$F(s)$	= transfer function	[—]
h_p	= particle-to-gas heat transfer coefficient	[W·m ⁻² ·K ⁻¹]
k	= thermal conductivity	[W·m ⁻¹ ·K ⁻¹]
k_e^0	= effective thermal conductivity of quiescent packed bed	[W·m ⁻¹ ·K ⁻¹]
Nu	= $h_p D_p / k_F$, Nusselt number	[—]
Pr	= $C_F \mu / k_F$, Prandtl number	[—]
R	= particle radius	[m]
Re	= $D_p U \varepsilon_b \rho_F / \mu$, particle Reynolds number	[—]
T	= temperature	[K]
U	= interstitial gas velocity	[m·s ⁻¹]
$\alpha_{a,z}$	= axial gas thermal dispersion coefficient	[m ² ·s ⁻¹]
α_F	= gas thermal diffusivity	[m ² ·s ⁻¹]
ε	= root-mean-square-error, defined by Eq. (12)	[—]
ε_b	= bed void fraction	[—]

μ	= gas viscosity	[Pa·s]
ρ	= density	[kg·m ⁻³]

<Subscripts>

F	= gas
S	= solid

<Superscripts>

I	= input
II	= response

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A STUDY OF THE STABILITY OF (W/O)/W-TYPE EMULSIONS USING A TRACER TECHNIQUE

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Separation techniques using liquid membrane have attracted special interest recently because of the development of low-cost separation processes. In particular, the multiple-emulsion system has the advantages of a large interfacial area and very thin liquid membrane. However, separation efficiency significantly decreases with breakage of the liquid membrane.

Only a small number of investigations have been made of the stability of (W/O)W-emulsions system in stirred vessels. The object of the present study is to investigate the stability of the aqueous solution-in-kerosene emulsion drops dispersed in outer water phase by using a tracer.

1. Experimental

An 800-ml vessel fitted with four baffles and two 6-bladed turbine-type impellers was used for the present study. Details of the experimental apparatus are given in the previous paper³⁾. Distilled water was used as the continuous phase. The dispersed phase was W/O-emulsion, prepared by dispersing an aqueous solution of tracer into kerosene containing Span-80 as emulsifying agent.

A tracer technique was employed. It involved deter-

mining the quantity of tracer leaking out of the inner dispersed droplets into the continuous phase due to the breakup of the emulsion drops. The tracers used were NaCl, NaSCN, CuSO₄, H₂SO₄, HCl, and/or NaOH, its concentration in the continuous phase being analyzed on a conductivity meter or an ion analyzer at a fixed agitation time. All experimental runs were conducted at 25±0.5°C.

2. Results and Discussion

In the present study, we assumed that the instability of the (W/O)/W-emulsion system could be measured by the breakage of W/O-emulsion drops, ξ , under fixed stirred conditions. Then the breakage was defined as follows:

$$\xi = C_o \phi_w / (C_i \phi_{w/o} \phi_w^i) \quad (1)$$

where $\phi_w + \phi_{w/o} = 1$ and the product of $\phi_{w/o}$ and ϕ_w^i is equal to the volume fraction of the inner aqueous solution.

In regard to the effect of salt tracer concentration in the inner aqueous solution on the stability of the (W/O)/W-emulsion, Kita *et al.*¹⁾ reported that the stability of emulsion increases with increase in NaCl concentration in the range of 0.3 to 0.5 wt%. On the other hand, it is also reported that the stability decreases as salt concentration in the continuous phase

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Fig. 1 Breakage fraction of emulsion drops against agitation time

Fig. 2 Breakage fraction of emulsion drops per unit specific interfacial area

increases⁴⁾. However, in a series of our preliminary experiments with various concentrations of NaCl in the inner aqueous phase the value of ξ varied little below 0.34 kmol/m^3 (2 wt%), while that for $C_i > 0.34 \text{ kmol/m}^3$ increased with C_i . Therefore, as the inner dispersed phase, a 0.171 kmol/m^3 (1 wt%) aqueous solution of NaCl was used in the present study.

Figure 1 shows the breakage fraction of W/O-emulsion drops as a function of agitation time. It can be seen that except for the initial period the breakage of emulsion drops proceeds at a constant rate. Thus, in the following experiments, the values of ξ were measured at $t=30 \text{ min}$. Figure 1 also shows that the ξ -value increases with impeller speed, N . In stirred liquid/liquid-dispersion systems, in general, larger N results in smaller drop size, i.e., large specific interfacial area, a . Accordingly, it is reasonable to discuss stability in terms of breakage per unit interfacial area. Estimating drop diameter according to the previous paper³⁾, we can calculate the value of ξ/a for a fixed value of $\phi_{w/o}$. The results are shown in Fig. 2 as a plot of ξ/a vs. $\bar{d}_{32}$. The figure shows that the smaller emulsion drops are more stable and that the values of ξ/a with the smaller impeller ($D_i=3.3 \text{ cm}$) are lower than those with $D_i=5.0$ and 6.7 cm . In addition, although the thickness of the oil membrane decreases with increase of ϕ_w^i , little effect of ϕ_w^i on ξ/a was found in the range studied.

Figure 3 shows the effect of concentration of Span-80 on the breakage of W/O-emulsion drops. According

Fig. 3 Breakage fraction against concentration of emulsifying agent

Fig. 4 Variation of breakage fraction with pH in inner aqueous phase

Fig. 5 Breakage fraction for inner aqueous solutions of H_2SO_4 , HCl and NaOH

to Kondo *et al.*²⁾, ξ -value suddenly decreased at about $C_s=1.0 \text{ wt}\%$. In Fig. 3, however, the ξ -value varies as the -1.5 power of C_s . This dependence of ξ on C_s suggests that the emulsion drops become rigid due to the adsorption of emulsifying agent on the oil-water interface.

In view of the practical applications of liquid membrane separation using the (W/O)/W-emulsion system, the breakage of emulsion drops was measured over a wide range of pH using CuSO_4 and NaSCN as tracer in the presence of sulfuric acid or sodium hydroxide. Figure 4 shows the effect of pH on ξ . As can be seen in the figure, solution more alkaline than pH 11.5 shows a drastic increase in ξ -value, while for $\text{pH} < 3$ there is also a significant increase in ξ .

Figure 5 shows the results obtained for the inner

aqueous solutions of H_2SO_4 , HCl and NaOH as the tracer. In the case of the aqueous solution of NaOH the breakage becomes very large, and it indicates that when $C_i=1 \text{ kmol/m}^3$ the greater part of the inner dispersed phase leaked out of the emulsion drops. On the other hand, using the acid solutions as the inner dispersed phase, ξ with H_2SO_4 is lower than with HCl . Also in Fig. 5, the ξ -value with the aqueous solution of sulfuric acid alone is considerably lower than that for the corresponding pH in Fig. 4. This fact suggests that breakage of the W/O-emulsion drops is affected not only by the hydrogen ion but also by the cupric and/or sulfate ions used as the tracer. It can be concluded that the stability of the (W/O)/W-emulsion depends on the ionic species and its concentration in the inner aqueous phase.

Nomenclature

a	= specific interfacial area of dispersed drops	$[\text{cm}^2/\text{cm}^3]$
C_i	= initial solute concentration in inner dispersed phase	$[\text{kmol/m}^3]$

C_o	= solute concentration in continuous phase	$[\text{kmol/m}^3]$
C_s	= concentration of emulsifying agent in oil	$[\text{wt}\%]$
D_i	= impeller diameter	$[\text{cm}]$
D_T	= diameter of stirred vessel	$[\text{cm}]$
$\bar{d}_{32}$	= Sauter mean diameter of emulsion drops	$[\text{cm}]$
N	= impeller speed	$[\text{rpm}]$
t	= agitation time	$[\text{min}]$
ξ	= breakage fraction of W/O-emulsion drops, defined by Eq. (1)	$[-]$
ϕ_w	= volume fraction of continuous water phase	$[-]$
$\phi_{w/o}$	= volume fraction of dispersed W/O-emulsion phase	$[-]$
ϕ_w^i	= volume fraction of inner water phase in W/O-emulsion phase	$[-]$

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ERRATA TO VOL. 14, NOS. 1-3 (1981)

No.	Page	Column	Line	erroneous	should be read
1	52		Fig. 6	B_o	B
2	157	Table 2	1-Pentanol ($c \times 10^5$) ($d \times 10^7$)	-0.2508 0.2392	0.2508 -0.2392
				Component	Component
				1 2	1 2
3	185	Table 2	Run No. 2	G.B. C.S. -A -A	C.S. G.B. -A -A
			No. 4	G.B. C.S. -C -C	C.S. G.B. -C -C