CONTINUOUS DEMULSIFICATION OF O/W EMULSIONS BY A MECHANICAL TECHNIQUE

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The industrial practice of hydrocarbon separation by liquid membrane permeation (LMP) requires the establishment of a simple, efficient technique for demulsification of O/W emulsions. In a previous report,[1] we proposed a new mechanical demulsification technique which applies strong agitation to the mixture of an O/W emulsion and a coexisting oil phase to cause phase inversion. This technique satisfactorily accomplished batch demulsification.[1] The present paper describes the application of the technique to the continuous demulsification of O/W emulsions.

1. Experimental

1.1 Preparation of O/W emulsions

O/W emulsions were prepared by use of a stirring vessel which had four baffles and a turbine impeller with six flat blades. The diameter of the vessel was 80 mm and the volume of agitated liquid was 400 ml. Isooctane and aqueous saponin solution were agitated in the vessel at 600 rpm for five minutes to prepare an O/W emulsion. More than three liters of emulsion were prepared for each demulsification run.

1.2 Demulsification procedure

Figure 1 shows a flow diagram for continuous breaking of O/W emulsions. A combination of a 10-liter premixer and a flow cell, which held a generator head equipped with high-speed homogenizer (HSH) (Nichion Irikakikai Co., NS-20TP), was used. The volume of the cell was 9 cm³. The maximum output power of the HSH was about 300 watts at 20,000 rpm. In the previous study,[1] continuous breaking was tried by use of a similar combination of premixer and flow cell. However, the reliability of the data was not satisfactory because flow rates fluctuated considerably. The main reason for the fluctuations was that, due to the use of a small premixer of 400 ml volume, operating periods, which were less than 4 s, were too short for high flow rates of 100 ml/s by HSH.

A 10-liter vessel, then, was newly used in this study.

Isooctane was used as coexisting oil and added to a given amount of original O/W emulsion to be demulsified. The two phases were agitated in the 10-liter vessel at about 400 rpm, forming a new O/W emulsion. The resultant O/W emulsion was pumped out by HSH through the flow cell in which demulsification occurred. Effluents from the cell consisted of two phases: isooctane phase and an O/W emulsion phase. The flow rate of each phase was measured by use of a graduated cylinder and a stopwatch.

2. Results and Discussion

Equation (1) defines the yield of demulsification:

$$Y = (Q_{ow1} - Q_{ow2})/(Q_{ow1} - Q_w) \qquad (1)$$

where Q_{ow1} is the volumetric flow rate of original O/W emulsion flowing into the cell and Q_{ow2} is the flow rate of O/W emulsion flowing out of the cell. Q_w is the flow rate of aqueous membrane solution. In the calculation of Y in Eq. (1), total flow rate was assumed to be constant, and also coexisting oil in the premixer was assumed to be homogeneously distributed in the original O/W emulsion. In fact, if the impeller was soaked in original emulsion phase at the beginning of agitation, the distribution of coexisting oil was satisfactory even if the volume fraction of coexisting oil was 70%.

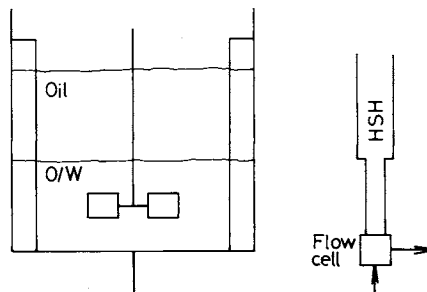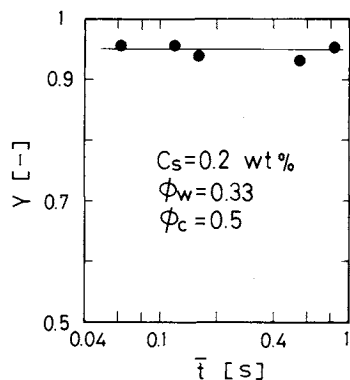Figure 2 shows the relation between yield and mean

Fig. 1. Schematic diagram for continuous breaking

Fig. 2. Relation between yield and mean residence time

Fig. 3. Effect of volume fraction of coexisting oil on yield

Fig. 4. Effect of volume fraction of membrane solution in original emulsion on yield

Fig. 5. Effect of C_s on yield

Key	Variable	Emulsi-fier	Demul-sifier	Oper-ation
△	ϕ_c:0.4-0.7		HSH typeA	
□	ϕ_w:0.2-0.5	SV		Cont.
○	C_s:0.1-0.5			
X		SV	HSH typeA	batch
▲	ϕ_c:0.4-0.7 N:170-340	HSH type A	HSH type A	batch
◊				
■	ϕ_w:0.3-0.5	HSH type B	HSH type B	batch
●	C_s:0.05-0.4			

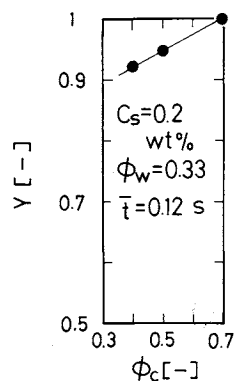
Fig. 6. Effects of C_t on yields

residence time for liquid mixture in the cell. Volumetric flow rate was varied through the variation of rotating speed of HSH. Operating periods for continuous breaking were not less than 40 s, and flow rates were stable in these runs. Yields were as high as 95% and almost constant throughout the range of mean residence time examined. At the highest speed of 20,000 rpm, the liquid flow rate was 150 ml/s. In this case, a residence time as short as 0.063 s was enough to cause efficient emulsion breaking; breaking seems to proceed very easily as soon as a liquid mixture is exposed to high shear.

Figure 3 shows the effect of volume fraction of coexisting oil, ϕ_c, on yield. Yield increased with increasing ϕ_c. At $\phi_c = 0.7$, yield was close to 100% and O/W emulsion after breaking showed higher transparency than the others did. Figure 4 shows the effect of volume fraction of aqueous membrane solution in original emulsion, ϕ_w, on yield. Yield decreased with increasing ϕ_w. In batch demulsification, the same effects of ϕ_c and ϕ_w on yield were obtained.[1] An increase in oil fraction in a O/W emulsion makes the emulsion unstable and often promotes phase inversion from O/W to W/O type.[1] Therefore, the increase in volume fraction of oil in the mixture flowing into the cell seems to have promoted demulsification as shown in Figs. 3 and 4.

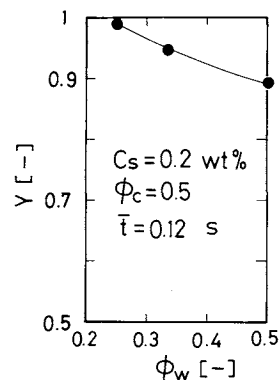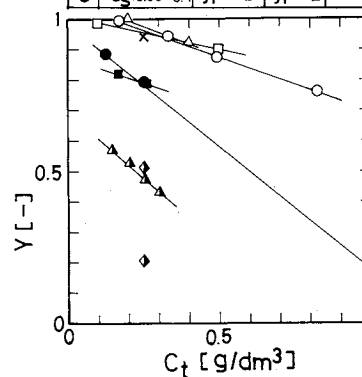Figure 5 shows the effect of saponin concentration in aqueous solution, C_s, on yield. The yield of

breaking decreased with increasing saponin concentration as was the case in batch demulsification.[1]

Figure 6 shows the effects of saponin concentration in total liquid, C_t, on the yields obtained in continuous demulsification shown in Figs. 3 to 5. It also includes the data obtained in batch demulsification.[1] Yields increased with decreasing C_t. It

must, however, be mentioned that C_t is not the only factor which has an effect on demulsification because, even at a constant value of C_t, yield increased with increasing stirring speed of homogenizer[1] and because demulsification did not occur without coexisting oil even at the value of C_t shown in Fig. 6.

Figure 6 also demonstrates that the yield of breaking strongly depends on the devices used in both emulsification and demulsification. When the stirring vessel (SV) was used as an emulsifier, the size distribution of oil droplets had a quite broad peak; the average diameter was about $10\,\mu m$. When high-speed homogenizers (HSH) were used, peaks were narrow; the mean value was about $2\,\mu m$ for HSH of standard type (type A) and about $1\,\mu m$ for improved type (type B). As might be expected, the emulsions which had smaller oil droplets were more stable during demulsification, while the demulsifiers that exerted strong agitation could demulsify emulsions more efficiently.

Nomenclature

C_s	= concentration of saponin in membrane solution	[wt%]
C_t	= concentration of saponin in total liquid mixture	[g/dm³]
N	= stirring speed	[s⁻¹]
Q_{ow1}	= volumetric flow rate of O/W emulsion flowing into cell	[m³]
Q_{ow2}	= volumetric flow rate of O/W emulsion flowing out of cell	[m³]
Q_w	= volumetric flow rate of aqueous membrane solution	[m³]
$\bar{t}$	= mean residence time in flow cell	[s]
Y	= yield of demulsification defined by Eq. (1)	[—]
ϕ_c	= volume fraction of coexisting oil in premixer	[—]
ϕ_w	= volume fraction of aqueous membrane solution in original O/W emulsion	[—]

Literature Cited

1) Kato, S. and J. Kawasaki: *J. Chem. Eng. Japan*, **20**, 232 (1987).

DENSITY-DEPENDENT LOCAL-COMPOSITION EFFECTS ON MIXING RULE OF CUBIC EQUATIONS OF STATE

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1. Introduction

The density-dependent local-composition model combined with equations of state seems rather promising for describing the phase behavior of strongly nonideal mixtures at high pressure. Attention has recently been focused on computer simulation to investigate the validity of the local composition model.[1-3,5-7] However, most computer simulation data are limited to simple mixtures. It is rather difficult to explain the complex molecular interactions in polar or associated mixtures.

The density-dependent local mole fractions of the

unified model proposed in our previous work[15] are defined as:

$$x_{12} = x_1 E_{12}/(x_1 E_{12} + x_2) \tag{1}$$

$$x_{21} = x_2 E_{21}/(x_1 + x_2 E_{21}) \tag{2}$$

$$x_{11} + x_{21} = 1, \qquad x_{12} + x_{22} = 1 \tag{3}$$

where E_{ij}'s are designated as nonconformal parameters, representing the deviation from the conformal reference state.

Its definition can be expressed as:

$$E_{ij} = \exp[-C_{ij}a_{ij}^o f(v)/RT] \tag{4}$$

where: C_{ij}'s are binary interaction parameters. a_{ij}^o is the attractive constant for the i–j pair in the