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## ANALYSIS OF WATER ENTRAINMENT INTO DISPERSED W/O EMULSION DROPS

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The effects of operating conditions on mechanical water entrainment into W/O emulsion drops in a (W/O)/W emulsion system were studied in a stirred tank in the absence of permeation due to osmotic pressure.

The water entrainment was influenced by surfactant concentration, water volume fraction in W/O emulsion, inner water drop size, salt concentration in the external water phase, and agitation speed in the stirred tank. There was a satisfactory correlation between the extent of water entrainment and the weight of surfactant per unit interfacial area. These observations suggested that water entrainment proceeded as a result of additional emulsification at the drop surface. This idea was confirmed by examining the water entrainment in an oil-water dispersion system where water entrainment occurred by emulsification. The effects of the operating conditions on water entrainment in the oil-water dispersion system were quite similar to those in the (W/O)/W emulsion system. In addition, the volume of water entrained per unit surface area of dispersed oil drops was in fair agreement with that in the (W/O)/W emulsion system. These results supported the proposed mechanism of water entrainment.

### Introduction

In extraction processes with liquid surfactant membrane where W/O emulsion is dispersed into aqueous solution, the lowering of the extract concentration in the inner aqueous phase results in the decrease of process efficiency. This problem occurs mainly by the permeation and mechanical entrainment of the external water. The former is caused by the concentration difference between internal and external aqueous solutions, and has been discussed in detail.<sup>2,6,7)</sup> The mechanical entrainment, however, is still not completely elucidated because of its complex mechanism.<sup>4,5,10)</sup>

Recently, Nakashio *et al.*<sup>6,7)</sup> investigated this problem quantitatively under conditions of no permeation. Fujinawa *et al.*<sup>2,3)</sup> studied the same subject for systems where mechanical entrainment and permeation proceeded simultaneously, and proposed operating conditions which suppressed entrainment.

They also showed that increasing the emulsion viscosity was effective in reducing the entrainment. Although the effects of various operating and emulsion-preparing conditions were examined in these papers, it is still obscure how drop surface contributes to water entrainment.

In the present study, the effects of operating conditions on mechanical entrainment were examined, using emulsions of various compositions. The extent of water entrainment was related to surfactant concentration per unit surface area, taking into account the contribution of additional emulsification at the drop surface. To establish the entrainment mechanism, the entrainment in an oil-water dispersion system was studied and compared with water entrainment in a W/O emulsion-water dispersion system, termed "(W/O)/W emulsion" in this paper. A mechanism of mechanical water entrainment was proposed on the basis of these experimental findings.

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## 1. Experimental

W/O emulsion was prepared by agitating kerosene solution containing Span 80 (Kao Co.) as a surfactant and aqueous solution of  $5 \text{ mol} \cdot \text{m}^{-3} \text{ Cu}(\text{NO}_3)_2$  in a homogenizer (Nippon Seiki Co.).  $\text{Cu}(\text{NO}_3)_2$  was utilized as a tracer to detect the emulsion breakage. The homogenizer agitation speed ( $n$ ), Span 80 concentration ( $C_s$ ), and volume fraction of water in the emulsion ( $\phi_w$ ) were varied in the range of  $33.3\text{--}167 \text{ s}^{-1}$ ,  $1\text{--}10 \text{ wt}\%$  and  $0.3\text{--}0.7$ , respectively. The agitation time was 10 min for all samples. About  $100 \text{ cm}^3$  of the emulsion was gently poured onto  $500 \text{ cm}^3$  of the external water phase, and the contents were agitated at impeller speeds ( $N$ ) ranging from  $2.5$  to  $5.0 \text{ s}^{-1}$ . All experiments were performed with a stirred tank made of glass and equipped with four stainless steel baffle plates. The inside diameter of the tank was  $0.105 \text{ m}$ . The impeller employed was a  $0.05 \text{ m}$  six-bladed fan turbine made of stainless steel, located at such a position that the upper end of the blade was in contact with the interface between the emulsion and external water. The temperature was kept at  $303 \text{ K}$  during the run. At a prescribed time after starting the agitation, samples were withdrawn from the tank and left for a while to separate W/O emulsion. The extent of water entrainment was calculated from the increase of water content in W/O emulsion as measured by the Karl Fisher method using an aquacounter AQ-5 (Hiranuma Sangyo Co.). The water drop size in W/O emulsion was measured by taking microphotographs. The W/O emulsion drop size was measured by taking photographs through the tank wall using an electronic flash. In both cases, the Sauter mean diameter ( $d_{32}$ ) was used as mean diameter.

## 2. Results

The water entrainment occurred immediately after starting the agitation and ceased in approximately 5 min. Since the breakage of W/O emulsion which was estimated from the leak of metal ions dissolved in the internal water phase was less than  $1\%$ , its contribution was neglected in the study. Water permeation due to the slight concentration difference between the inner and external phase was not observed during the run.

In the figures shown below, the W/O emulsion drop diameter ( $d_{w/o}$ ) and the relative increase of internal water-phase volume ( $V_i/V_i^0$ ) were measured 30 min after starting agitation, whereas the inner water drop diameter ( $d_w$ ) was measured before starting agitation.

### 2.1 Effects of surfactant concentration

Figure 1 shows the variation of  $d_{w/o}$  and  $V_i/V_i^0$  with surfactant concentration  $C_s$ . Emulsion drop diameter  $d_{w/o}$  decreased as  $C_s$  increased, whereas water-phase

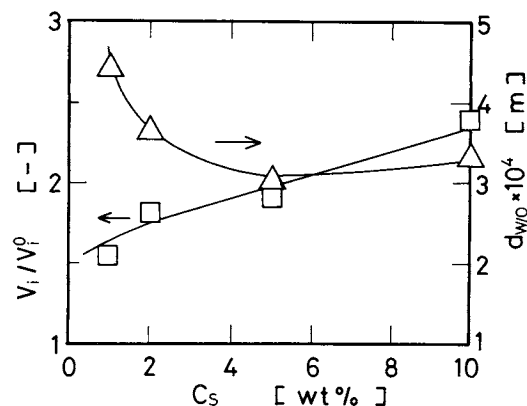


Fig. 1. Effects of surfactant concentration on  $d_{w/o}$  and  $V_i/V_i^0$  ( $\phi_w = 0.5$ ,  $N = 3.3 \text{ s}^{-1}$ ,  $n = 83.3 \text{ s}^{-1}$ )

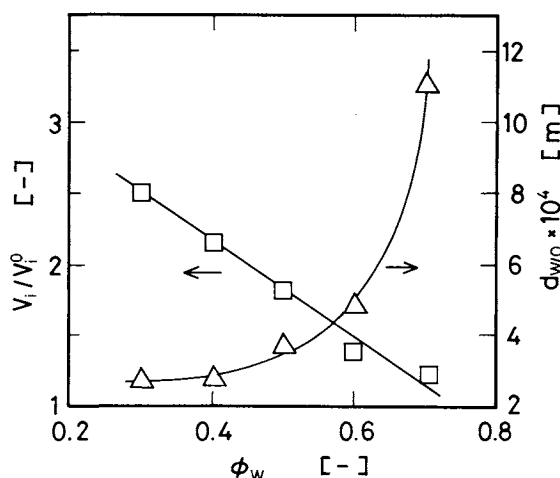


Fig. 2. Effects of water volume fraction in W/O emulsion on  $d_{w/o}$  and  $V_i/V_i^0$  ( $C_s = 2 \text{ wt}\%$ ,  $N = 3.3 \text{ s}^{-1}$ ,  $n = 83.3 \text{ s}^{-1}$ )

volume ratio  $V_i/V_i^0$  increased. The effects of surfactant concentration shown in Fig. 1 suggest that water entrainment is associated with the increase of surfactant molecules and surface area of emulsion drops.

### 2.2 Effects of water volume fraction in W/O emulsion

Figure 2 shows the variation of  $d_{w/o}$  and  $V_i/V_i^0$  with the water volume fraction  $\phi_w$  in W/O emulsion. The increase of emulsion drop size is a result of viscosity rise.<sup>9)</sup> Since the surfactant concentration in oil phase was kept constant in preparing the emulsion, the total content of surfactant molecules decreased when  $\phi_w$  was raised. The increase of  $\phi_w$  also reduced the total surface area of emulsion drops. These effects might contribute to the decrease of water entrainment.

### 2.3 Effects of inner water drop size

Figure 3 shows the effects of water drop diameter  $d_w$  on  $d_{w/o}$  and  $V_i/V_i^0$ . The water entrainment increased as  $d_w$  increased, whereas  $d_{w/o}$  decreased. As pointed out by Fujinawa *et al.*,<sup>1)</sup> the decrease of  $d_w$  at constant  $\phi_w$  and  $C_s$  results in a reduction of the number of surfactant molecules per unit interfacial area between oil and water. In addition, the decrease

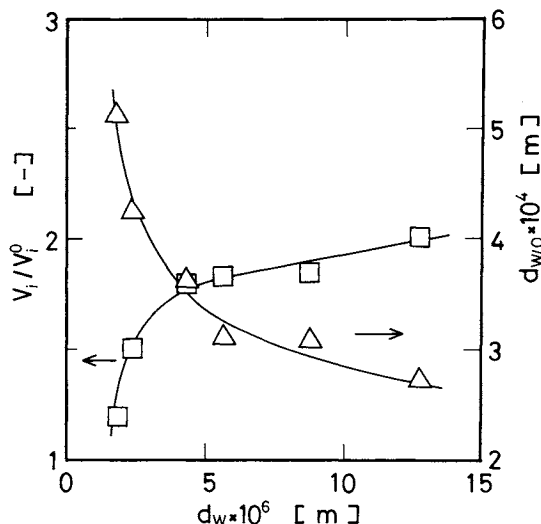


Fig. 3. Effects of inner water drop size on  $d_{w/o}$  and  $V_i/V_i^0$  ( $C_s = 2 \text{ wt}\%$ ,  $\phi_w = 0.5$ ,  $N = 3.3 \text{ s}^{-1}$ )

of  $d_w$  increased the emulsion drop size due to viscosity increase, which then reduced the total surface area. These factors might cause the decrease of  $V_i/V_i^0$ .

## 2.4 Effects of electrolyte concentration in the external water phase

The effects of electrolyte concentration ( $C_e$ ) on  $d_{w/o}$  and  $V_i/V_i^0$  were examined using  $0\text{--}50 \text{ mol} \cdot \text{m}^{-3}$  aqueous solution of  $\text{NiSO}_4$  and  $\text{CuSO}_4$  as the internal and external water phases respectively. To prevent water permeation by osmotic pressure, electrolytes concentration in both water phases were equalized. The drop diameter ( $d_{w/o}$ ) was almost constant, whereas  $V_i/V_i^0$  decreased as  $C_e$  increased. The electrolytes in the external water phase may have a role in depressing the water entrainment.

## 2.5 Effects of agitation speed in a stirred tank

Figure 4 shows the effects of agitation speed ( $N$ ) in a stirred tank on  $d_{w/o}$  and  $V_i/V_i^0$ . To prevent steep secondary entrainment at high agitation speed, the impeller in these runs was located at the center of the contents and the electrolyte concentration in inner and external water phase was adjusted to  $50 \text{ mol} \cdot \text{m}^{-3}$ . Emulsion drop diameter ( $d_{w/o}$ ) decreased as agitation speed increased, whereas the extent of water entrainment increased. The increase of water entrainment is presumably due to increased drop surface area and enhanced contact between the drop and external water.

## 3. Discussion

### 3.1 Relation between water entrainment and surfactant concentration at drop surface

As illustrated in the preceding section, it was proved that the increase of water entrainment ( $V_i/V_i^0$ ) was closely associated with the increase of surfactant concentration and total surface area of emulsion

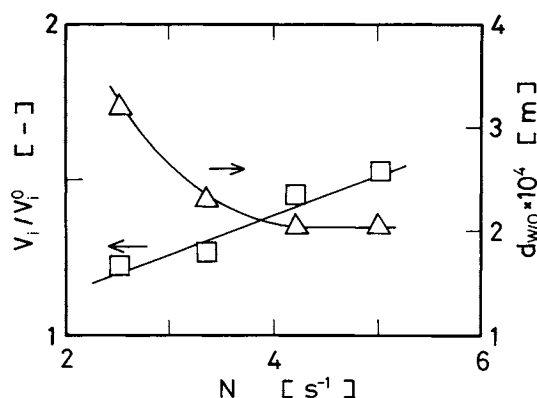


Fig. 4. Effects of agitation speed in a stirred tank on  $d_{w/o}$  and  $V_i/V_i^0$  ( $C_s = 2 \text{ wt}\%$ ,  $\phi_w = 0.5$ ,  $n = 83.3 \text{ s}^{-1}$ )

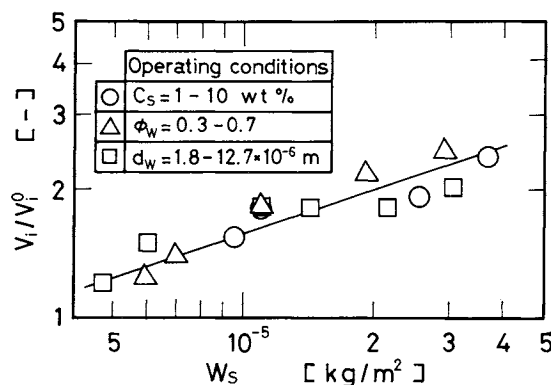


Fig. 5. Relation between extent of water entrainment and surfactant weight per unit interfacial area ( $N = 3.3 \text{ s}^{-1}$ )

drops. To study these effects quantitatively, surfactant weight per unit interfacial area ( $W_s$ ) was estimated by the following equation:

$$W_s = (C_s/100) \cdot (1 - \phi_w) \cdot \rho_o / 6(\phi_w/d_w + 1/d_{w/o}) \quad (1)$$

In this equation all surfactant molecules were assumed to exist on the oil–water interface although some may be present in the bulk of oil phase.

The observed values of  $V_i/V_i^0$  in each run are plotted against  $W_s$  in Fig. 5. It is apparent that an increase of surfactant molecules at the interface results in an increase of water entrainment.

### 3.2 Comparison with water entrainment in oil–water dispersion system

To obtain more information concerning the water entrainment mechanism, the water entrainment in an oil–water dispersion system was studied, using the same components as in the (W/O)/W emulsion system. The oil-phase volume in this case was equalized to that used in preparing W/O emulsion.

The effects of  $C_s$  and  $N$  on drop diameter  $d_o$  and oil volume increase  $V_o/V_o^0$  are shown in Figs. 6 and 7 respectively. The increase of  $C_s$  and  $N$  raised the extent of water entrainment. This behavior was similar to that observed in the (W/O)/W emulsion system. The oil phase after stirring turned to a stable

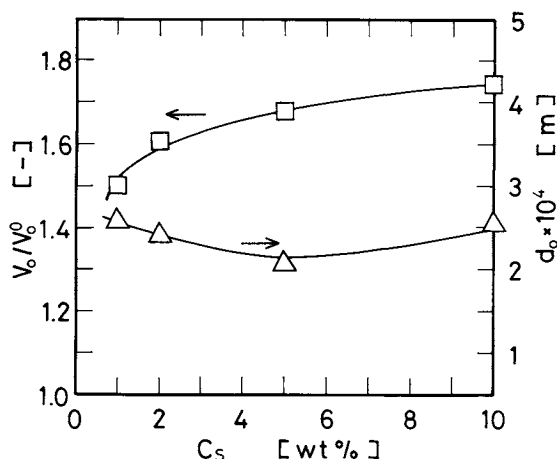


Fig. 6. Effects of surfactant concentration on  $d_o$  and  $V_o/V_o^0$  in oil-water dispersion system ( $N=3.3 \text{ s}^{-1}$ )

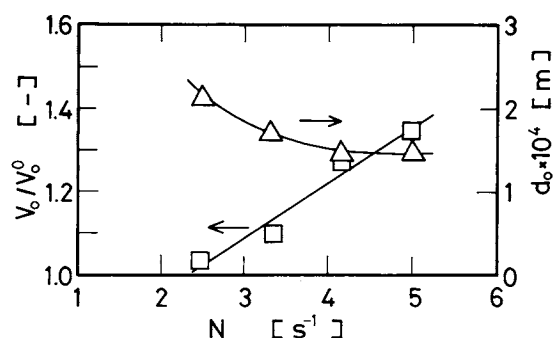


Fig. 7. Effects of agitation speed in a stirred tank on  $d_o$  and  $V_o/V_o^0$  in oil-water dispersion system ( $C_s=2 \text{ wt}\%$ )

white mixture, which demonstrated that water entrainment in the oil-water dispersion system was caused by emulsion formation. From these results, water entrainment in the (W/O)/W emulsion system was presumed to occur by additional emulsification at the interface of W/O emulsion drops and external water phase during the early stage of dispersion.

### 3.3 Contribution of drop surface area of the W/O emulsion to water entrainment

From the discussion above, the surface of dispersed drops is considered to play an important role in water entrainment. To discuss quantitatively the entrainment in the oil-water dispersion and (W/O)/W emulsion systems, the volume increase of dispersed phase was compared for the same oil and external water volume. The entrainment in the (W/O)/W emulsion system was, as shown in Fig. 8, more than that in the oil-water dispersion system in all cases. However, water entrainment per unit surface area of dispersed drops,  $V_{\text{ent},\text{W/O}}/S_{\text{W/O}}$  and  $V_{\text{ent},\text{o}}/S_o$ , were in good agreement as shown in Fig. 9. This result supported the water entrainment mechanism proposed for the (W/O)/W emulsion system.

From the experimental findings presented in this study, some points concerning the mechanical water

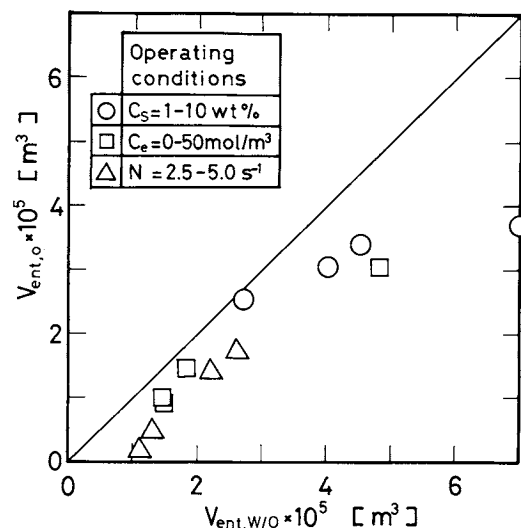


Fig. 8. Comparison of water entrainment in (W/O)/W emulsion and oil-water dispersion systems ( $\phi_W=0.5$ )

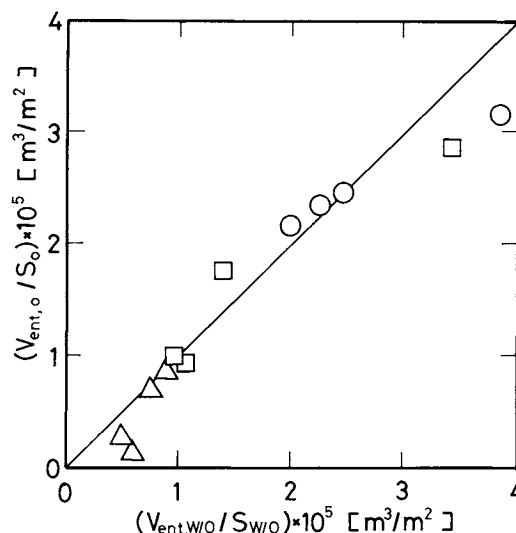


Fig. 9. Comparison of water entrainment per unit surface area of dispersed drops in (W/O)/W emulsion and oil-water dispersion systems (Keys are the same as in Fig. 8)

entrainment will be noted as follows.

Entrainment begins in the early stage of agitation and ceases after approximately 5 min in most cases. Therefore, mechanical water entrainment proceeds during initial unsteady state where larger drops are split into smaller ones. The pouring method devised by Fujinawa *et al.*<sup>3)</sup> is thought to reduce the unsteady-state period mentioned above by supplying the emulsion dropwise using a pipette and to decrease the resultant water entrainment. Next, the extent of water entrainment is controlled mostly by the surfactant concentration. To suppress additional emulsification at the drop surface, excess surfactant should not be used. For the same purpose, large drop size is desirable because of reduced surface area, although it is not desirable from the viewpoint of extraction rate. The optimum agitation rate must be selected to

obtain a sufficient rate while keeping water entrainment as low as possible. Another way to decrease the water entrainment is to raise the emulsion viscosity. The addition of a viscous fluid like liquid paraffin to oil phase clearly reduces the degree of entrainment.<sup>2,8,9)</sup> The increase of emulsion viscosity by increasing water-phase holdup and decreasing water drop size might also contribute to the suppression of entrainment observed in Figs. 2 and 3.

## Conclusion

The effects of operating conditions on mechanical water entrainment into W/O emulsion drops dispersed in water were studied and the following results were obtained.

1) Mechanical water entrainment could be depressed by increasing water volume fraction in the W/O emulsion and electrolytes concentration in the external water phase, and by decreasing surfactant concentration, inner water drop size and agitation speed in a stirred tank. The extent of water entrainment could be correlated well with surfactant concentration per unit interfacial area between oil and water.

2) The volume of water entrained per unit surface area of dispersed drops in the (W/O)/W emulsion system was in fair agreement with that in the oil-water dispersion system where water entrainment occurred by emulsification. These findings suggested that water entrainment into the W/O emulsion proceeded as a result of emulsification at the drop surface.

## Nomenclature

$C_e$	= electrolyte concentration in external water phase	[mol · m <sup>-3</sup> ]
$C_s$	= Span 80 concentration in oil phase	[wt%]
$d_o$	= mean diameter of dispersed drops in oil-water dispersion	[m]
$d_w$	= mean diameter of inner water drops in W/O emulsion	[m]

$d_{w/o}$	= mean diameter of W/O emulsion drops	[m]
$N$	= impeller speed in a stirred tank	[s <sup>-1</sup> ]
$n$	= homogenizer agitation speed	[s <sup>-1</sup> ]
$S_o$	= total surface area of dispersed drops in oil-water dispersion	[m <sup>2</sup> ]
$S_{w/o}$	= total surface area of dispersed W/O emulsion drops in (W/O)/W emulsion	[m <sup>2</sup> ]
$V_{ent,o}$	= volume of water entrained in oil-water dispersion	[m <sup>3</sup> ]
$V_{ent,W/O}$	= volume of water entrained in (W/O)/W emulsion	[m <sup>3</sup> ]
$V_i$	= volume of internal water phase in W/O emulsion	[m <sup>3</sup> ]
$V_o$	= volume of dispersed phase in oil-water dispersion	[m <sup>3</sup> ]
$V_{w/o}$	= volume of W/O emulsion	[m <sup>3</sup> ]
$W_s$	= surfactant weight per unit interfacial area	[kg · m <sup>-2</sup> ]
$\rho_o$	= density of oil phase	[kg · m <sup>-3</sup> ]
$\phi_w$	= water volume fraction in W/O emulsion	[—]

<Superscript>

<sub>0</sub> = initial value

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