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Microemulsions as Liquid Media for Material Separation

by

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ABSTRACT

The functions of the microstructures in water-in-oil microemulsion are elucidated. The electrostatic interaction in the water-pools of the microstructures plays a key role in the solubilization of ionic solutes. A large internal interface of microemulsion contributes to the solubilization of less polar solutes. The curvature of the microstructures affects the local environment of less polar solutes entrapped in the internal interface. For polar macromolecules such as proteins, the microstructures have a function to recognize the size of solutes. The solubilization dynamics was also studied. These knowledge permits tailoring microemulsion for solubilization of solutes and chemical reactions in the microstructures.

Key Words: Microemulsion, Microstructure, Solubilization, Extraction rate

1. INTRODUCTION

Microemulsions are thermodynamically stable, macroscopically homogeneous dispersion of the microstructures composed of water, hydrocarbon and surfactant, which provide nanoscale compartments for solute molecules. This compartmentalized liquid has attracted a great deal of interest in using such system for the selective separations of substances and the microreactors of materials syntheses. Extensive studies have been performed on the solubilization of solute molecules in the microstructures (aggregates). However, the role of the aggregates in the solubilization has not been well understood. This work aims at the elucidation of the role of the aggregates by focussing on a typical water-in-oil microemulsion composed of sodium bis (2 ethylhexyl) sulfosuccinate (AOT) and hydrocarbon solvents, which are equilibrated with NaCl-brine bulk solution.

2. EXPERIMENTAL

AOT supplied by Tokyo Kasei and proteins supplied by Sigma were used without further purification. The other materials of reagent grade were used as supplied. The solubilization of solutes was measured by usual methods used in the two bulk phases system (AOT/ solvent/ NaCl-brine system).
Fig. 1  Effects of salinity and organic solvents on size of microemulsion aggregates at 25°C. [AOT] = 0.05M. □ n-dodecane,
○ n-decane, △ isooctane, ■ n-heptane,
○ n-hexane, ▲ cyclohexane, ▼ toluene.

Fig. 2  Osmotic compressibility vs. packing fraction of aggregates.
r: hard sphere radius.

Fig. 3  Specific viscosity vs. packing fraction of aggregates.
\[ \eta_s = \left( \eta - \eta_{\text{solv}} \right) / \eta_{\text{solv}} \]
The osmotic compressibility and the size of aggregates were determined by static light scattering (SLS) and small angle X-ray scattering (SAXS) methods, respectively. The change in protein conformation was detected by circular dichroism (CD).

3. CHARACTERISTICS OF AOT-MICROEMULSION SYSTEM

The characteristics of the AOT microemulsion in the Winsor II region, i.e., the effects of salinity and organic solvent species on the size of the aggregates, are summarized in Fig. 1. The radius $R$ of the spherical aggregates in dilute state measured by SAXS can be easily controlled by salinity and solvent species. This ease of the control arises from the rotation of the ethanic bond between branched two hydrocarbon groups of an AOT-molecule [1]. The radius $R$ can be related to the water-to-AOT mole-ratio $W_o$ in the microemulsion phase:

$$R = 0.16W_o + 1.2nm$$

The radius $R_w$ of the water-pool of an aggregate is equivalent to $0.16W_o$.

The osmotic compressibility $\chi$ and the specific viscosity $\eta_{sp}$ of the microemulsion are shown against the packing fraction of the aggregates $\Phi_{ms}$ in Figs. 2 and 3. The solid curves in Fig. 2 represent the $\chi$ value calculated from the Carnahan-Starling equation of states for hard sphere system, and explains well the results observed by SLS. The $\eta_{sp}$ value at zero-shear rate also agrees with that for the colloidal solution of monodispersed silica particles [2]. It is concluded from these results that the microemulsion aggregates behaving as hard spheres provide the nanoscopic compartments of water-microphase (the water-pool) for solubilizing solute molecules in wide ranges of $\Phi_{ms}$.

Fig. 4 Effect of electric charge states of amino acids on distribution coefficients in AOT/n-heptane/brine system at 25°C. (a) Gly; (b) Trp.
I = ionic strength: [Na$^+$]
4. ROLES OF AGGREGATES IN SOLUBILIZATION OF SMALL MOLECULES

AOT molecules are anionic, and thus cationic solutes can be solubilized in the water-pools of the aggregates through strong electrostatic interaction [3]. Typical solutes are amino acids RCHNH2COOH, whose charge state can be regulated by altering the pH in the aqueous bulk solution. Figure 4 shows typical examples of the distribution coefficients $D_s$ (= J-solute conc. in the microemulsion divided by that in the brine) for glycine (Gly) and tryptophan (Trp) [4]. In the middle ranges of pH, these amino acids are in zwitter ionic states (±). In this range, the value of $D_{Gly}^+$ can be interpreted by postulating that Gly is entrapped uniformly in the water-pools of the aggregates, whereas in low pH, Gly+ is concentrated in the electrical double layer, yielding higher $D_{Gly}^+$ value. Trp, which is much more hydrophobic than Gly, is entrapped in the interface of the aggregates (micro-interface), resulting in much higher $D_{Trp}^+$ than $D_{Gly}^+$. Thus, the area of the micro-interfaces is essential to the solubilization of Trp.

Figure 5 shows the effects of salinity and organic solvent species on $D_{Trp}^+$. These effects on $D_{Trp}^+$ are uniquely determined by $W_o$, i.e., the curvature of the aggregates. The fluorescence spectra for Trp due to hydrophobic indole ring indicate that the local environment around the indole ring of Trp varies from nonpolar to polar with decreasing the curvature [4]. Thus, the local environment around Trp and the partition of Trp can be controlled by altering the curvature of the aggregates (see Fig. 5).
5. ROLE OF AGGREGATES IN SOLUBILIZATION OF LARGE MOLECULES

Proteins are bioactive macromolecules, which can be solubilized in the microemulsion phase. It was ascertained from CD-spectra that \( \alpha \)-chymotrypsinogen (CTN) is one of the typical proteins which are hardly denatured by the adsorption of AOT-molecules on the protein surface.

The fractions of CTN extracted to the microemulsion \( E \), which was measured in short term (10 min) after contacting the microemulsion with the brine solution containing CTN, are shown in Fig. 6 against the AOT-to-CTN mole-ratio, \( \rho = \frac{[\text{AOT}]}{[\text{CTN}]} \), the subscript \( c \) representing the feed state. Here, \( [\text{AOT}] \) represents the AOT concentration in the microemulsion phase. Both \( E \) and \( [\text{AOT}] \) values are almost zero until a critical \( \rho \)-value, followed by abrupt increases and approaching a saturated value with increasing \( \rho \). This result indicates that the CTN molecules in the brine solution adsorb almost all AOT-molecules present in the system below the critical \( \rho \)-value. Just over the critical \( \rho \)-value, CTN is extracted to microemulsion phase accompanying large amount of water. As shown in Fig. 6, the size of the CTN-AOT aggregates in the microemulsion phase measured by SAXS was extraordinarily large compared with the AOT-aggregates free from CTN. Thus, the CTN-AOT aggregates contain large amounts of water and AOT molecules. Just below the critical \( \rho \)-value, the CTN-molecules in the aqueous phase generate large aggregates, which are extracted to the organic phase by adding extra amount of AOT to the system. With increasing \( \rho \), the size of AOT-CTN aggregates decreases to approach that of the AOT-aggregates in the absence of CTN. Thus, the AOT-CTN aggregates are subdivided into finer aggregates, and when \( \rho \) is large, each AOT-aggregate provides the compartment for solubilizing a CTN-molecule.

The distribution coefficient for CTN, \( D_{\text{CTN}} \), was proportional to the AOT concentration in the microemulsion phase. Figure 7 shows the effects of salinity and organic solvent species on \( D_{\text{CTN}}/ [\text{AOT}] \).
As shown in Fig. 8, these effects on \( D_{\text{CTN}}/ [AOT] \) reduce to the effect of \( W_o \), i.e., of the water-pools of the aggregates. The result in Fig. 8 can be divided into three domains: (a) Domain of constant \( D_{\text{CTN}}/ [AOT] \), (b) Domain of strong decrease in \( D_{\text{CTN}}/ [AOT] \) with decreasing \( W_o \), and (c) domain of constant low \( D_{\text{CTN}}/ [AOT] \) -value. In domain (a), the size of the water-pools is large enough to solubilize CTN. CTN in the brine adsorbs AOT molecules, resulting in amphiphilic species. Thus, the distribution of CTN is proportional to the total area of the micro-interface, i.e., \( D_{\text{CTN}}/ [AOT] \). In domain (c), a CTN-molecule adsorbing some AOT-molecules in the brine solution is estimated to dissolve in the organic solvent by adsorbing additional AOT-molecules. The fine microemulsion aggregate does not accommodate a CTN-molecule, because its size is small enough to reject the CTN-entrapment. Thus, in the middle domain (b), each water-pool is estimated to have the function to accommodate a CTN-molecule.

In domain (b), the size of the water-pools would be smaller than the effective size of a CTN-molecule. The original microemulsion aggregates should expand to accommodate a CTN molecule in the water pool. The increase in the free energy of the micro-interface due to the expansion can be expressed by the elastic energy required for the expansion. The elastic energy per unit area in the absence CTN is given by

\[
f = \left( \frac{k_{\text{sp}}}{2} \right) \left( 1/R - 1/R_o \right)^2 + k_{\text{nud}}/R^2
\]

where, \( R_o \) is the radius of natural curvature. Then, the total elastic energy in the system \( F_o \) is expressed by

\[
F_o = 4\pi R^2 N f
\]

where \( N \) is the number of the aggregates in the absence of CTN, and is expressed by \( (\Sigma s/4\pi) (\Sigma s/3V_w W_o)^{\frac{1}{3}} [AOT] \). Here, \( \Sigma s \) and \( V_w \) represent the area occupied by a surfactant molecule and the molecular volume of a water-molecule. At equilibrium, \( f \) must take a minimum value, because \( 4\pi R^2 N \) is constant. Then, \( F_o \) is written as

\[
F_o = (\Sigma s/2)(\Sigma s/3V_w W_o)^{\frac{1}{3}}[AOT] \lambda (1+\lambda) k_{\text{sp}}
\]

\[
\lambda = 2k_{\text{nud}}/k_{\text{sp}}
\]

and the radius \( R_e \) at equilibrium is given by

\[
R_e = R_o (1+\lambda)
\]

We assume for the sake of simplicity that the water content in the aggregates containing CTN is negligibly small. The number and the radius of the aggregates containing CTN are denoted by \( N_c \) and \( R_c \). Then,

\[
4\pi R^2 N + 4\pi R^2 R_c N_c = \Sigma s [AOT], \quad 4\pi R^2 N/3 = V_w [H_2O]
\]
The total energy in the system containing CTN is

\[ F_c = 4\pi R^2 N c f_R - Re + 4\pi Re^2 N c f_R = Re \]  

From Eqs. (2) - (7), the free energy change due to the aggregate expansion, \( \Delta F = F_c - F_0 \), is approximated when \( N_c \ll N \):

\[ \frac{\Delta F}{N c} = 2\pi k_{sp}(1 + \lambda)(1 - 2\lambda) \{ \frac{Re}{1 - 2\lambda} \}^2 \frac{2\lambda}{1 - 2\lambda} \]  

When the AOT-aggregate accommodates at most one CTN molecule, the distribution of CTN is proportional to \( N \). Then, \( D_{CTN} \) is expressed by

\[ D_{CTN} \propto N \exp(-\Delta F/NckT) \]

or

\[ D_{CTN}/[AOT] \propto W_0^{-2}\exp(-\Delta F/NckT) \]  

Here, \( Re \) is approximated as

\[ Re = 3V_w W_0 / \Sigma s \]  

The change of \( D_{CTN}/[AOT] \) with \( W_0 \) in the domain (b) can be fitted well by Eq. (9) with the value of several \( kT \) for \( k_{sp} \). This result indicates that a CTN-molecule is entrapped in the water-pool of an AOT-aggregate by expanding the aggregate volume. In other word, the AOT-aggregates have size-recognition ability for the solubilization of large guest molecules.

In contrast to CTN, cytochrome c (Cytc) adsorbs many AOT-molecules, resulting in strong denaturation. Due to this, the conformation of Cytc is completely different from natural conformation. Then, Cytc is converted to strong amphiphilic state, and is entrapped in the micro-interface of the AOT-aggregates [5]. The micro-interface of the AOT-aggregates becomes essentially important for the solubilization of such denatured proteins.

6. DYNAMICS OF SOLUBILIZATION

Solute transfer rate between the microemulsion and the brine phases was measured with the aid of the Lewis cell. The microemulsion was equilibrated with the brine phase before use. The solute flux \( J \) is expressed by

\[ J = K(D_j C_{j,aq} - C_{j,org}), \quad 1/K = D_j/k_{aq} + 1/k_i + 1/k_{org} \]  

where \( C \) represents the concentration of solute \( j \), \( K \), \( k_{aq} \) and \( k_{org} \) are the overall mass transfer coefficient, the mass transfer coefficients in the aqueous and the organic phases, respectively. \( k_i \) is the permeation rate coefficient through the macro-interface between the microemulsion and the bulk brine.
phases. The subscripts, $a_q$ and $org$, represent the brine and the microemulsion phases.

The flux measured was controlled by the interfacial rate process. The obtained $k_i$ values for several solutes were $10^{-4}$ to $10^{-5}$ cm/s in order of magnitude. These $k_i$ values are much less than $k_{aw}$ and $k_{aw}$. The observed $k_i$ values for Trp, potassium cation $K^+$ and anionic iodide $I^-$ in the n-heptane solvent system are plotted in Fig. 9 against the diameter of the aggregates, $D_{sph} = 2(R + 1c)$. Here, $1c (=0.8 \text{nm})$ is the length of the hydrocarbon chain tail of AOT-molecule. The diameter was changed by altering salinity. The $k_i$ values for n-heptane solvent system are proportional to $D_{sph}$ irrespective of solute species. The $k_i$ was found to be independent of $[AOT]$. Thus, the flux $J$ is proportional to $[AOT]$ because $D_i \propto [AOT]$. If the interfacial rate process is dominated by the aggregate formation due to thermal undulation of the micro-interface, the flux must be independent of $[AOT]$, because the adsorption of AOT at the macro-interface is saturated. It is, therefore, concluded that the aggregate formation does not dominate the interfacial rate process.

The solute transfer would proceed via several steps as shown in Fig. 10. The steps (b) and (c) are the fusion process between the macro-interface and the aggregates, and the exchange process of solute, respectively. $k_i$ is independent of three kinds of solutes, which are localized in different positions with each other. Thus, the step (c) is not rate-determining step. Since the steps (a), (d) and (e) are fast, the rate-determining step is the fusion process (b).

The effect of solvent species on $k_i$ is shown in Fig. 11 against $W_o$. The effect of salinity in the n-
heptane solvent system is also shown in this figure. The dependence of $k_i$ on solvent species is much greater than that of salinity in the n-heptane solvent system. This result indicates that strong penetration of the solvent molecules into the micro-interface of the aggregates (e.g., solvent CCl₄) decreases the fusion rate. Thus, the solvent species plays an important role in the solubilization of solutes.

7. CONCLUDING REMARKS

The basic information for tailoring microemulsion is presented. Many functions of the compartmentalized liquids such as microemulsion will be extracted by tailoring the microstructures toward separation of solute molecules and microreactor of materials syntheses.

REFERENCES