the oil and water phases, respectively. It is apparent that the surfactants with ethylene oxide chain lengths in the range of 1 to 8 are more soluble in the oil than in the water phase, because the K$_i$ is larger than 1.0. Therefore, the surfactants with ethylene oxide chain lengths less than 5 produce W/O macroemulsion when used at concentrations above the cmc, while the surfactants with ethylene oxide chain lengths greater than 5 produce O/W macroemulsions. It should be noted

<table>
<thead>
<tr>
<th>EO chain length</th>
<th>K$_i$(C$_o$/C$_w$)*1</th>
<th>Emulsion type at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5,430</td>
<td>W/O</td>
</tr>
<tr>
<td>2</td>
<td>1,390</td>
<td>W/O</td>
</tr>
<tr>
<td>3</td>
<td>319</td>
<td>W/O</td>
</tr>
<tr>
<td>4</td>
<td>102</td>
<td>W/O</td>
</tr>
<tr>
<td>5</td>
<td>40.7</td>
<td>Three phases*2</td>
</tr>
<tr>
<td>6</td>
<td>16.9</td>
<td>O/W</td>
</tr>
<tr>
<td>7</td>
<td>5.49</td>
<td>O/W</td>
</tr>
<tr>
<td>8</td>
<td>1.98</td>
<td>O/W</td>
</tr>
<tr>
<td>9</td>
<td>0.704</td>
<td>O/W</td>
</tr>
<tr>
<td>10</td>
<td>0.260</td>
<td>O/W</td>
</tr>
</tbody>
</table>

*1: Crook's data$^{11}$
*2: The system is separated into three phases of isooctane, water, and surfactant

Fig. 1 Types of various macroemulsions.

Fig. 2 Partition isotherms of homogeneous OPE$_4$, OPE$_5$, OPE$_6$, and OPE$_8$ in the isooctane-water system at 25°C$^9$.

Table 2 Partition coefficients (K$_i$) of homogeneous OPE$_4$ for the isooctane/water system at 25°C below the cmc$^9$. 

P.O.O.Type

A-polymer solution
B-polymer solution

P.O.O.Type

Fig. 1 Types of various macroemulsions.
that unassociated monomeric OPEs with ethylene oxide chain lengths in the range of 6 to 8 are more soluble in the oil than in the water phase, but these emulsifiers produce O/W macroemulsions. In order to understand this relationship between the partition behavior of emulsifiers and the type of macroemulsion produced, it is necessary to determine the partition isotherms of surfactants in the oil-water system over the entire concentration range below and above the cmc. Fig. 2 depicts the partition isotherms of OPEs in the isooctane-water system at 25°C.

It is well known that the partition isotherm of a surfactant in an aqueous-organic two-phase system exhibits an abrupt change of slope when the equilibrium concentration of the solute attains the cmc\(^{12,13}\). The break points in the partition isotherms indicate the beginning of micelle formation. At concentrations below the cmc, partition coefficients for OPE\(_6\) and OPE\(_8\) are kept constant regardless of concentration, whereas those for OPE\(_4\) and OPE\(_5\) slightly increase with increasing concentration. Therefore, in the latter case, it seems likely that dimerization occurs in the organic phase. For the system OPE\(_4\)-isooctane-water, the surfactant concentration in the water phase (C\(_w\)) is held constant at concentrations above the cmc, which suggests that micelles are formed in the oil phase. On the contrary, for the systems OPE\(_6\)-isooctane-water and OPE\(_8\)-isooctane-water, the surfactant concentration in the water phase is held constant at concentrations above the cmc, which indicates that micelles are formed in the water phase. Above the cmc the micellar phase disperses in the oil phase for the systems OPE\(_4\)-isooctane-water where W/O macroemulsions are formed, while it disperses in the water phase for the systems OPE\(_6\)-isooctane-water, OPE\(_8\)-isooctane-water where O/W macroemulsions are formed.

Thereby, it seems that the phase in which the micellar phase disperses as small aggregates of surfactant molecules is the continuous phase in the macroemulsion at the present.

The microemulsions of two immiscible liquids contain appropriate amounts of surfactants or cosurfactants (alcohol and/or amphiphilic compounds). Such microemulsions, the droplet diameters of which are about 100–1000 Å\(^{14,15}\), are liquid-liquid dispersion systems, and are thermodynamically stable single phases\(^{16}\), differentiating them from macroemulsions as shown in Table 1. The microemulsion can also be classified as O/W or W/O similar to macroemulsion systems. Such systems have several advantages over macroemulsions for industrial applications. The very small droplet size in microemulsions also leads to a large surface-to-volume ratio in an oil-water system. This is important for chemical reactions in which the rate of reaction depends on the interfacial area. Moreover, there is a microemulsion called the middle-phase microemulsion, which contains large amounts of both oil and water simultaneously and shows an extremely low interfacial tension between oil and water\(^{17}\). It is frequently considered to consist of ill-defined oil and water regions coexisting in the absence of long-range order, but the structure of the middle phase microemulsion is presently a matter of controversy\(^{18,19}\).

### 4 Stability and Breakdown

The formation of macroemulsions means that the interface area between oil and water (in other words, surface area of macroemulsion particle) increases in the process of globule formations. When the interface area increases, resulting in increasing the free energy at the surfaces, then the system becomes unstable thermodynamically. Therefore, the macroemulsion produced inevitably changes to thermodynamically stable direction (two-phase separation), in other words, to a breakdown of macroemulsion. To prevent this destruction, an emulsifier (a surfactant) plays an important role. The function of an emulsifier will be classified as follows:

1. Decreases interfacial tension by its adsorption at the interfaces
2. Prevents the coalescence of droplets due to the formation of adsorbed film (liquid film)
3. Prevents the coagulation of droplets by the repulsion by the charges on the droplet surfaces caused by the addition of electrolytes.

It goes without saying that stability and breakdown of the dispersion systems is two-faced relationship, in general, it is well known that macroemulsions undergo a change to be a two-phase separation through destruction processes such as coalescence, creaming, and coagulation. Recently, Tomomasa et al.4) and Nakajima et al.5) emphasize the destruction due to the molecular diffusion22) mentioned later.

4-1 Creaming

Creaming is the special case in which the globules collect in a concentrated layer at the top of a macroemulsion. Devis et al.23) say that if the droplets of dispersed liquid in emulsion are larger than 1 μ in radius, they will settle preferentially to the top (or bottom) of a vessel under the influence of gravity.

This is also the process concentrated partly due to the sedimentation or creaming of the droplets caused by a density difference between the dispersing medium and dispersed phase. The flocculation (or sedimentation) is subject to the equation by Stokes.

\[
V = \frac{2a^2(\rho_0 - \rho)g}{9\eta}
\]

where \( V \) is the creaming velocity, \( a \) is the radius of the droplets, \( \rho_0 \) and \( \rho \) are the densities of dispersed phase and dispersing medium, \( g \) is the gravitational acceleration, and \( \eta \) is the viscosity of the dispersed phase. As can be seen from the above equation, therefore, in order to decrease the creaming velocity, we have to pay attention to the following facts:

1. Decrease in the particle size of globules
2. Decrease in the density difference between two immiscible liquids
3. Increase in the viscosity of dispersing medium (continuous phase).

If numbers 1 and 2 above are restricted to the products, it is necessary to decrease the particle size of globules, for example, by using some physical (mechanical) techniques mentioned later.

4-2 Coagulation

Even if the coagulation occur, the droplets have not entirely lost their identity, and then the system can be redispersed only by an external force such as stirring. The coagulation will result from the London dispersion force between macroemulsion droplets, and the following equation is applied.

\[
V_A = \frac{A}{6}\left(\frac{2a^2}{R^2-4a^2} + \frac{2a^2}{R^2} + \ln\frac{R^2-4a^2}{R^2}\right)
\]

where \( A \) is the Hamaker constant, \( R \) is the interparticle distance between droplets, and \( a \) is the average radius of droplets.

As the coagulation process makes progress, the creaming or exclusion of liquid will be promoted. Therefore, in order to prevent coagulation, it is necessary to increase an electrostatic repulsion force by adding an electrically charged material; which means one particle gets out of contact with another particle. In general, the surface of droplets are electrified due to the following reasons;

1. By the counter ions of emulsifiers adsorbing on the droplet surfaces
2. By another ions dissolved in the continuous phase
3. By a large difference of dielectric constant between dispersed phase and dispersing medium.

Therefore, we only have to increase the factor above-mentioned to prevent coagulation.

4-3 Coalescence

In the course of time, coalescent macroemulsions tend to destroy the interfacial films and form a large particle due to the coagulation. When the coalescence process makes progress,

surrounding the globules
the interfacial area decreases, and the system is completely separated into two phases after all. Even if the creaming or coagulation process occurs, according to circumstances macroemulsion particles are redispersed easily by stirring and/or shaking. However, once the coalescence process occurs, the macroemulsion can not return to its former state unless reemulsification with the large amounts of emulsifier is performed. This coalescence process is said to be related to the strength of adsorbed films formed on the macroemulsion droplet surfaces.

4-4 Molecular diffusion (Ostwald ripening)

Higuchi et al.22) have described that if there exist different particles in size in an emulsion, the smaller particles will tend to dissolve, and the larger particles will tend to grow at the expense of the former due to the difference in solubility limit caused by Kelvin rule. This phenomenon is recognized in the system alkyl (polyoxyethylene) ether/alkane/water5).

4-5 Evaluation of Stability

a. Coagulation of O/W macroemulsion

The classical Derjarguin-Landau-Verwey-Overbeek (DLVO) theory was designed to explain the stability of suspension systems such as aqueous gold, sulfur or selenium, metal sulfides, etc. The DLVO theory takes into account the balance of two forces related to coalescence, which is the balance of London-van der Waals attraction with electrostatic repulsion owing to overlap of electric diffuse double-layers when the two charged particles (perfect rigid bodies) approach each other. Strictly speaking, emulsion (macro and micro) particles are not a perfect rigid body, however, this theory can be valid when the particle size of emulsion droplets is sufficiently small not to cause convection currents during their migration. The total potential energy (V(H)) of interaction between two particles is London-van der Waals attraction potential (VA) and electrostatic repulsion potential (VR) owing to the electric diffuse double-layer described as the following equation:

\[ V(H) = V_A + V_B \] (3)

When VA is larger than VR (in other words, Vmax is small), an emulsion becomes unstable, whereas VR is larger than VA, the potential curve shows a maximum (Vmax) as shown in Fig. 3; which means that the potential barrier would result in prevention of collision of particles and the emulsion is maintained in a stable state.

As aforementioned, this theory does not always apply to all emulsion systems. Because an emulsion is a liquid-liquid dispersion system, this theory is not valid when the particle size is not sufficiently small.

![Fig. 3 Potential curve for interactions between two spherical colloidal particles.](image)

- VR: Electrostatic interaction energy
- VA: Van der Waals interaction energy
deformation due to strain and/or coagulation occurs or density difference and/or convection currents result in the inside of the particles. In order to contact for two particles, one particle must go over the potential barrier \( V_{\text{max}} \) as shown in Fig. 3, namely the particle should hold an energy more higher than \( V_{\text{max}} \). The probability holding energy \( V \) is proportional to the following.

\[
\exp \left( \frac{-V}{kT} \right)
\]

(4)

Therefore, the probability holding the energy larger than \( V_{\text{max}} \) is proportional to the following equation.

\[
\int_{V_{\text{max}}}^{\infty} \exp \left( \frac{-V}{kT} \right) dV = kT \exp \left( \frac{-V_{\text{max}}}{kT} \right)
\]

(5)

Finally, coalescence probability\(^{24}\) will be proportional to the following equation.

\[
\exp \left( \frac{-V_{\text{max}}}{kT} \right)
\]

(6)

It should be considered that the coalescence probability will be evaluated as a function of temperature.

To evaluate the stability of an emulsion at the early stage of the coalescence process;

1. Measures the \( V_{\text{max}} \) at different temperatures, and then estimates it from the incline of coalescence probability-temperature curve
2. Measures the coalescence probability of samples which have been given a thermal treatment (several heating and cooling process) at a given temperature, and then estimates it from the slope of relationship curve between the repetition numbers and the probability.

b. **Coagulation of W/O macroemulsion**

Murase\(^{25}\) says that the stability of W/O macroemulsion is evaluated in terms of the type of curve given by differential scanning calorimetry (DSC). If the particles of an emulsion are distributed by coagulation, Gauss distribution is not seen in the curves of DSC in the cooling process (which means the peak should be slightly close to 0°C), or a new peak should appear at temperatures higher than \(-40°C\).

Therefore, the following examinations would be necessary to evaluate the coagulation of W/O macroemulsion.

1. Perform DSC measurements in the cooling process, and then examines supercooling state of the sample
2. Perform DSC measurements at \(-30°C\).

5 **Selection of emulsifier**

5.1 **Formation of Emulsions**

If the apparatus with the ability to apply a strong shear stress is used or alcohol which is a good balance between hydrophilic and hydrophobic properties like normal propanol are added, macroemulsion having short life span can be produced without any addition of an emulsifier. If an emulsions are used as a fuel, for example, it is not necessary to be stable for long time, and it only has to decrease particle size to show good fluidity just when it is sprayed into the combustion chamber\(^{26}\)~\(^{28}\). In general, however, as the preparation of the emulsion with a good stability of the rest state is desirable, it is necessary to add surfactants (emulsifiers) and it is important to decrease the interfacial tension between oil and water. In the case without any surfactant, the interfacial tension between them is too large to mix well, for example, the interfacial tension between alkane and water is well known to be 50 mN/m. By addition of a surfactant, the interfacial tension decreases by increasing its concentrations. The decline of interfacial tension means that the energy required to spread its interface area (namely an emulsion is produced) is a small, and it is easy to get a large area...
by giving a suitable physical technique (e.g., stirring). There is a good relationship between the interfacial tension and the particle size of emulsion. When the interfacial tension becomes less than 30 mN/m, an emulsion is produced by a common stirring and/or shaking. When the interfacial tension is less than 2 mN/m, an emulsion is produced spontaneously\(^29\). Moreover, when the interfacial tension becomes to about \(10^{-3}\) mN/m, microemulsion as shown in Table 1 is produced\(^{30,31}\).

### 5.2 HLB

The most important factor to determine the type of emulsion is the selection of emulsifier (surfactant). One of the most widely used methods of selecting emulsifier was initiated by Griffin\(^{32}\) and is known as the hydrophilic-lipophilic balance (HLB) method. Shinoda et al.\(^{33}\) say that an HLB number is a number assigned to a molecule as such without any consideration of the properties of the two solvents present; this is unfortunate since the actual HLB of adsorbed surfactant at the oil/water interface changes with the types of oil, temperature, additives in oil and water phases and etc.

One of the methods, Davis’s method\(^{34}\) is shown by the following:

\[
\text{HLB} = 7 + \Sigma (\text{hydrophilic group number}) - \Sigma (\text{lipophilic group number})
\]

(7)

HLB group numbers are shown in Table 3.

HLB method by Griffin\(^{32}\) can also be applied to mixed surfactant systems.

\[
\text{HLB}_M = \frac{W_A \times \text{HLB}_A + W_B \times \text{HLB}_B}{W_A + W_B}
\]

where HLB\(_M\) is the HLB number of mixtures, \(W_A\) and \(W_B\) are weight fraction, respectively, HLB\(_A\) and HLB\(_B\) are the HLB number of a single surfactant, respectively. This equation is available to obtain a suitable condition of emulsification, however, the HLB number obtained in practice is shifted to a higher value than a weighted average because of increasing hydrophilicity owing to a mixed micelle formation\(^{35}\).

Relationships between HLB numbers and solubility against water, or main utilization are shown in Tables 4 and 5.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>HLB group numbers.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrophilic group numbers</td>
<td></td>
</tr>
<tr>
<td>(-\text{SO}_4\text{Na})</td>
<td>38.7</td>
</tr>
<tr>
<td>(-\text{CO}_2\text{K})</td>
<td>21.1</td>
</tr>
<tr>
<td>(-\text{CO}_2\text{Na})</td>
<td>19.1</td>
</tr>
<tr>
<td>(-\text{N(tertiary amine)})</td>
<td>9.4</td>
</tr>
<tr>
<td>Ester (sorbitan ring)</td>
<td>6.8</td>
</tr>
<tr>
<td>Ester (free)</td>
<td>2.4</td>
</tr>
<tr>
<td>(-\text{COH})</td>
<td>2.1</td>
</tr>
<tr>
<td>(-\text{OH (free)})</td>
<td>1.9</td>
</tr>
<tr>
<td>(-\text{O-})</td>
<td>1.3</td>
</tr>
<tr>
<td>(-\text{OH (sorbitan ring)})</td>
<td>0.5</td>
</tr>
</tbody>
</table>

| Lipophilic group numbers | |
| \(-\text{CH}\) | |
| \(-\text{CH}_2^-\) | \(-0.475\) |
| \(-\text{CH}_3^-\) | |
| \(-\text{CH}^-\) | |

| Derived group numbers | |
| \(\text{CH}_2\text{CH}_2\text{O}^-\) | 0.33 |
| \(\text{CH}_2\text{CH}_2\text{OH}^-\) | \(-0.15\) |

<table>
<thead>
<tr>
<th>Table 4</th>
<th>HLB number ranges and solubility in water.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HLB number</td>
<td>Solubility in water</td>
</tr>
<tr>
<td>(1.5-3)</td>
<td>Not disperse</td>
</tr>
<tr>
<td>(3-6)</td>
<td>Slight disperse</td>
</tr>
<tr>
<td>(6-8)</td>
<td>Emulsify with stirring</td>
</tr>
<tr>
<td>(8-10)</td>
<td>Obtain a stable emulsion</td>
</tr>
<tr>
<td>(10-13)</td>
<td>Obtain a translucent solution</td>
</tr>
<tr>
<td>13 and more</td>
<td>Obtain a transparent solution</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 5</th>
<th>HLB number ranges and their application.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HLB number</td>
<td>Application</td>
</tr>
<tr>
<td>(1.5-3)</td>
<td>Antifoaming Agent</td>
</tr>
<tr>
<td>(4-6)</td>
<td>W/O Emulsifier</td>
</tr>
<tr>
<td>(7-9)</td>
<td>Wetting Agent</td>
</tr>
<tr>
<td>(8-18)</td>
<td>O/W Emulsifier</td>
</tr>
<tr>
<td>(13-15)</td>
<td>Detergent</td>
</tr>
<tr>
<td>(15-18)</td>
<td>Solubilizer</td>
</tr>
</tbody>
</table>
5-3 HLB-Temperature (PIT)

The concept of an HLB-temperature system is more effective to select an emulsifier than that of the HLB system.

Shinoda et al.\textsuperscript{33) say that the HLB of a nonionic surfactant is a function of temperature, because the interaction between water and a hydrophilic group or oil and a lipophilic group of surfactant changes with temperature. The HLB temperature (or PIT, which means phase inversion temperature in emulsion) is a characteristic property of an emulsion at which the hydrophile-lipophile property of nonionic surfactant just balances\textsuperscript{33)}. The effect of additives on the solvent, the effect of mixed emulsifiers or of mixed oils, etc. are all reflected in the PIT and automatically adjusted in its determination, and thus, illustrates the change of HLB of the emulsifier at the interface\textsuperscript{33). As the instability of the emulsion is sensitive to the PIT, the selection of a suitable emulsifier by the PIT data is accurate. They also say that the optimum temperature difference between the storage temperature of the emulsion and the PIT is the variable; the emulsifier having the PIT which is lower than 30\textdegree - 65\textdegree C of the storage temperature will perform well.

The comparison between the HLB temperature and the HLB number with regard to the information of various factors is summarized in Table 6\textsuperscript{36}).

It is also well known that the PIT is shifted to higher temperature than the estimated temperature in the case of mixtures of emulsifiers\textsuperscript{35),37}, or increases with emulsifier concentration\textsuperscript{10),38}.

### 6 Preparation

Preparations of emulsions are classified either as a chemical technique or a physical technique according to whether or not they are prepared by the use of the brute force method (mechanically forced energy). Generally, a physical method is available to mass production emulsions due to producing emulsions continuously, whereas a chemical method is suitable to produce homogeneous and fine droplets of emulsions.

#### 6-1 Physical and/or mechanical technique

Many pieces of emulsification equipment have been developed and improved such as the colloid mill, homogenizer and ultrasonic emulsification method. Various devices designed to produce emulsions and microparticles are summarized in Table 7\textsuperscript{39}).

There has been a desire to develop a new simple emulsification technology for producing monodispersed emulsions. Nakashima et al.\textsuperscript{40) have recently proposed a new technique for

<table>
<thead>
<tr>
<th>Table 6</th>
<th>The comparison between the PIT (HLB Temperature) and the HLB number in regard to the information on various factors*\textsuperscript{36}).</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIT (HLB Temperature)</td>
<td>Factors</td>
</tr>
<tr>
<td>○</td>
<td>Hydrophilic-lipophilic balance of surfactant</td>
</tr>
<tr>
<td>○</td>
<td>Types of oils</td>
</tr>
<tr>
<td>○</td>
<td>Additives in water and/or oil phase</td>
</tr>
<tr>
<td>○</td>
<td>Concentration of emulsifier</td>
</tr>
<tr>
<td>○</td>
<td>Phase volume</td>
</tr>
<tr>
<td>○</td>
<td>Temperature</td>
</tr>
<tr>
<td>○</td>
<td>Emulsion types</td>
</tr>
<tr>
<td>○</td>
<td>Correlation with the other properties</td>
</tr>
<tr>
<td>○</td>
<td>In the case of ionic surfactant</td>
</tr>
</tbody>
</table>

*: ○ Accurate information is available ; ●, Less accurate information is available ; ×, Almost no information is available.
Preparing monodispersions, which makes use of a microporous glass membrane (CaO-Al₂O₃-B₂O₃-SiO₂ type glass with microphase separation) with very narrow pore size distribution. According to this technology, uniform particle size emulsions can be obtained, and also any emulsion particle size ranging from 0.1 to 10 microns can be designed by switching to glass membranes with different pore sizes. By forcing an oil phase through the microporous glass membrane with uniformly controlled pores and dispersing the oil phase into the water phase, stable monodispersed emulsions can be produced. The following three conditions are said to be always necessary in order to prepare monodispersions in the steady state.

1. The porous membrane must have a narrow pore size distribution and be strong enough not to deform or compact, even if high pressure is applied.
2. The membrane should never be wetted with dispersion phase.
3. An appropriate amount of surfactant suitably selected for each dispersion must be added into the continuous water phase.

This membrane emulsification will open up new possibilities for producing an excellent liquid dispersion.

It is well-known to be difficult to prepare monodispersed water-in-oil type emulsions, even a high pressure homogenizer is not available to produce water-in-oil type microemulsion due to the nozzle being choked up with oil.

Kandori et al.⁴¹)⁴²) have prepared fine and monodispersed water-in-oil (W/O) type emulsions by using a porous glass membrane filter with a copolymer type surfactant. They have prepared W/O type emulsions by two kinds of the glass membrane filter emulsification techniques using continuous and batch methods. The apparatus they used for the continuous method is shown in Fig. 4 (a)⁴¹).

The toluene solution containing a known concentration of poly (oxyethylene-oxypropylene) surfactant, which is HO (C₂H₅O)₁₃-(C₃H₇O)₃₀-(C₂H₅O)₁₃-H, is passed through the glass membrane filter set in a stainless steel column module at a constant flow rate of 23 ml/min by pump 2. Water is then fed in by pressing from the outside to the inside of the filter at a constant flow rate of 4 ml/min with pump 1 through the uniform pores. In the case of the batch method, the filter, the bottom end of which is sealed by fusion and connected to line 1 by a teflon tube at Point A in Fig. 4 (a), is immersed in a toluene solution of poly (oxyethylene-oxypropylene) surfactant as shown in Fig. 4 (b). Afterwards water presses into a surfactant/toluene solution from the inside of the filter using the same procedure as for the continuous method. The change of water pressure during emulsification is monitored by a pressure gauge, and critical pressure of water penetration (Pc) through the filter is measured for both methods. It should be noted that Pc values are independent of the length of the filter for both methods. As a result, the mean diameters of water droplets are 0.66–0.77 μm by the continuous method and 1.59–1.87 μm by the batch method, and the monodispersity ratios

<table>
<thead>
<tr>
<th>Apparatus</th>
<th>Mode of operation</th>
<th>Drop formation</th>
<th>Energy density</th>
<th>Range of drop size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical stirrer</td>
<td>Batch</td>
<td>Laminar flow Tubulence</td>
<td>Low</td>
<td>10–20</td>
</tr>
<tr>
<td>Bortex mixer</td>
<td>Batch</td>
<td>Tubulence</td>
<td>Low</td>
<td>10–200</td>
</tr>
<tr>
<td>Homo mixer</td>
<td>Batch</td>
<td>Tubulence</td>
<td>Moderate</td>
<td>1–100</td>
</tr>
<tr>
<td>High pressure homogenizer</td>
<td>Continuous</td>
<td>Tubulence Cavitation</td>
<td>High</td>
<td>0.1–10</td>
</tr>
<tr>
<td>Hydro shear</td>
<td>Continuous</td>
<td>Tubulence</td>
<td>High</td>
<td>0.2–20</td>
</tr>
<tr>
<td>Colloid mill</td>
<td>Continuous</td>
<td>Laminar flow</td>
<td>Moderate</td>
<td>1–100</td>
</tr>
<tr>
<td>Flow jet mixer</td>
<td>Batch</td>
<td>Tubulence</td>
<td>Moderate</td>
<td>10–100</td>
</tr>
<tr>
<td>Ultrasonic</td>
<td>Batch</td>
<td>Cavitation</td>
<td>High</td>
<td>0.1–10</td>
</tr>
</tbody>
</table>

Table 7 Various devices designed to produce emulsions and microparticles³⁹).


are 1.017–1.025 by the continuous method and 1.019–1.032 by the batch method.

The dispersion stability of W/O type emulsions prepared by these column filter techniques are extremely good above 7.5 wt% of the copolymer type surfactant. No creaming and coalescence have occurred for those emulsions after one month.

6.2 Chemical technique

About 40 years ago, Becher described four standard techniques (Agent-in-water method, Agent-in-oil method, Nascent soap method, Alternate addition method) in relation to a chemical method to produce an emulsion.

Now, the most famous procedure among chemical techniques is HLB-Temperature method by Shinoda.

Surfactant-phase emulsification is a very useful technique to produce an oil-in-water emulsions having fine and uniform droplets without highshear equipment. Since the surfactant-phase emulsification method utilizes neither a three-phase region nor a lamellar liquid crystalline phase, the tedious adjustment of HLB is not needed. Nonionic surfactants such as oleyl poly (oxyethylene) ethers, water, and polyols were dissolved in a water bath, to form an isotropic surfactant solution, and then oil was added dropwise to the surfactant solution with stirring. An oil-in-surfactant clear gel is formed by addition of a certain amount of oil. A fine oil-in-water emulsion is obtained by dilution of the gel with water. Sagitani et al. declare that polyols are essential components for operating this method; alkanediols such as 1,3-butandiol, 1,4-butandiol, and 1,2-butandiol have been found to give finer oil-in-water emulsions (dv=0.45 µm) than those of the other polyols such as glycerol, polyglycerol 500, polyethylene glycol 400, 600, and D-sorbitol.

There are also very interesting methods such as liquid crystal emulsification. In this method, a dispersed phase (oil) is added to the liquid crystalline phase to form a gel-like oil-in-liquid crystal (O/LC) emulsion, followed by dilution with water to form a fine three-phase emulsion in which individual oil droplets are surrounded by the liquid crystalline phase. This liquid crystal emulsification technique is useful for oils possessing a high melt-
7 Preparation of multiphase microemulsions

Microemulsions are homogeneous mixtures of hydrocarbons and water with large amounts of surfactants, and are thermodynamically stable isotropic dispersions as aforementioned. In most surfactant formulations involving microemulsions, an alcohol and/or other amphiphilic cosurfactant is used in combination with the primary surfactant. The most fundamental role of alcohol is its ability to destroy liquid crystalline and/or gel structures which disturb the formation of a microemulsion. In fact, Winsor-type phase behavior in surfactant/oil/water systems could never be detected at a low temperature in the absence of alcohols.

The phase behavior of microemulsions clearly shows that a variety of phases can exist in equilibrium with one other. While in equilibrium, each phase will involve a different structure. The commonly observed Winsor-type systems indicate that the microemulsions can exist in equilibrium with excess oil, excess water, or both (Fig. 5).

A Winsor-I-type system consists of a lower-phase microemulsion and excess oil; a Winsor-II-type system consists of an upper-phase microemulsion and excess water. The factors that affect the transitions between different types of systems include the temperature, the salinity, the molecular structure of surfactant and cosurfactant, the nature of the oil, and the oil-to-water ratio. For example, the transition (lower → middle → upper) shown in Fig. 5 takes place by increasing salinity, cosurfactant concentration, surfactant concentration, molecular weight of surfactant, or brine/oil ratio, but by decreasing temperature, or oil chain length. Under adequate conditions, the microemulsion system is miscible with both oil and brine. However, beyond its solubilization limit, the microemulsion system partitions into three phases, namely, a surfactant-rich middle phase, a surfactant-poor brine phase, and an oil phase. This surfactant-rich middle phase (middle-phase microemulsion) is called a Winsor-III-type microemulsion. The system of most interest are generally located in the neighborhood of this region.

This section deals specifically with the properties and the structure of microemulsions.
formed with some typical surfactants.

7.1 Phase Behavior

Winsor\textsuperscript{56}) introduced a unifying concept which has proved useful in correlating many experimental observations. His primary concept is that the R-ratio of cohesive energies, stemming from the interaction of the interfacial layer with oil, divided by the energies resulting from the interaction with water, determines the curvature of the interface. This concept (R-theory), which is qualitative in nature, is based on the relative magnitude of the interaction energies (or cohesive energies of Hildebrand’s terminology\textsuperscript{57}) of the amphiphilic (C) with oil (O) and with water (W):

\[ R = \frac{A_{CO}}{A_{CW}} \]  

Recently, this concept has been advanced by Verzaro et al.\textsuperscript{58}), who developed the equation:

\[ R = \frac{A_{CO} - A_{OO} - A_{LL}}{A_{CW} - A_{WW} - A_{HH}} \]  

Here R is the R-ratio introduced by Winsor; A\textsubscript{CO} and A\textsubscript{CW} are the molecular interactions promoting miscibility between C and O or C and W, in other words, the cohesive energies; A\textsubscript{OO}, A\textsubscript{LL}, A\textsubscript{WW}, and A\textsubscript{HH} are the lipophilic- and hydrophilic-type contributions promoting segregation of the components as separate phases.

Most microemulsion systems include a high concentration of a cosurfactant, such as alcohol in the system to destroy any liquid crystalline material\textsuperscript{59}). Equation 2 can be rewritten in that case in the form:

\[ R = \frac{(A_{CL1} + A_{CW}) - A_{OO} - (A_{LL1} + A_{LL2} + A_{LL2})}{(A_{CLW} + A_{CW}) - A_{WW} - (A_{HH1} + A_{HH2})} \]

where C1 is the surfactant, C2 the cosurfactant, L1 and L2 the hydrophobic portions, and H1 and H2 their hydrophilic portions.

When the lipophilic-type contribution of the system increase (the numerator becomes larger than the denominator), a W/O-type microemulsion results. When the hydrophilic-type contribution of the system increases (the numerator becomes smaller than the denominator), a O/W-type microemulsion results. When the hydrophilic and lipophile tendencies of the system are equilibrated, R is equal to 1. This case corresponds especially to the Winsor-III-type microemulsion optimal system, where the volumes of oil and water solubilized in the middle phase, which exists in equilibrium with both oil and water, are equal; the so-called middle-phase microemulsion forms. Even at R=1, a lamellar structure (a liquid crystalline and/or gel) is formed by more or less regular arrangement of the surfactant molecules in parallel leaflets allowing alternate solubilization of oil and water\textsuperscript{56}). In order to form a middle-phase microemulsion with a water-soluble surfactant (whose A\textsubscript{CW} is quite large), the property of the system must become hydrophobic by changing the factors (salinity, temperature, etc.) which affect the R-ratio of the system. For example, when the salinity increases, the ionic strength of aqueous solutions increases: this disturbs the dissociation of the counterions of an ionic surfactant, it makes surfactant molecules more hydrophilic; as a result, the decrease in A\textsubscript{CW} and the increase in A\textsubscript{CO} occur simultaneously. The temperature rise results in the increase of solubility of surfactant in water; the A\textsubscript{CW} increases and the A\textsubscript{CO} decreases simultaneously, therefore the amount of an inorganic electrolyte (salinity) must be increased to form a middle-phase microemulsion.

We have studied the effect of salinity on the phase behavior of a sodium alkyl sulfate/n-alkane/cosurfactant/brine system\textsuperscript{60}). With increasing salinity, a Winsor-type phase transition takes place in the latter system. When the alkyl chain length in surfactant (SCN) decreases, the salinity range where the middle-phase microemulsion forms increases.

The optimum salinity for middle-phase microemulsion formation increases with increasing temperature and/or the alkyl chain length in n-alkanes (alkane carbon number, ACN),
but it decreases with increasing SCN and/or alkyl chain length in the cosurfactant (cosurfactant carbon number, CCN).

The solubilization parameter at the optimum (equal volumes of oil and water in the middle-phase microemulsion) increase with an increase in SCN and/or CCN, but decreases with an increase in ACN.

**Table 8** shows the effects of SCN and of ACN on the middle-phase microemulsion formation in a sodium alkyl sulfate/alkane/n-hexanol (4 wt %) brine system.

When ACN-SCN<3, the middle-phase microemulsion is formed. For ACN-SCN>4, however, it is not formed even at 17 wt % and more of salinity.

Israelachvili and Pashley have proposed that the hydrophobic interaction free energy ($G_H$) between two hydrophobic particles is given by

$$G_H = -20 \frac{R_1 R_2}{(R_1 + R_2)^2} e^{-D/D_0} \text{ (kcal/mol)}$$

where $R_1$ and $R_2$ are the radii (nm) of two unequal spheres, $D$ the distance (nm) between two particles, and $D_0$ the distance at which $G_H$ becomes equal to 1/e.

If the hydrophobic portions of surfactant molecules and oil have radii $R_1$ and $R_2$ respectively, a decrease in ACN and SCN would lead to an increase in $G_H$. This means that the hydrophobic interaction between the hydrophobic portions of surfactant molecules and oil becomes small. Therefore, in the case of ACN-SCN>4, in other words, when using an alkane containing long alkyl chains and a surfactant having short alkyl chains, the interaction between oil and surfactant molecules ($A_{CO}$) becomes smaller than that between oil molecules ($A_{OO}$); the numerator of equation 10 becomes smaller than the denominator, so $R$ cannot attain the value 1.

When SCN is rather large (for instance, C18), a single-phase microemulsion without any excess phase is observed. The $R$-ratio of the system will be dependent not only on the balance of hydrophilic-hydrophobic interaction, but also on the magnitudes of the respective strengths. In the case of an ionic surfactant containing the same hydrophilic groups, such as sodium, alkyl sulfate, the magnitude of the respective strengths is larger for the surfactant which is able to form a middle-phase microemulsion at lower salinity than for that which can only form it at higher salinity. The effect of electrolyte on the dissociation of counterions is lower for long ACN than for short ACN, so the value of $A_{CW}$ becomes large and the value of $A_{CO}$ also becomes large.

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**Table 8** Effects of SCN and ACN on the middle phase microemulsion formation in sodium alkyl sulfate/n-alkane/n-hexanol/brine system at various temperature (25~35℃).

<table>
<thead>
<tr>
<th>ACN/SCN</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>9</td>
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<td>o</td>
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<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
</tbody>
</table>

○: Formed, ●: Unformed
7.2 Transition States of Microemulsions with Changing Salinity

The salinity range at which the middle-phase microemulsion forms becomes wider with decreasing SCN. Therefore, in order to investigate in detail the phase behavior with increasing salinity, we prepared a microemulsion with the sodium octyl sulfate (SOS) containing shorter alkyl chains. (21)

Fig. 6 depicts the changes in the volume fractions of the SOS/n-hexanol/n-decane/brine multiphase microemulsions with salinity.

As can be seen in Fig. 6 Winsor type I appears at salinity values lower than 10.3%. Winsor type II forms at salinity values higher than 15.7%. In the salinity region between 10.3% (S1) and 15.7% (SII), Winsor type III is observed.

At the two characteristic salinities (S1 and SII) where Winsor I--Winsor III--Winsor II phase transitions take place, the phase volume of the middle-phase microemulsion attains a maximum. At some intermediate salinity between S1 and SII (optimum salinity for middle-phase microemulsion formation), however, the phase volume attains a minimum.

It is generally thought that a phase transition which is Winsor I type to Winsor III type and/or Winsor III type to Winsor II type occurs suddenly at the respective optimum salinity.

One should note that two different types of microemulsion are in contact with each other in the vicinity of the characteristic salinities (S1 and SII). A lower-phase and a middle-phase microemulsion (ML and MM) coexist at the salinity zone (Z1) from 10.3% (S1) to 10.7% (S1'). A middle-phase and an upper-phase microemulsion (MM and MU) coexist at the salinity zone (ZII) from 15.3% (SII') to 15.7% (SII).

Fig. 7 presents the reciprocal of the diffusion coefficient (D−1) as a function of the magni-
tude of the scattering vector \( q \),
\[
q = \left( \frac{4 \pi n}{\lambda} \right) \sin \left( \frac{\Theta}{2} \right)
\]  
(12)

where \( n \) is the refractive index of the solution, \( \lambda \) the wavelength of light, and \( \Theta \) the scattering angle.

The \( D^{-1} \) value of a spherical structure without interparticle interactions does not depend on \( q \), while \( D^{-1} \) values of spherical structures with interparticle interactions and of nonspherical ones depend on \( q \)62),63). It can be seen in Fig. 7 (a) that scattering from any type of multi-phase microemulsion at which the salinity is very far from the two characteristic salinities (\( S_I \) and \( S_{II} \)) shows no dependence on the scattering vector. In Fig. 7 (b), however, as the characteristic salinities are approached, the \( D^{-1} \) values of Winsor-I- and Winsor-II-type systems come to depend on \( q \). Even within the three-phase region, as the salinity moves away from the optimum salinity (13.0%) for middle-phase microemulsion formation, a dependence of \( D^{-1} \) upon \( q \) is found. This may be due to increasing interparticle interactions. By the way, we used 90° as the scattering angle in the following dynamic light scattering (DLS) measurements.

Fig. 8 shows the changes in the diffusion coefficient of each microemulsion within the salinity zones (\( Z_I \) and \( Z_{II} \)) where two different types of microemulsion exist.

In \( Z_I \) (from 10.3% to 10.7%), the diffusion coefficients of both the lower-phase and middle-phase microemulsions increase with increase in salinity. On the other hand, the \( D \) values of both the middle-phase and upper-phase microemulsions decrease with decreasing salinity in \( Z_{II} \) (from 15.3% to 15.7%).

Data of artition ratio, moisture content reveal that two different types of microemulsions coexist within the salinity zones (\( Z_I \) and \( Z_{II} \)).

7.3 Swelling and Contraction with Temperature of Particles of Middle-Phase Microemulsions

We have studied the change in diameter of the middle-phase microemulsion with a temperature rise from 27.5°C to 28.0°C64). Just after the sample tube (\( C_{12}E_4/tetradecane/water \) system), at 27.5°C, is immersed into a thermostat controlled at 28.0°C, the solution in the tube is a bluish-transparent solution and the particle diameters are 20 nm. After that, the solution becomes turbid rapidly. After 4 min, the particle diameters in the solution increase to over 80 nm. A few minutes later, the solution becomes bluish-transparent once again, and the

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Fig. 8 Changes of diffusion coefficient (D) with changing salinity within the salinity zones \( Z_I \) and \( Z_{II} \) at 35°C.

\( \bigcirc \) denotes \( M_L \), \( \Box \) \( M_M \), and \( \bullet \) \( M_U \).
particle diameters in the solution are 25 nm, just like at 28.0°C. A similar tendency is recognized in results for other temperature ranges measured, namely, both swelling and contraction in the size of microemulsion particles take place when the temperature of a system is changed. The swelling may be due to the change in the hydrophilic-lipophilic balance of a system with changing temperature, and the contraction may be due to very low interfacial tensions between the microemulsion phase and the excess oil and/or water phases.

8 Interfacial electric phenomena in some O/W type microemulsion systems

Since the objective of a scientist may be to accelerate or to hinder a physico-chemical process like flocculation, a knowledge of the electrical properties of the double layer of a dispersed phase is clearly valuable asset. One of the most appropriate parameters in this respect, and one which can now be easily measured, is the zeta potential, which exists at the effective boundary between a particle (or droplet) and its surrounding medium.

The stability of hydrophilic dispersions is governed by the balance of the forces of attraction and repulsion between the individual particles in the system. In an oil-in-water type emulsion stabilized by ionic and/or amphoteric surfactants, these forces can be identified as the van der Waals forces of attraction and electrical forces of repulsion arising from interaction between the electrical double layers of the emulsion droplets.

Only a few studies on the direct measurements of the surface charge density and/or surface potential in microemulsion system have been reported in the literature, to our knowledge. Direct measurement of the electrophoretic mobility in microemulsions is expected to be useful in evaluating existing thermodynamic models for phase behavior of microemulsions and in improving the understanding of electrostatic interactions in both the charged palisade layer and between droplets.

The charge that develops at the surface of a colloidal particle might arise from any of several mechanisms, depending on the nature of the particle and that of its surrounding medium. In the case of particles dispersed in liquids, two of the most important factors are the ionization (dissociation) of functional groups at the surface and the differential adsorption of ions of different charges from solution.

The development of a net charge at the particle surface affects the distribution of ions in the surrounding interfacial region, resulting in an increased concentration of counter ions close to the surface. Thus, an electrical double layer is formed around each particle.

The double layer is considered to consist of two parts: an inner region that includes ions bound relatively strongly to the surface by adsorption, and an outer or diffuse region in which ion distribution is determined by a balance of electrostatic forces and random thermal motion. The potential close to the surface of the particle, therefore, decays as the distance from the surface increases, eventually reaching zero in bulk solution.

An individual particle and its most closely associated ions move through the solution as a unit and the potential at the boundary of this unit, at the surface of shear between the particle with its ion atmosphere and the surrounding medium, is known as the zeta potential.

Knowing the electrophoretic mobility (U), ζ-potential is evaluated from the Henry’s equation.

\[
\zeta = -\frac{\eta U}{\varepsilon_0 \varepsilon_r f(\kappa a)}
\]

with

\[
\kappa = \left[ \frac{2 N_A e l}{\varepsilon_0 \varepsilon_r kT} \right]^{1/2}
\]

where \( \eta \) is the viscosity of the medium, \( \varepsilon_0 \) the permittivity of a vacuum, \( \varepsilon_r \) the relative permittivity of the medium, \( f(\kappa a) \) is the Henry coefficient, which depends on radius of particle, \( \kappa \) is the Debye-Hückel parameter, \( e \) is the elementary electric charge, \( N_A \) is Avogadro’s num-
ber, I is the ionic strength of the medium, k is the Boltzmann constant, and T is the absolute temperature.

According to the numerical value of $\kappa a$, the Henry factor $f(\kappa a)$ can be expressed by the equations

$$f(\kappa a) = 1 - \frac{3}{\kappa a} + \frac{25}{(\kappa a)^2} - \frac{220}{(\kappa a)^3} + \ldots, \quad \kappa a \geq 25,$$

$$f(\kappa a) = 1 + \frac{(\kappa a)^2}{16} - \frac{5(\kappa a)^3}{48} - \frac{(\kappa a)^4}{96} + \frac{(\kappa a)^5}{96} + \ldots$$

$$- \left[ \frac{(\kappa a)^2}{8} - \frac{(\kappa a)^3}{96} \right] \exp \left( \kappa a \right) \cdot \int_{\infty}^{\kappa a} \frac{\exp(-t)}{t} \, dt, \quad 0 < \kappa a < 5,$$

with

$$\int_{\infty}^{\kappa a} \frac{\exp(-t)}{t} \, dt = -E_i(\kappa a)$$

and

$$-E_i(\kappa a) = \gamma + \ln(\kappa a) - \frac{\kappa a}{1!} - \frac{(\kappa a)^2}{2 \cdot 2!} - \frac{(\kappa a)^3}{3 \cdot 3!} - \frac{(\kappa a)^4}{4 \cdot 4!} - \frac{(\kappa a)^5}{5 \cdot 5!} + \ldots$$

where $\gamma$ is the Euler constant, 0.5772156654.

$$f(\kappa a) = 0.00664425 \kappa a + 0.7398574, \quad 5 \leq \kappa a \leq 25,$$

Electrophoretic mobilities (U) were measured with the Zetasizer IIc and III (Malvern, Co.) which are laser Doppler electrophoresis apparatus. These apparatus are equipped with a multibit 8 Malvern Correlator with delayed channel and 15 mW He-Ne laser ($\lambda$=633 nm).

**8.1 Anionic surfactant systems**

First, we investigated the zeta potential of microemulsions of the sodium dodecyl sulfate (SDS)/n-hexanol/n-octane/brine system. The diameter increases with the increase of salinity, but the zeta potential shows a maximum at a given salinity.

We must consider why the zeta potential shows a maximum with increasing salinity. The zeta potential is related approximately to the surface charge density ($\sigma$) of the microemulsion:

$$\zeta = \frac{\sigma (c)}{\varepsilon \varepsilon_0 \kappa (c)}$$

This is obtained by linearizing the exact $\sigma/\zeta$ relationship, given below in equation 19, with respect to $\sigma$.

As can be seen in equation 18, when the concentration of the electrolyte in the solution changes, both the direct effect (due to the changes of surface charge density and adsorption amount) and the indirect (shield) effect (due to the change of electric double layer) change accordingly. We first consider the direct effect. The surface charge density can be obtained from the values of zeta potential measured on the basis of the following equation:

$$\sigma = \sqrt{8 \varepsilon c N \alpha} \frac{e \kappa T}{\varepsilon_0} \sinh \left( \frac{e \zeta}{2 \varepsilon_0 k T} \right)$$

where $c$ is the concentration of charged molecules (mol/l), $N_A$ is the Avogadro number, and $e$ is the elementary charge. The surface charge density displays a maximum with increasing salinity. This means that the zeta potential is considerably affected by the direct effect. Quantity $\sigma$ is also given by

$$\sigma = N \times \left( \frac{1}{S} \right)$$

where $N$ is the number of charged molecules (surfactant and cosurfactant) adsorbed on microemulsion surfaces, and $S$ is the total surface area of the microemulsion. Equation 20 means that the increase of $N$ results in the increase of $\sigma$, while the increase of $S$ results in the decrease of $\sigma$. The $N$ and $S$ calculated from the data of the diameter and surface charge den-
Table 9 Changes of zeta potential, surface charge density, occupied area of charged molecule (surfactant), diameter, aggregation number of O/W microemulsion of the SDS/n-octane/n-hexanol system at 30°C.

<table>
<thead>
<tr>
<th>Salinity (M)</th>
<th>Zeta potential (mV)</th>
<th>Surface charge density (C/m²)</th>
<th>Occupied area (Å²)</th>
<th>Diameter (Å)</th>
<th>Surfactant per unit microemulsion</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.068</td>
<td>−33.7</td>
<td>−0.0210</td>
<td>762</td>
<td>340</td>
<td>477</td>
</tr>
<tr>
<td>0.072</td>
<td>−40.4</td>
<td>−0.0268</td>
<td>597</td>
<td>351</td>
<td>648</td>
</tr>
<tr>
<td>0.075</td>
<td>−43.4</td>
<td>−0.0298</td>
<td>537</td>
<td>373</td>
<td>814</td>
</tr>
<tr>
<td>0.078</td>
<td>−41.7</td>
<td>−0.0290</td>
<td>552</td>
<td>391</td>
<td>870</td>
</tr>
<tr>
<td>0.082</td>
<td>−37.4</td>
<td>−0.0261</td>
<td>613</td>
<td>478</td>
<td>1170</td>
</tr>
</tbody>
</table>

With increasing salinity, the S becomes large as shown in Table 9, and the N also becomes large, because of the increasing number of surfactant molecules adsorbed on the microemulsion surfaces.

Consequently, when the degree of increase of the number of charged molecules N is larger than that of the total surface area S, the increase of surface charge density ƒÐ and hence the increase of zeta potential occurs. Since the degree of increase of S is larger than that of N, the decrease of ƒÐ and hence the decrease of zeta potential takes place.

8.2 Amphoteric surfactant systems

Amphoterics surfactants can exist in cationic, amphoteric and anionic forms, depending upon the pH value of the aqueous solutions. Previously, we have investigated the pH-dependence of multiphase microemulsions in amphoteric surfactant, oil, cosurfactant and brine (containing added acid or base) systems. Our results show that microemulsion formation is affected by the degree of dissociation of the surfactant. When the pH changes, the charge density at the hydrophilic groups of the surfactant films is expected to change. One of the valid methods to evaluate the charges on the surface of microemulsion particles is mobility measurement, because the zeta potential and surface charge density can be calculated from the mobility. Therefore, we have investigated the pH-dependence of the zeta-potential and particle size of O/W type microemulsion forming in solutions amphoteric surfactant (N², N³–dimethyl–N³–lauroyl lysine, DMLL)/1-pentanol/octane/brine.

Fig. 9 exhibits the pH-dependence of the zeta-potential of the O/W type microemulsion. The values of the zeta-potential change from positive to negative with increasing pH and become zero at pH 3.9.

Fig. 10 shows the particle diameter results for O/W type microemulsions for which the zeta-potential measurements were made.

The diameter has two maxima, at pH 3 and pH 8, where two different forms of DMLL (cationic and amphoteric types, amphoteric and anionic types) coexist, depending on the pH values as described in a previous paper.

The relationship between zeta-potential and surface charge density when a 1-1 electrolyte is used in the water phase is expressed by the following formula:

\[
\sigma = \frac{\varepsilon \varepsilon_0 \kappa K T}{e} \cdot 2 \sinh \left( \frac{e \zeta}{2 K T} \right) \left[ 1 + \frac{2}{\kappa a^\alpha \cosh^2 \left( e \zeta/4 K T \right) \ln \left( \cosh \left( e \zeta/4 K T \right) \right)} \right]^{1/2}
\]

(21)

where \(\sigma\) is the surface charge density and \(\zeta\) is the zeta-potential. For the special case when the absolute values of zeta are quite small, so that the Debye-Hückel approximation applies, equation 21 becomes

\[
\sigma = \varepsilon \varepsilon_0 K \zeta \left( 1 + \frac{1}{\kappa a} \right)
\]

(22)

The surface charge densities obtained from Eq. (22) are plotted against pH in Fig. 11.
It should be noted that the surface charge densities also change from positive to negative with increasing pH.

As mentioned previously\(^{69}\), the phase behavior of the microemulsion formed by DMLL depends on the pH value. It is suggested that the ionic character of DMLL influences the phase behavior of microemulsions. DMLL can exist in cationic, amphoteric (zwitterionic), and anionic forms depending on the pH values of the aqueous solutions. These forms are related by the equations

\[
\begin{align*}
\text{RCHCOOH} & \quad \text{pK}_{a1} & \quad \text{RCHCOO}^- & \quad \text{pK}_{a2} & \quad \text{RCHCOO}^- \\
\text{HN}^+(\text{CH}_3)_2 & \quad \text{H}^+ & \quad \text{HN}^+(\text{CH}_3)_2 & \quad \text{H}^+ & \quad \text{N}(\text{CH}_3)_2 \\
\end{align*}
\]

where \(\text{R}=\text{C}_{11}\text{H}_{23}\text{CONH}(\text{CH}_2)_4\). If these equilibria are established without any kind of interaction (e.g., electrostatic interaction), the relationship between pH and dissociation constants is expressed simply as

\[
\begin{align*}
\text{pK}_{a1} &= \text{pH} - \log \frac{\alpha}{1 - \alpha}, \quad (24) \\
\text{pK}_{a2} &= \text{pH} + \log \frac{\beta}{1 - \beta}, \quad (25) \\
\end{align*}
\]

where \(\alpha\) and \(\beta\) are the ionization degrees of carboxyl groups and of dimethylammonium groups, respectively. The dissociation constants of DMLL were \(\text{pK}_{a1}=2.2\) and \(\text{pK}_{a2}=9.8\) at 25°C\(^{70}\). The mole fractions of amphoteric, cationic and anionic types of DMLL at each pH, calculated by equations 26–28 and derived from equations 24, 25 are shown in Fig. 12.

\[
\begin{align*}
X_+(\pm) &= \left[ 1 + \frac{10^{-\text{pH}}}{10^{-\text{pK}_{a1}}} + \frac{10^{-\text{pK}_{a2}}}{10^{-\text{pH}}} \right]^{-1}, \\
X_+ &= \left[ 1 + \frac{10^{-\text{pK}_{a1}}}{10^{-\text{pH}}} \left( 1 + \frac{10^{-\text{pK}_{a2}}}{10^{-\text{pH}}} \right) \right]^{-1}, \quad (27)
\end{align*}
\]
where $X(\pm)$, $X(\mp)$ and $X(-)$ are the mole fractions of zwitterionic, cationic and anionic type DMLL, respectively.

As is shown in Fig. 12, the isoelectric region is found to be at pH 5~7. In this range of pH, the net charge derived from the head groups of DMLL becomes nearly zero (the mole fraction of the zwitterionic form become almost equal to one). However, it should be noted that the surface charge densities of DMLL become negative in the isoelectric region, as can be seen in Fig. 11. This suggests the preferential adsorption of chloride ions compared to sodium ions. It can be postulated that the charges on the microemulsion surface are derived from the DMLL and the bindings of inorganic ions adsorbed on the microemulsion surface. Therefore, we have tried to make a quantitative analysis of the surface charge densities of DMLL microemulsions. The surface charge densities of the model are derived below. Assuming Langmuir-type adsorption of anionic type DMLL molecules which have no counterions on the surface of the microemulsion, Na$^+$ and H$^+$ will bind competitively at the carboxyl groups which are in the negative (COO$^-$) form. Furthermore H$^+$ will bind to the $\left(\text{N(CH}_3\text{)}_2\right)$ groups, and next Cl$^-$ will bind at these groups in the positive form, $\left(\text{HN}^+(\text{CH}_3)_2\right)$. Thus, we can express the surface charge density ($\sigma$) of the model microemulsion as the following equation.

\begin{equation}
\sigma = \frac{\frac{n_H}{K_{a2}} \exp \left(-\frac{e \Psi_0}{kT}\right) + K_{Na} n_{Na} \exp \left(-\frac{e \Psi_0}{kT}\right)}{1 + \frac{n_H}{K_{a2}} \exp \left(-\frac{e \Psi_0}{kT}\right) + K_{Na} n_{Na} \exp \left(-\frac{e \Psi_0}{kT}\right)} + \frac{eN}{1 + \frac{K_{a2}}{n_H} \exp \left(-\frac{e \Psi_0}{kT}\right) + K_{Cl} n_{Cl} \exp \left(-\frac{e \Psi_0}{kT}\right)}.
\end{equation}

where, $N$ is the adsorption number per unit area of the surface of microemulsion, $K_{a2}$ is
the dissociation constants of head groups of DMLL, $K_{Na}$ and $K_{Cl}$ are the binding constants of $Na^+$ and $Cl^-$ to the DMLL, $n_{H}$, $n_{Na}$ and $n_{Cl}$ are the numbers of $H^+$, $Na^+$ and $Cl^-$ in unit volume of water phase, and $\Psi_0$ is the surface electric potential.

Assuming that the $\zeta$-potential is equal to the surface potential of microemulsion, equation 29 becomes

$$\sigma = -\frac{eN}{1+\frac{10^{-pH}}{10^{-pK_{a1}}}+K_{Na}C_{Na}exp\left(-\frac{e\zeta}{kT}\right)+K_{Na}C_{Na}exp\left(-\frac{e\zeta}{kT}\right)\cdot eN \left(1+\frac{10^{-pK_{a2}}}{10^{-pH}}+K_{Cl}C_{Cl}exp\left(\frac{e\zeta}{kT}\right)\right).$$

(30)

where $K_{a1}$ is the dissociation constants of head groups of DMLL, $C_{Na}$ and $C_{Cl}$ are the mole units of $n_{Na}$ and $n_{Cl}$.

As the surface charge density at the isoelectric regions is quite small as shown in Fig. 11, the ratios of surface covering of $Na^+$ and $Cl^-$ are considered to be also small. Therefore, when $1 \gg K_{Na}C_{Na}exp\left(-\frac{e\zeta}{kT}\right)$ and $1 \gg K_{Cl}C_{Cl}exp\left(\frac{e\zeta}{kT}\right)$ are hold, equation 30 can be approximated as

$$\sigma \approx -\frac{eN}{1+\frac{10^{-pH}}{10^{-pK_{a1}}}exp\left(-\frac{e\zeta}{kT}\right)} + \frac{eN}{1+\frac{10^{-pK_{a2}}}{10^{-pH}}exp\left(\frac{e\zeta}{kT}\right)} + eNK_{Na}C_{Na}exp\left(-\frac{e\zeta}{kT}\right) - eNK_{Cl}C_{Cl}exp\left(\frac{e\zeta}{kT}\right).$$

(31)

The meaning of the terms on the right-hand side of equation 31 is given below. The first term and the second term are the charge densities arising from the carboxyl groups (COO-) and the dimethylammonium groups, (HN+(CH3)2), respectively. The third and the fourth terms are the charge densities derived for $Na^+$ and $Cl^-$ respectively. As is shown in Fig. 9 and 11, the $\zeta$-potential and the surface charge density become zero at pH 3.9. So we find

$$K_{Na} - K_{Cl} = \frac{1}{C} \left[\frac{1}{1+\frac{10^{-pH}}{10^{-pK_{a1}}}} - \frac{1}{1+\frac{10^{-pK_{a2}}}{10^{-pH}}}\right] = -0.20 \text{ (M}^{-1}\text{)},$$

(32)

where $C=C_{Na}=C_{Cl}=0.10 \text{ M}$. Furthermore, since the net charge of DMLL becomes almost zero in the vicinity of pH 6, we have,

$$K_{Na}exp\left(-\frac{e\zeta}{kT}\right) - K_{Cl}exp\left(\frac{e\zeta}{kT}\right) = \frac{e\sigma}{eC} \cdot \frac{1}{N}.$$  (33)

Substituting the values of pH, the $\zeta$-potential, and the surface charge density into equations 32 and 33 and assuming that $K_{Na}>0$, the following relations are introduced.

$$0 < K_{Na} < 0.91,$$

(34)

$$0.20 < K_{Cl} < 1.11,$$

(35)

$$K_{Cl} - K_{Na} = 0.20,$$

(36)

$$N > 0.79.$$  (37)

We have calculated $\sigma$ for many sets of $N$, $K_{Na}$ and $K_{Cl}$. Some examples of the obtained results for the cosurfactant concentrations of 8.0% are shown in Fig. 13 in comparison with the experimental data (open circles in the figure). In this calculation, we have assumed $N$ is independent on the pH value.

As can be seen in Fig. 13, the theoretical curves also change from positive to negative with changing pH, and become zero at pH 3.9. When $N$ is greater than 0.2 nm$^2$, the calculated values of $\sigma$ at various values of $N$ become larger than the experimental values (open circles) in the acid and in alkaline regions. This means that $N$ will be reduced by increasing hydrophilicity of DMLL and by the electrostatic forces of repulsion between the head groups of
DMLL with increasing mole fraction of cationic DMLL or anionic DMLL. Moreover, although it is very difficult to estimate exact values of $K_{Na}$ and $K_{Cl}$, the theoretical curves calculated with larger values of $K_{Na}$ and $K_{Cl}$ (such as $K_{Na}=0.8 \text{ M}^{-1}$ and $K_{Cl}=1.0 \text{ M}^{-1}$) do not agree well with the experimental curves. So we conclude that the value of $K_{Na}$ is nearly equal to zero.

We estimate that the values of $N$ are greater than 0.2 nm$^{-2}$ from the plots in Fig. 13. The surfactant number on the surface of unit microemulsion ($N_s$) is evaluated from the following equation

$$N_s = 4\pi a^2 \cdot N.$$ (39)

In fact, the surfactant numbers vary from a few hundreds to a few ten thousands$^{44}$. It
should be noted that we can evaluate more precise values when we specify the diameter of the microemulsion.

The novel numerical analysis on this amphoteric surfactant O/W type microemulsion are described in our previous papers\textsuperscript{72,73}. Effects of multivalent metallic ions on the binding constants and aggregation numbers of the amphoteric surfactant O/W type microemulsion are also described in our previous papers\textsuperscript{74−76}. On the other hand, the binding constants of inorganic electrolytes and aggregation numbers of O/W type microemulsion with a nonionic surfactant are published elsewhere\textsuperscript{77,78}.

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【総説】マクロおよびマイクロエマルション

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この総説では、マクロエマルションとマイクロエマルションの違い、マクロエマルションの構造と物性、マイクロエマルションの構造と物性、マクロエマルションの安定化と破壊、マクロエマルションの物理的調製法と化学的調製法、乳化剤の選択、多相マイクロエマルションの調製、マイクロエマルションの界面電気的挙動について論述されている。

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【報文】シクロヘキサソノンとメチルエチルケトン
類存在下のアクリルアミドの挙動

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シクロヘキサソノン、メチルエチルケトン、あるいはその誘導体存在下のアクリルアミド（AAm）の反応性をテトラヒドロフラン中、様々な温度で検討したところ、カルボニル基とアミド基の間の相互作用が存在し、これら相互作用により AAm の反応性が向上していることを見出した。同反応条件において、ケトン類の存在しない場合には AAm は未反応である。また、AAm と t-ブチルメチルケトンあるいはポリメチルブチルケトンとの混合物について 13C NMR スペクトルの測定を行い、カルボニル基とアミド基の間の相互作用を直接評価した結果、混合物中の AAm のカルボニル基炭素の化学シフトは、単独のそれよりいずれも若干低磁場に移動する傾向があることが判明した。この結果から、ケトンとアミドとの間の水素結合に基づく相互作用が、AAm の反応性向上の主な理由と予想される。

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