Demulsification of Water-in-Oil Emulsion by an Electrostatic Coalescence Method

Tetsuji Hirato*, Kazuya Koyama**, Takahiro Tanaka***,
Yasuhiro Awakura* and Hiroshi Majima*

Various factors affecting the demulsification rate of emulsion were examined by means of an electrostatic coalescence method using emulsion which consisted of an organic phase containing tri-n-octylamine (TNOA) and Span 80 or ECA 4360J and an internal aqueous phase containing Na_2CO_3 . Increases in applied voltage, Na_2CO_3 concentration, and W_1/O ratio result in an increase in demulsification rate, while increases in surfactant (including Span 80 and ECA 4360J) concentration, agitation speed of homogenizer and homogenizing time cause a decrease in demulsification rate. Changes in TNOA concentration do not have a significant effect. The regeneration of emulsion was examined using organic solution recovered from a Mo(VI) extraction circuit. It was found that the regeneration of emulsion containing Span 80, is generally difficult, while that containing ECA 4360J is relatively easy.

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I. Introduction

In recent years, a separation-concentration process, using an emulsion liquid membrane of the W/O/W type, has been receiving much attention. To operate this process continuously, it is necessary to demulsify the W/O emulsion after the extraction of metal values. In other words, in order to recycle the organic phase, the aqueous phase containing stripped metal values must be separated from the organic phase by breakdown of the emulsion.

The electrical method of applying an electrostatic field of high voltage is recognized as an efficient demulsification method⁽¹⁾⁻⁽⁶⁾. Although some fundamental studies on the demulsification of emulsion utilizing an electrostatic coalescence method have been reported, only a limited number of papers are related to the extraction process of metal values⁽⁴⁾⁽⁵⁾. The present authors have studied the application of an emulsion-type liquid membrane technique to recover U(VI)⁽⁷⁾ and Mo(VI)⁽⁸⁾. Industrial application of the emulsion-type liquid membrane process requires a study of the demulsification of emulsion and the recycling of the organic phase.

For this reason, the present authors conducted a fundamental study of the demulsification of water-in-oil emulsion in a high voltage d.c. field. In this study, the effects of various factors on the demulsification of emulsion containing TNOA as an extractant were investigated. In addition, the recycle of organic phase derived from Mo(VI) extraction was examined.

II. Experimental Procedures

The procedures for preparation of W/O emulsion and extraction of metal values are the same as those reported in the previous papers⁽⁷⁾⁻⁽⁹⁾. The surfactant used in this study was either Span 80 (Nakalai Tesque Inc.) or ECA 4360J (Exxon Chemical Japan Ltd.). Unless otherwise stated, the emulsion was prepared by using 1 kmol m^{-3} Na_2CO_3 solution as the internal aqueous phase and 0.02 kmol m^{-3} TNOA-5 mass% Span 80-kerosene solution as the organic phase. The volume ratio, W_1/O , of the internal aqueous phase to the organic phase was maintained at unity in this work.

Figure 1 shows schematically the apparatus used in this study for demulsification. A glass separatory funnel was adapted to a rectangular glass tube having dimensions, 50 mm length $\times$ 10 mm $\times$ 10 mm. Two platinum electrodes were fixed to opposite walls of the tube at a distance of 10 mm. 40 ml of water-in-oil emulsion was charged to the glass vessel, and the demulsification experiment was commenced by applying pulses of high voltage to the electrodes, using a d.c. electrostatic field. The high voltage generator (Noise Laboratory, ESS-625S) could deliver voltages up to a maximum of 25 kV for time intervals ranging from 0.6 to 10 s. Unless otherwise stated, the applied voltage was kept at 10 kV and at a 0.6 s pulse cycle. The aqueous phase recovered by demulsification of emulsion was continuously discharged by means of a stopcock at the bottom of the glass tube. The interface between the aqueous phase and the emulsion was kept at 5 mm below from the lower end of the Pt electrodes during the experiment. The volume of aqueous phase recovered was measured periodically in order to calculate the percent demulsification according to the following equation:

* Department of Metallurgy, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan.

** Graduate Student, Kyoto University.

*** Formerly, Undergraduate Student, Kyoto University. Present address: Kubota Ltd.

Fig. 1 Schematic illustration of apparatus used for the demulsification experiment.

Demulsification(%)

$$= \frac{\text{(volume of recovered aqueous solution)}}{\text{(volume of internal aqueous solution)}} \times 100 \quad (1)$$

The organic phase recovered from the emulsion was used again to prepare emulsion for the extraction. The procedures of the extraction experiment are the same as those reported in the previous papers⁽⁷⁾⁽⁸⁾.

III. Experimental Results and Discussion

1. Demulsification of water-in-oil emulsion

The effect of applied voltage in the range, 5 to 25 kV, on the demulsification of emulsion was studied. The relationship between the percent demulsification and the demulsification time is shown in Fig. 2. At each voltage, the percent demulsification increases linearly with demulsification time until the percent demulsification reaches 60–70%. Thereafter, the rate of demulsification decreases gradually. As is clear in this figure, both the initial rate of demulsification and maximum percent demulsification increase with increasing applied voltage. Demulsification was barely noticeable at 2 kV. The maximum percent demulsification, established in the present study, was 98% for 0.9 ks of demulsification, but the recovered organic phase was turbid.

The initial rate of demulsification which was estimated by the tangent of the rate curve at time, zero, was used to evaluate the effect of various factors on demulsification

Fig. 2 Effect of applied voltage on demulsification rate.

rate. Initial rates corresponding to the results shown in Fig. 2 were plotted against applied voltage, as shown in Fig. 3. As is clear in this figure, the initial demulsification rate is proportional to the applied voltage. A similar result has been reported by Kataoka and Nishiki⁽⁴⁾. It appears that a higher demulsification rate can be obtained using a higher applied electrostatic voltage.

As can be seen in Fig. 2, the demulsification rate is retarded after 60–70% demulsification. It is very likely that the volume ratio of organic phase to internal aqueous phase increases gradually with the progress of demulsification, and as a result, the effectiveness of the electrostatic force is decreased.

To test this reasoning, a demulsification experiment was conducted by using emulsion in which the aqueous phase content was increased by settling. The experiment was performed as follows. Freshly-prepared emulsion

Fig. 3 Relationship between initial demulsification rate and applied voltage.

Fig. 4 Recovery of initial demulsification rate by removing the supernatant after settling of the combined demulsified emulsion.

was demulsified to 60% at 10 kV. The recovered organic phase, which contained undemulsified emulsion, was allowed to settle overnight. After the supernatant organic phase was decanted, the remaining emulsion was subjected to demulsification at an applied voltage of 10 kV. The experimental results are depicted in Fig. 4. For the sake of comparison, the demulsification of fresh emulsion at an applied voltage of 10 kV for 0.36 ks is also shown in this figure. The initial demulsification rates are almost identical. This result supports the reasoning presented above.

Demulsification experiments were conducted to examine the effect of agitation speed during the preparation of emulsion using a homogenizer. Demulsification rate decreases with an increase in agitation speed, from 133 to 200 s^{-1} . The effect of homogenizing time on the rate of demulsification was also studied for time periods of from 0.18 to 0.6 ks. The demulsification rate decreases with prolonged homogenizing time. The average droplet diameter of the internal aqueous phase in the emulsion decreases with an increase in homogenizing time and with agitation speed of the homogenizer⁽⁹⁾. It may reasonably be understood that the decrease in diameter of droplets causes a decrease in the rate of demulsification.

The effect of volume ratio of internal phase to organic phase was also examined. Figure 5 shows the results for volume ratios of 1/2, 1/1 and 2/1. The demulsification rate increased slightly with an increase in volume ratio of internal phase to organic phase. The increase in W_1/O ratio results in shortening of the distance between droplets of the internal aqueous phase. The increase in W_1/O ratio also results in an increase in interfacial area between the organic phase and the internal aqueous phase. This causes a decrease in density of surfactant at the inter-

Fig. 5 Effect of W_1/O ratio on demulsification rate.

face. Thus, the results shown in Fig. 5 can be explained reasonably well.

Figure 6 shows the effect of TNOA concentration on demulsification. In these experiments, the concentrations of TNOA were in the range, 0 to 0.1 $\text{kmol} \cdot \text{m}^{-3}$. It was found that the demulsification rate is almost independent of TNOA concentration.

Previously, the authors observed that the stability of emulsion during extraction is greatly lowered by the addition of TNOA at a concentration above 0.05 $\text{kmol} \cdot \text{m}^{-3}$

Fig. 6 Effect of TNOA concentration on demulsification rate.

or by a decrease in the volume ratio, $W_1/O^{(9)}$. The results of this study are quite different from that based on stability of emulsion. It should be noted that the ease with which demulsification occurs using an electrostatic field does not necessarily correspond to the stability of emulsion during extraction.

The effect of Span 80 concentration on demulsification rate was investigated in the concentration range, 1 to 10 mass%. The results obtained are depicted in Fig. 7. Demulsification rate decreases with an increase in Span 80 concentration. A demulsification experiment was conducted using the surfactant, ECA 4360J, which is a polyamine, in place of Span 80. The experimental results are depicted in Fig. 8. For the sake of comparison, the demulsification rate curve corresponding to 1 mass% Span 80 is displayed in the same figure. It was found that demulsification is more difficult with ECA 4360J than Span 80 at the concentration levels, shown in Fig. 8. It was also observed that the demulsification rate curve is linear only in the range, 0–40% demulsification.

These results indicate that a high demulsification rate is expected when emulsion is prepared with surfactant of low concentration. On the contrary, at low concentration, the stability of emulsion is poor⁽⁹⁾. Therefore, an optimal concentration of surfactant may be determined by consideration of both extraction and demulsification results.

The effect of Na_2CO_3 concentration, in the internal aqueous phase, on demulsification behavior was studied using Na_2CO_3 concentrations of 1.0, 1.5, and 2.0 $\text{kmol}\cdot\text{m}^{-3}$. The results are illustrated in Fig. 9. Demulsification rate increases with increasing Na_2CO_3 concentration. Addition of Na_2CO_3 in an internal aqueous phase results

in an increase in the specific gravity difference between the organic phase and internal aqueous phase. This may promote demulsification.

In order to examine the demulsification behavior of emulsion used in an actual extraction process, the following experiment was performed. Emulsion prepared with 1.0 $\text{kmol}\cdot\text{m}^{-3}$ Na_2CO_3 solution as the internal aqueous phase and 0.02 $\text{kmol}\cdot\text{m}^{-3}$ TNOA-2 mass% ECA 4360J-

Fig. 8 Effect of ECA 4360J concentration on demulsification rate.

Fig. 7 Effect of Span 80 concentration on demulsification rate.

Fig. 9 Effect of Na_2CO_3 concentration on demulsification rate.

Fig. 10 Effect of extraction time on demulsification rate.

kerosene solution as the organic phase, was contacted with $1.0 \text{ kg} \cdot \text{m}^{-3}$ Mo(VI)- $33 \text{ kg} \cdot \text{m}^{-3}$ H_2SO_4 solution to extract Mo(VI). Following extraction for a defined period of time, the emulsion was separated from the external aqueous phase and subjected to the demulsification experiment. Experimental results are depicted in Fig. 10. For reference, the demulsification rate curve of fresh emulsion is given in the same figure. The post-extraction demulsification rate was much greater than the rate of fresh emulsion. An evolution of gas bubbles was detected when used-emulsion was subjected to the demulsification experiment. By contacting the evolved gas bubbles with an aqueous solution of calcium hydroxide, a white, turbid solution was generated. This finding suggests that the evolved gas is CO_2 . The pH in the internal solution is lowered by H^+ transported with Mo(VI) and sulfate ions, and this decrease in pH is conducive to the evolution of CO_2 gas in the internal phase. The formation of CO_2 gas bubbles enhances the demulsification of emulsion.

2. Recycle of organic phase demulsified in an electrostatic field

In order to operate an emulsion-type liquid membrane process, it is necessary to recycle the organic phase recovered after extraction. It is important to examine the effects of demulsification and scrubbing on the extraction-stripping ability of the recycled organic phase.

Therefore, the effects of various factors on extraction behavior were examined using a liquid membrane in which the organic phase recovered from the emulsion was used repeatedly. In the following experiments, the

emulsion was demulsified at an applied voltage of 15 kV for 1.8 ks. The concentrations of Span 80 and ECA 4360J were based on the stability of emulsions during extraction.

Figure 11 shows the results of the Mo(VI) extraction experiments using a recycled organic phase, which contains Span 80 as the surfactant. $2 \text{ kmol} \cdot \text{m}^{-3}$ Na_2CO_3 solution and $1 \text{ kg} \cdot \text{m}^{-3}$ Mo(VI)- $33 \text{ kg} \cdot \text{m}^{-3}$ H_2SO_4 solution were used as internal aqueous solution and external aqueous solution, respectively. The first extraction experiment was performed for 1.8 ks using an emulsion prepared with fresh organic solution. This extraction is identified in this report as '1st run'. After the 1st run, the emulsion was separated from the external aqueous phase, and then demulsified at an applied voltage of 15 kV. Using the organic phase recovered from the emulsion, a new emulsion was prepared for the next extraction experiment and labelled, '2nd run'. After the 2nd run, the emulsion was demulsified again in the same way, and the organic phase recovered was used to prepare a new emulsion for the 3rd extraction experiment ('3rd run').

As is clear in Fig. 11, the percent extraction of Mo(VI) decreases with an increase in the number of extractions, when Span 80 is used as surfactant. When the applied voltage was changed from 15 kV to 5 and 25 kV, no significant change in the percent extraction of the 2nd run was detected. Similar extraction experiments for U(VI) were performed using the recycled organic phase containing 5 mass% Span 80. The percent extraction of U(VI) was lowered by use of the recycled organic phase, to a greater extent than that exhibited by the Mo(VI) extraction.

Similar studies were conducted using ECA 4360J instead of Span 80. In these tests, 2 mass% ECA 4360J was

Fig. 11 Extraction of Mo(VI) using the recycled organic phase containing 5 mass% Span 80.

Fig. 12 Extraction of Mo(VI) using the recycled organic phase containing 2 mass% ECA 4360J.

used as surfactant and $2 \text{ kmol} \cdot \text{m}^{-3} \text{ Na}_2\text{CO}_3$ solution as the internal aqueous phase. The experimental procedures employed were the same as those for Span 80. The experimental results are shown in Fig. 12. Although the extraction rate of Mo(VI) seems to decrease slightly, no significant change in the percent extraction is detected between the runs. Therefore, it appears that an organic phase containing ECA 4360J as surfactant can be used repeatedly to prepare emulsion, following a cycle of the liquid membrane process. The effect of applied voltage on the percent extraction of Mo(VI) was also examined using the recycled organic phase containing 2 mass% ECA 4360J. No significant change in the percent extraction was detected. Similar results were obtained in the U(VI) extraction experiments using a recycled organic phase of the same composition.

In order to understand the loss in percent extraction, which was observed when Span 80 was used as surfactant, the effect of each unit process in the recycle of the organic phase on the extraction of metal values was examined. The unit processes considered include extraction, demulsification, scrubbing of the organic phase, and supernatant recovery by the centrifuge. The results are presented in Fig. 13. The notations, EM, EX, DE, SC and CE used in this figure, express the respective unit processes, i.e., emulsification, extraction, demulsification, scrubbing of the organic phase and supernatant recovery by the centrifuge. For reference, results of the 1st and 2nd runs of Fig. 11 are also shown in Fig. 13. The extraction rate and the maximum percent extraction of Mo(VI) are less than those of the 1st run, when using the emulsion prepared with an organic phase recovered from a fresh emulsion without extraction. The extraction rate

Fig. 13 Extraction of Mo(VI) using emulsion prepared by various processing steps.

is almost the same as that of the 2nd run, but the maximum percent extraction is greater. These results can be attributed to the stability of the emulsion. It appears that the extraction performance of the organic phase is dependent on the extraction and demulsification processes.

One extraction experiment was performed with an emulsion which was prepared using an organic phase scrubbed with Na_2CO_3 solution. The scrubbing process effectively removes Mo(VI) remaining in the organic phase which is recovered by demulsification. The experimental results are represented by symbol, $\square$, in Fig. 13. Solvent scrubbing does not appear to have a significant effect on extraction rate as evidenced by results which are similar to those of the 2nd run. Since the organic phase recovered by demulsification still contained a small amount of undemulsified emulsion, the supernatant of the organic phase, recovered by the centrifuge, was used to prepare an emulsion. The experimental results corresponding to this emulsion are represented by a symbol, $\bullet$, in Fig. 13. There is no significant improvement in extraction rate over the 2nd run. It is believed that the amount of surfactant available for preparation of emulsion becomes limiting as the demulsification processes, and this causes the instability of emulsion. To overcome this problem, 1 mass% Span 80 was added to the demulsified organic phase which was then used in the next extraction experiment of Mo(VI). The experimental results are depicted by a symbol, $\blacksquare$, in Fig. 13. The extraction rate decreased as compared with that of the 2nd run.

From these findings, it is appears at this stage, that repeated use of the organic phase in the extraction of U(VI) or Mo(VI) is limited when Span 80 and Na_2CO_3

are used as the surfactant and the stripping agent, respectively. ECA 4360J is a better surfactant than Span 80 from the aspect of recycling of organic phase, in the extraction of Mo(VI) or U(VI), utilizing an emulsion-type liquid membrane technique.

IV. Conclusions

The relationship between demulsification time and the percent demulsification of Mo(VI) and U(VI), using emulsion which consisted of an organic phase containing TNOA and Span 80 or ECA 4360J and an internal aqueous phase containing Na_2CO_3 , was studied by means of an electrostatic coalescence technique.

The initial demulsification rate increases with increasing applied voltage, Na_2CO_3 concentration, and W_1/O ratio. Increases in Span 80 or ECA 4360J concentration, agitation speed of homogenizer and homogenizing time depress demulsification. The variation in TNOA concentration does not affect significantly demulsification. The demulsification of the emulsion containing ECA 4360J is more difficult than that of the emulsion containing Span 80. Demulsification of the loaded emulsion occurs with greater ease than that of the fresh emulsion. The emul-

sion containing ECA 4360J effects adequate extraction of both Mo(VI) and U(VI) with the recycled organic phase, while the extraction ability of the emulsion containing Span 80 decreases gradually with a repeated use of the organic phase. Thus, ECA 4360J is found to be a more suitable surfactant than Span 80 in the liquid membrane process studied in this paper.

REFERENCES

- (1) T. P. Martin and G. A. Davis: *Hydrometallurgy*, **2** (1976/77), 315.
- (2) H. Ino, N. Imaishi, M. Hozawa and K. Fujinawa: *Kagaku Kogaku Ronbunshu*, **9** (1983), 263.
- (3) K. Fujinawa, M. Morishita, M. Hozawa, N. Imaishi and H. Ino: *J. Chem. Eng. Japan*, **17** (1984), 632.
- (4) T. Kataoka and T. Nishiki: *Kagaku Kogaku Ronbunshu*, **12** (1986), 16.
- (5) T. Kataoka and T. Nishiki: *Kagaku Kogaku Ronbunshu*, **13** (1987), 700.
- (6) T. Hano, T. Ohtake and K. Takagi: *J. Chem. Eng. Japan*, **21** (1988), 345.
- (7) T. Hirato, I. Kishigami, Y. Awakura and H. Majima: *Hydrometallurgy*, **26** (1991), 19.
- (8) T. Hirato, K. Koyama, Y. Awakura and H. Majima: *Mater. Trans., JIM*, **31** (1990), 213.
- (9) T. Hirato, T. Suyama and H. Majima: *J. Japan Inst. Metals*, **53** (1989), 1041.