PREPARATION AND DEMULSIFICATION OF W/O EMULSION CONTAINING AQUEOUS ALKALINE SOLUTION

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Introduction

Recently, the separation and enrichment of acidic compounds like phenols, organic acids and antibiotics by use of liquid surfactant membrane (henceforth LSM) have become of interest with the increase in environmental concern and the development of new biotechnology[9]. In such a system, an alkaline solution is used as an internal aqueous solution of W/O emulsion to promote the dissociation of acidic compounds transported. The W/O emulsion is then demulsified to recover the component separated. Only a few investigations, however, on electrostatic demulsification have been carried out by use of an aqueous alkaline solution[1, 8, 10].

In this work, we investigated the preparation and demulsification of W/O emulsion containing an aqueous alkaline solution and compared the results with those obtained by using an aqueous acidic solution as reported in previous papers[5-7].

1. Experimental

The W/O emulsion was prepared by mixing the same volume of organic solution containing surfactant and aqueous solution containing 0.3 kmol/m^3 sodium hydroxide with homogenizer (Nihon Seiko) at 50 s^{-1}. An average Sauter diameter of aqueous drop was 3.0 μm. The solvent used was Shellsol 71L or a mixture of Shellsol 71L and liquid paraffin. The nonionic surfactants used were Span 80, Paranox 100 and 2C$_{18}\Delta^9$GE from Wako Chemical Co., Exxon Chemical Co. and Kyushu Univ.[3], respectively.

The batch demulsifier was similar to that reported in our previous papers[5-7]. The electrode was prepared by filling the 8 mm-diameter glass tube with saturated aqueous sodium chloride solution into which a 2 mm-diameter copper wire was inserted and then sealing the glass tube. The glass-sealed electrode was vertically placed. The copper disk electrode, 41 mm in diameter, was set at the bottom and grounded. A.C. 15kV at 60Hz was applied between the two electrodes at 30°C in all experiments.

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2. Results and Discussion

2.1 Preparation of stable W/O emulsion

Various combinations of surfactant and internal aqueous solution were tested to obtain a stable emulsion. **Table 1** summarized the results. It has been reported in metal separation that stable emulsion containing a mineral acid as an internal solution can be obtained by using any of these surfactants[4]. However, stable emulsion containing strong alkaline solution could be prepared only by using Paranox 100, a polyamine derivative, as shown in Table 1. Ester moieties in Span 80 and 2C$_{18}\Delta^9$GE may be hydrolyzed with strong alkaline solution. Surfactants of polyamine derivatives have been used to date in demulsification studies[1, 2, 8, 10] of W/O emulsion containing an alkaline solution. In the work presented in the previous papers, perhaps a stable emulsion could not be obtained with other surfactants. We concluded that Paranox 100 was the best surfactant for alkaline solution.

2.2 Demulsification of W/O emulsion

Figure 1 shows typical examples of the time-course of electrostatic demulsification. The extent of demulsification was defined as the volume fraction of the separated aqueous phase against the initial internal aqueous phase. The organic solvent used was a mixture of Shellsol 71L and liquid paraffin. The demulsification was accelerated by gently agitating the emulsion. The demulsification was not completed without agitation. Feng et al.[1] observed a similar effect of agitation in W/O emulsion containing sodium hydroxide solution. The following experiments were conducted at an agitation speed of 1 s^{-1} because re-emulsification occurred above more than 1 s^{-1}.

In our previous papers[5, 6, 7], we examined how the demulsification rates were affected by both emulsion preparation and demulsification conditions.

The dependencies on the same operating conditions were investigated for W/O emulsions of alkaline solution. The results are summarized in **Table 2**, along with those obtained in acidic solutions[5]. The demulsification rate, dV_w/dt, was evaluated at the extent of 50 % demulsification in the same way as described in the pre-

Table 1. Preparation of W/O emulsion

Surfactant	Internal solution			Stability of W/O emulsion
Span 80 (1-6 wt%)	NaOH	0.05-0.3	kmol/m³	Phase separated
Span 80 (4 wt%)	Na₂CO₃	0.05-0.3		Good
2C₁₈Δ⁹GE (1-7 wt%)	NaOH	0.05-0.3		Phase separated
2C₁₈Δ⁹GE (4 wt%)	Na₂CO₃	0.05-0.3		Good
Paranox 100 (4-6 wt%)	NaOH	0.05-0.3		Good
Paranox 100 (4 wt%)	Na₂CO₃	0.05-0.3		Good

Solvent = Shellsol 71 L
Agitation speed of homogenizer = 50 s⁻¹,
Agitation time of homogenizer = 300 s.
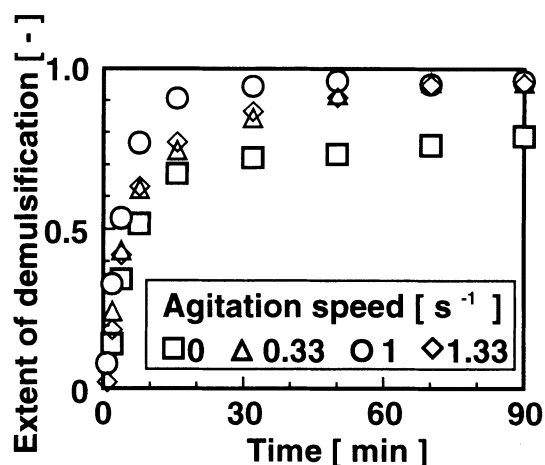Volume ratio(W:O) = 1:1

Fig. 1 Time-course of demulsification

Fig. 2 Comparison of observed and calculated demulsification rates

Table 2. Dependencies of demulsification rate on various operating conditions

Operating condition	Internal phase	
	NaOH solution	CuSO₄ solution[5, 6]
Temperature	$\exp(-31300/RT)$	$\exp(-22500/RT)$
Oil-phase viscosity	$\mu\,\text{oil}^{-0.5}$	$\mu\,\text{oil}^{-3.2}$
Water-drop diameter	$d_w^{1.6}$	$d_w^{3.5}$
Aqueous-phase holdup	$\exp(5.70\,\phi_w)$	$\exp(-19.6\,\phi_w)$
Surfactant concentration	$\exp(-0.528\,C_s)$	$\exp(-0.111\,C_s)$
Applied voltage	$E^{0.6}$	-
Concentration of electrolytes in aqueous solution	$0.281 - 0.608\,C_w$	$0.042 + 0.123\,C_w$

vious paper[5]. As shown in Table 2, the dependencies in alkaline and acidic solution systems differed considerably. Especially, the holdup of aqueous phase and the concentrations of electrolytes in the internal solution exhibited opposite effects. Interaction between the surfactant and alkaline species may occur at the interface. This is a subject for future study.

The correlating equation of the demulsification kinetics was derived as follows by summarizing the experimental results shown in Table 2.

$$dV_w / dt = 9.50 \times 10^3 \exp(-31{,}300/RT)\,\mu_{oil}^{-0.5}\,d_w^{1.6}$$
$$\times \exp(5.7\,\phi_w)\exp(-0.528\,C_s)\,E^{0.6}(0.281 - 0.608\,C_w)$$

Figure 2 compares the observed and calculated demulsification rates. Relatively good agreement was obtained.

Conclusion

The preparation and demulsification of W/O emulsion containing an aqueous alkaline solution were studied to apply the LSM process to the separation of acidic compounds. Paranox 100 was the best surfactant from the viewpoint of emulsion stability. An examination of various experimental conditions in electrostatic demulsification suggested that the ranges of operating conditions are considerably limited compared with those of emulsions containing acidic or neutral aqueous solution.
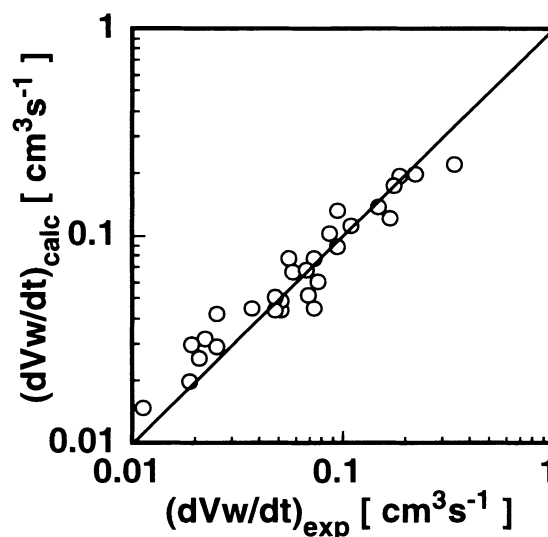
Nomenclature

C_s	=	surfactant concentration	[wt%]
C_w	=	concentration of electrolyte in internal aqueous solution	[kmol/m³]
d_w	=	water-drop diameter in W/O emulsion	[μm]
E	=	applied voltage	[kV]
R	=	gas constant	[J/(mol·K)]
T	=	temperature	[K]
t	=	time	[s]
V_w	=	volume of aqueous phase separated	[cm³]
μ_{oil}	=	oil-phase viscosity	[mPa·s]
ϕ_w	=	aqueous phase holdup	[-]

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