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## SELECTION OF BREAK-UP TRACER FOR EVALUATION OF STABILITY OF LIQUID SURFACTANT MEMBRANE

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In liquid surfactant membrane (LSM) processing, it is important to obtain more stable LSM. Many studies of the stability of LSM formed by Span 80 or polyamine have been carried out using a tracer technique.<sup>1-5,8,9)</sup> However, different break-up tracers were used by the researchers, so that the influence of various factors on the stability of LSM has not necessarily been clarified so far.

In the previous paper,<sup>4)</sup> use of nickel ion as the break-up tracer for LSM formed by Span 80 was proposed when nickel and copper ions were dissolved in the internal aqueous solution.

In the present work, the tracer technique for evaluating the stability of LSM was examined in detail and its validity, which is based on the assumption that the tracer permeation through LSM besides the break-up of LSM is negligibly small, was also examined.

### 1. Experimental

Surfactants<sup>4)</sup> used were Span 80, polyamine and a derivative of L-glutamic acid di-oleyl ester (henceforth 2C<sub>18</sub>A<sup>9</sup>GE). The experimental method was the same as that described in the previous paper.<sup>4)</sup> The break-up tracer used was metal nitrate. The external aqueous solution contained manganese nitrate as the occlusion tracer.

Extent of break-up of LSM was defined by Eq. (1):

$$\varepsilon = \frac{V_{we} C_{te}}{V_{wi}^0 C_{ti}^0} \quad (1)$$

The distribution equilibrium of the metal used as

the break-up tracer was measured at 303 K between toluene and deionized water.

### 2. Results and Discussion

**Figure 1(a)** shows the relation between extent of break-up of LSM,  $\varepsilon$ , and time when using Span 80 as the surfactant, copper nitrate as the break-up tracer and manganese nitrate as the occlusion tracer. **Figure 1(b)** shows the characteristic behavior of the break-up in the initial stage of the experiment.

From Fig. 1(a), it was found that as the surfactant concentration,  $C_s$ , increased,  $\varepsilon$  decreased. However,  $\varepsilon$  increased when the concentration exceeded 28.7 mol/m<sup>3</sup>. This result seems strange because it is considered that the LSM should be more stable with increasing  $C_s$ . Hence, it is considered that the apparent increase of  $\varepsilon$  with  $C_s$  is caused by the transport of copper by the surfactant from internal to external aqueous solution. In the range of  $C_s > 28.7$  mol/m<sup>3</sup> in Fig. 1(b), the relation between  $\varepsilon$  and time can be divided into two regions according to its slope. This suggests that the drop size of the W/O emulsion changes in the initial period of mixing and that a certain time is required to attain steady-state dispersion as pointed out by Hong and Lee<sup>6)</sup> and Kataoka *et al.*<sup>7)</sup>

The rate constants of break-up of LSM in both regions are defined by the following equations. **Figure 2** shows the effect of  $C_s$  on  $k_{b0}$  and  $k_{bs}$ .

$$k_{b0} = \left( \frac{d\varepsilon}{dt} \right)_{t=0} \quad (2)$$

$$k_{bs} = \left( \frac{d\varepsilon}{dt} \right)_{t>120} \quad (3)$$

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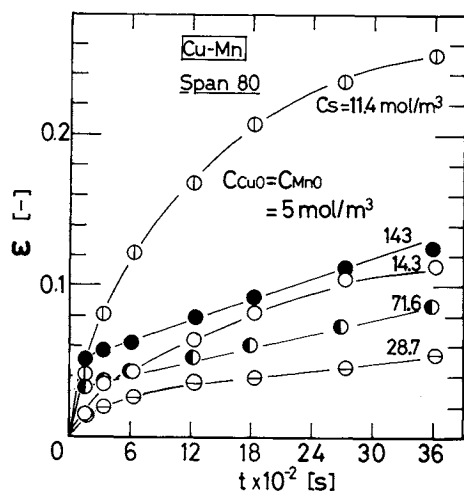


Fig. 1(a). Relation between extent of break-up of LSM and time when using Span 80 as surfactant, copper nitrate as break-up tracer and manganese nitrate as occlusion tracer

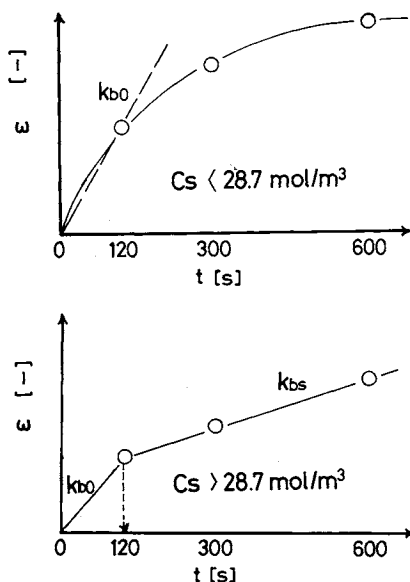


Fig. 1(b). Characteristic behavior of break-up in initial stage of experiment

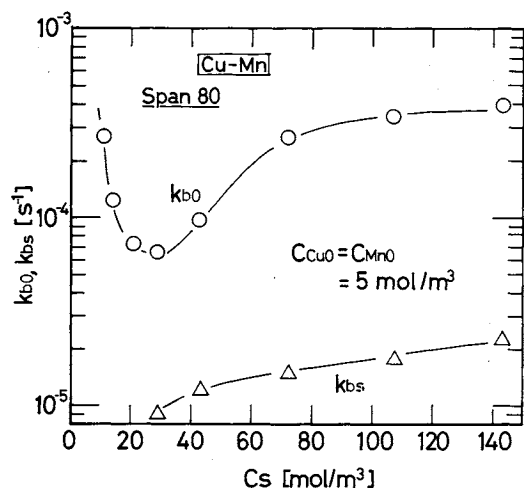


Fig. 2. Effect of  $C_s$  on  $k_{bo}$  and  $k_{bs}$

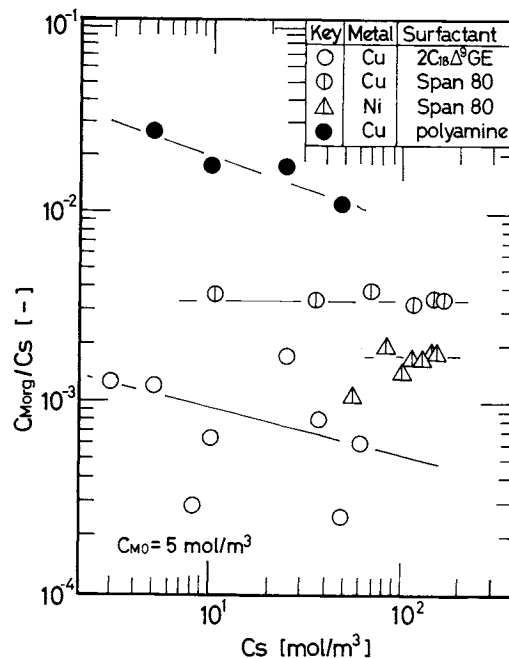


Fig. 3. Distribution equilibrium of copper and nickel

where  $k_{bs}$  is defined only when the value of  $\varepsilon$  increases linearly with elapsed time.

To examine the possibility of copper transport by the surfactant, the distribution equilibrium of copper between the aqueous solution and the toluene solution containing the surfactant was measured.

Figure 3 shows the result for distribution equilibrium of copper and nickel. In Fig. 3, the experimental data concerning  $2C_{18}\Delta^9GE$  are considerably scattered due to the limitation of analytical accuracy, but copper is found to be scarcely extracted with  $2C_{18}\Delta^9GE$ . On the other hand, Span 80 and polyamine extract copper into the toluene solution. At present, the chemistry of the interactions between copper and the surfactants is difficult to be clarified because both Span 80 and polyamine are mixtures of many components.

As a result, it is considered that  $k_{bo}$  in the range of  $C_s > 28.7 \text{ mol/m}^3$  indicates the dissolution rate of copper from the organic solution in the W/O emulsion to the external aqueous solution when the W/O emulsion was first added into the external aqueous solution, because the organic solution already contained copper as mentioned above. On the other hand,  $k_{bo}$  in the range of  $C_s < 28.7 \text{ mol/m}^3$  indicates the break-up of W/O emulsion because the extent of copper extracted is relatively small and  $k_{bo}$  decreases with increasing  $C_s$ . The value of  $k_{bs}$ , which appears only in the range of  $C_s > 28.7 \text{ mol/m}^3$ , indicates the transport rate of copper by Span 80 from internal to external aqueous solution because in this range LSM formed by Span 80 is considered to be stable as will be mentioned below.

From these results, the use of copper nitrate as the

break-up tracer is not suitable. Subsequently, use of other metals such as nickel, magnesium and zinc was examined and distribution equilibria of the metals were measured. It was found that polyamine and  $2C_{18}\Delta^9GE$  did not extract these metals into the organic solution although they were extracted with Span 80, and that the extent of nickel extracted was a little smaller than those of the others as shown in Fig. 3. Therefore, use of metal nitrate alone as the break-up tracer of LSM formed by Span 80 is not adequate.

The distribution equilibrium of each metal under the coexistence of copper and nickel nitrates is shown in Fig. 4, from which it is seen that Span 80 interacts selectively with copper. It is expected that the use of nickel nitrate as the break-up tracer under the coexistence of copper and nickel is possible.

The effect of  $C_s$  on  $k_{b0}$  and  $k_{bs}$  under the coexistence of copper and nickel in the internal aqueous solution is shown in Fig. 5. As expected, a large difference in  $k_{b0}$  between copper and nickel was observed and the values of  $k_{b0}$  and  $k_{bs}$  for copper were similar to those in Fig. 2. It is concluded that under the coexistence of copper and nickel the leakage of nickel from internal to external aqueous solution is caused by the break-up of LSM formed by Span 80.

Finally, because polyamine and  $2C_{18}\Delta^9GE$  do not extract nickel nitrate as mentioned above, the use of nickel nitrate as the break-up tracer is possible. Therefore, as reported in the previous paper,<sup>4)</sup> it is considered that the break-up rate of LSM obeys a first-order expression when a surfactant does not interact with the tracer.

#### Nomenclature

$C_{Morg}$	= metal concentration in organic solution	[mol/m <sup>3</sup> ]
$C_s$	= surfactant concentration	[mol/m <sup>3</sup> ]
$C_t$	= break-up tracer concentration	[mol/m <sup>3</sup> ]
$k_{b0}$	= rate constant of break-up in initial period	[s <sup>-1</sup> ]
$k_{bs}$	= rate constant of break-up in steady-state dispersion	[s <sup>-1</sup> ]
$V_w$	= volume of aqueous solution	[m <sup>3</sup> ]
$t$	= time	[s]
$\varepsilon$	= extent of break-up	[—]

#### <Subscripts>

$e$	= external aqueous solution
$i$	= internal aqueous solution

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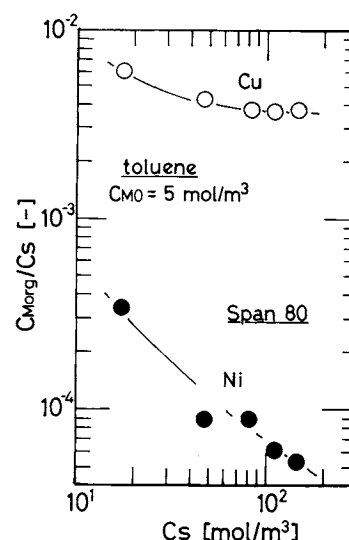


Fig. 4. Distribution equilibrium of each metal ion under coexistence of copper and nickel

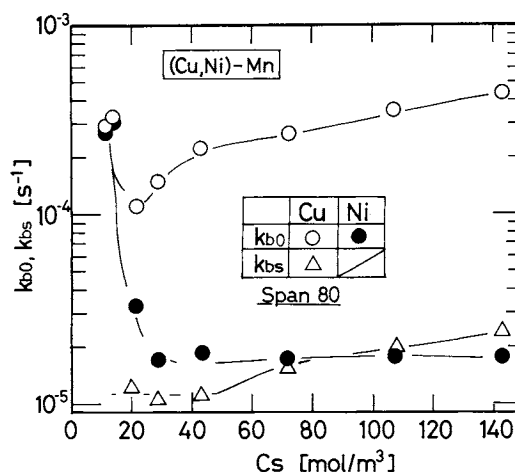


Fig. 5. Effect of  $C_s$  on  $k_{b0}$  and  $k_{bs}$  under coexistence of copper and nickel in internal aqueous solution

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