REGENERATION OF STYRENE-DIVINYLBENZENE COPOLYMER MICROCAPSULES CONTAINING TRI-*n*-OCTYL AMINE

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Regeneration of microcapsules was carried out by stripping the extracted propionic acid with distilled water and aqueous NaOH solution based on data obtained for a liquid-liquid system. Concerning the stripping behavior with distilled water, the stripping reactions can be successfully expressed as the reverse formula of the extraction reactions. The stripping ratio was found to be a function of the concentrations of the extracted propionic acid in organic solution and the propionic acid in aqueous solution at equilibrium. For aqueous NaOH solution, on the other hand, the stripping could be expressed by the following stoichiometric reaction in the organic solution in both the liquid-liquid and the microcapsule systems.

Perfect stripping was achieved when the molar ratio of NaOH to propionic acid was larger than unity.

The microcapsule extraction system showed the same extraction capacity after repetitive extraction and stripping of propionic acid.

Introduction

Recently, one of the most attractive features in fermentation engineering has been the solvent extraction technique for separation and concentration of fatty acids from dilute solutions. High-molecular weight amines such as tri-*n*-octyl amine (hereafter abbreviated as TOA) have been employed as extractants, that react with fatty acids to form complexes in organic solution^{3, 4, 7, 8}.

A separation technique using extractant-impregnated macroporous resins and Levetrel resins for diluent solutions has been developed in hydrometallurgy^{1, 5, 6, 10, 12}. These resins have many advantages: high selectivity owing to the extractant impregnated in the pores of the resin, ease of separation between solution and resins, and simple equipment that operates like packed columns. On the other hand, such resins have serious problems; not all of the molecules of impregnated extractant react, owing to the effect of steric hindrance, and selectivity can be low, due to inactivation of the extractant².

As described in our previous paper¹³, microcapsules containing TOA as the core material were prepared via *in situ* polymerization and the extraction characteristics of propionic acid (hereafter referred to as HPr) in the aqueous solution were estimated. In that study, TOA molecules enclosed in microcapsules were observed to easily form the HPr-TOA complex, and the microcap-

sule extraction system was found to have the same extraction capacity as that for the liquid-liquid system.

For practical use of the microcapsule extraction system, the extracted HPr should be easily stripped and the microcapsules should maintain the same extraction capacity for repeated use. There is, however, little information concerning the stripping characteristics of the fatty acid in the microcapsule extraction system.

The purpose of this study is to clarify the stripping characteristics of HPr with distilled water and aqueous NaOH solution, based on data for the liquid-liquid system. Furthermore, the extraction capacity was investigated in the repeated uses for the extraction and the stripping.

1. Experiment

1.1 Preparation of microcapsule

Styrene-divinylbenzene (hereafter referred to as St-DVB) copolymer microcapsules were prepared by *in situ* polymerization under a nitrogen atmosphere at 343 K. The details of the experimental procedure were the same as in our previous work¹³.

The conditions for preparation of microcapsules in this work are listed in Table 1.

1.2 Regeneration experiment

1) Measurement of stripping equilibrium in the liquid-liquid system

The organic solution to dissolve TOA-HPr complexes was prepared in the following procedure. Equal

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Table 1. Preparation conditions of microcapsules

Dispersed phase	Total monomer concentration	1.85 mol·dm ⁻³
	Divinylbenzene/Styrene weight ratio	0.20
	TOA concentration in n-dodecane	1.14 mol·dm ⁻³
Continuous phase	Arabic Gum content	2.0 wt%
Operation condition	Stirring speed	6.82 s ⁻¹
	Temperature	343 K
	Duration Time	28.8 ks

volumes of the aqueous and the organic solutions of known concentrations were shaken in an Erlenmeyer flask and allowed to attain equilibrium at 303 K for 86.4 ks. Two liquid phases were then separated. The amounts of extracted HPr were determined according to the manner mentioned previously¹³⁾.

Two kinds of stripping solution were used: distilled water and aqueous NaOH solution. The relations between the stripping ratio and the equilibrium concentration of HPr in the aqueous solution were investigated at various amounts of distilled water. The effect of NaOH concentration in the aqueous solution on stripping was investigated in the case of aqueous NaOH solution as the stripping solution.

The concentration of the stripped HPr was measured by the difference between initial and equilibrium concentrations of NaOH in aqueous solutions, which were determined by neutralization titration with aqueous standard solution of sulfuric acid, using phenolphthalein as an indicator.

2) Regeneration of microcapsules

The extraction procedure using microcapsules was the same as that described in the previous paper¹³⁾. Microcapsules that extracted HPr were dispersed in the stripping solutions and were shaken in a thermostatic bath at 303 K. When aqueous NaOH solutions were used as the stripping solution, the concentration of NaOH was varied from 0.07 mol·dm⁻³ to 1.5 mol·dm⁻³. The stripped HPr was determined from the difference of the NaOH concentrations in the aqueous solution. When distilled water was used, the stripped HPr was measured from the difference between initial and final HPr concentrations in the aqueous solution.

3) Extraction characteristic of microcapsules in repeated use

2.0 mol·dm⁻³ aqueous HPr solutions were used at the extraction stage. At the stripping stage, 0.6 mol·dm⁻³ aqueous NaOH solutions were used as the stripping solutions. The microcapsules that extracted HPr were air-dried and served for the stripping experiment. After the stripping, microcapsules were washed with distilled water until the pH of the filtrate was neutral. The microcapsule concentration was kept to be 20 kg·m⁻³ in both the extraction stage and the stripping stage.

Fig. 1 Effect of volume of distilled water on stripping ratio in the liquid-liquid system

2. Results and Discussion

2.1 Regeneration of microcapsules extracted HPr with distilled water

If we assume that the extraction equilibrium of HPr is reversible and that the association order of complexes between TOA and unstripped HPr is determined by the HPr concentration in the aqueous solution, we can say that a new equilibrium state will be established when distilled water is used as the stripping solution.

On this subject, two points need clarification. The first point is to elucidate the stripping equilibrium of HPr in the liquid-liquid system. This is the key to an understanding of the regeneration of microcapsules with distilled water. The second is to investigate the regeneration of microcapsules in the microcapsule extraction system.

1) Stripping equilibrium of HPr in the liquid-liquid system

The experiments were carried out by varying the distilled water volume to study the effect of the aqueous equilibrium concentration of HPr on the stripping ratio. The results are shown in **Figs. 1 and 2**.

Figure 1 represents the effect of distilled water volume on the stripping ratio E' . The volume of the organic solution was held on at 0.025 dm³ for all runs. The stripping ratio increased with an increase in distilled water volume. Perfect stripping, however, was not attained in most cases. A higher stripping ratio at the same volume of distilled water was obtained both at lower TOA concentration and at lower initial HPr concentration in the organic solution.

Figure 2 illustrates a representative relationship between distilled water volume and HPr concentration in the aqueous solution at equilibrium. HPr concentration in the aqueous solution decreased with increasing distilled water volume. From **Figs. 1 and 2**, a higher stripping ratio was obtained by lowering HPr concentration in the aqueous solution.

The results, as can be seen in **Figs. 1 and 2**, indicate the establishment of a new equilibrium state of HPr

Fig. 2 Representative results in stripping with distilled water

between the organic and the aqueous solutions, and the stripping equilibria of HPr with distilled water can be summarized by the following equations.

$$\left. \begin{aligned} \overline{(\text{HA})\text{B}(\text{HA})}_{n-1} &= \overline{(\text{HA})\text{B}(\text{HA})}_{n-2} + \text{HA}; K'_{n,1} \\ \overline{(\text{HA})\text{B}(\text{HA})}_{n-2} &= \overline{(\text{HA})\text{B}(\text{HA})}_{n-3} + \text{HA}; K'_{n-1,1} \\ \overline{(\text{HA})\text{B}(\text{HA})} &= \overline{(\text{HA})\text{B}} + \text{HA}; K'_{2,1} \\ \overline{(\text{HA})\text{B}} &= \overline{\text{B}} + \text{HA}; K'_{1,1} \end{aligned} \right\} \quad (1)$$

where $K'_{n,1}$ is given by

$$K'_{n,1} = C_A^n \bar{C}_B / \bar{C}_{n,1} \prod_{i=1}^{n-1} K'_{i,1}$$

and the upper bar refers to the organic phase.

Considering the mass balances of HPr and TOA, the following equations were obtained, respectively.

$$V_{org} \bar{C}_{A,0} = C_A V_{aq} + \bar{C}_B V_{org} \sum_{n=1}^N \left(n C_A^n / \prod_{i=1}^n K'_{i,1} \right) \quad (2)$$

$$\bar{C}_{B,0} = \bar{C}_B \left(1 + \sum_{n=1}^N \left(C_A^n / \prod_{i=1}^n K'_{i,1} \right) \right) \quad (3)$$

The apparent associated number, Z' , in the stripping equilibrium is the number of moles of unstripped HPr associated with a mole of TOA and is calculated from the above equations.

$$\begin{aligned} Z' &= (V_{org} \bar{C}_{A,0} - V_{aq} C_A) / V_{org} \bar{C}_{B,0} \\ &= \sum_{n=1}^N \left(n C_A^n / \prod_{i=1}^n K'_{i,1} \right) / \left\{ 1 + \sum_{n=1}^N \left(C_A^n / \prod_{i=1}^n K'_{i,1} \right) \right\} \end{aligned} \quad (4)$$

Equation (4) shows the same definition of the apparent associated number in the extraction as that from Kawano *et al.*^{7,9)}

Figures 3 and 4 illustrate the effect of HPr equilibrium concentration in the aqueous solution on the apparent association order of HPr-TOA complex for all observed data. The apparent association orders, Z' , were determined from HPr concentration in the organic solution at the equilibrium state with Eq. (4). The values, Z' ,

Fig. 3 Apparent association order of HPr-TOA complex as a function of aqueous HPr concentration at stripping equilibrium
Effect of initial HPr concentration in organic solution

Fig. 4 Apparent association order of HPr-TOA complex as a function of aqueous HPr concentration at stripping equilibrium
Effect of initial TOA concentration in organic solution

Table 2. Equilibrium constants in the extraction

$K_{1,1}$	$= 1.01 \text{ m}^3 \cdot \text{kmol}^{-1}$
$K_{2,1}$	$= 5.14 \text{ m}^3 \cdot \text{kmol}^{-1}$
$K_{3,1}$	$= 5.56 \text{ m}^3 \cdot \text{kmol}^{-1}$

lie on one line no matter how the initial conditions of stripping, $\bar{C}_{A,0}$ and $\bar{C}_{B,0}$ are changed. The solid lines in Figs. 3 and 4 represent the extraction equilibrium curves evaluated by the second equation of Eq. (4) using the values listed in Table 2. Equilibrium constants, $K_{n,1}$ ($n = 1, 2, 3$), were determined by a graphical method^{9,14)}. The observed data satisfactorily agree with the calculated ones. In the stripping of mineral acids like hydrochloric acid and nitric acid, excessively extracted acid ($Z > 1$) was easily stripped with distilled water¹¹⁾. For fatty acids like HPr, the stripping ratio was determined by the relation between the equilibrium concentration in the aqueous solution and the association order of HPr-TOA complex. This can be attributed to the difference in the

Fig. 5 Representative results of regeneration of HPr extracted microcapsules

association state of TOA complexes between mineral acid and fatty acid⁹⁾.

2) Regeneration of microcapsules with distilled water

Figure 5 shows the effect of the concentration of dispersed microcapsules in distilled water on the stripping ratio. The weight of microcapsules was 2.0 g in all runs. The amounts of extracted HPr in microcapsules were evaluated by the procedure mentioned below in connection with the stripping using aqueous NaOH solution. As this figure shows, the stripping ratio decreased with increasing the microcapsule concentration. In other words, higher values of the stripping ratio are obtained at larger volumes of distilled water. This was the same result as that for the liquid-liquid system. Moreover, the stripping ratios of longer duration were higher than those of shorter duration.

Considering the results mentioned above, the stripping results were evaluated using the relation between the final HPr concentration in the aqueous solution and the association order of HPr-TOA complexes. The solid keys in Fig. 3 are the results for the regeneration of microcapsules. The solid circles and the solid triangles represent the results of 1-day duration and of 9-day duration, respectively. The results, except for the data at C_A above $0.2 \text{ mol}\cdot\text{dm}^{-3}$, showed higher values than those predicted, even the data after 9-day duration. This implied that the stripping rate in the microcapsule extraction system was much slower than that in the liquid-liquid system. Hence stripping equilibrium was not attained in the microcapsule system even after 9-day duration.

2.2 Regeneration of microcapsules containing extracted HPr with aqueous NaOH solution

In the extraction of acids with long-chain alkylamines, amines must first be protonated and the pairing anions are extracted from the aqueous solution into the organic solution to form complexes. Hence it seems possible to strip acids by removing protons from protonated amines with an aqueous alkaline solution. Aqueous NaOH solutions were used as the alkaline solution. The results obtained are discussed below in detail.

1) Stripping equilibria of HPr with aqueous NaOH solution

Fig. 6 Influence of initial NaOH concentration in aqueous solution on stripping ratio, taking no account of NaOH distribution

Fig. 7 Influence of initial NaOH concentration in aqueous solution on stripping ratio, taking account of NaOH distribution

Figure 6 represents the effect of the initial concentration of NaOH on the stripping ratio in the liquid-liquid system for $C_{A,0} = 0.25 \text{ mol}\cdot\text{dm}^{-3}$ and $0.58 \text{ mol}\cdot\text{dm}^{-3}$. It is seen from Fig. 6 that the stripping ratio of HPr increased with an increase in NaOH concentration and became larger than unity. We do not think that the deviation of E' is caused by errors in determination of the NaOH concentration in the aqueous solution, because the errors inherent in the titration method are of the order of a few per cent. There are two ways of interpreting the obtained results in Fig. 6. One is that excess NaOH is required to deprotonate ammonium salt. The other is the distribution of NaOH between the organic and the aqueous solutions. However, it is hard to consider the former case, because TOA ammonium anion is monovalent. Hence, the distribution of NaOH should be taken into account after the stripping reaction is completed.

Figure 7 illustrates the stripping results, taking account of the distribution of NaOH between two immiscible liquids. The distribution of NaOH was measured by contacting aqueous NaOH solution with 0.20

Fig. 8 Distribution of NaOH between microcapsules and aqueous NaOH solution

Fig. 9 Effect of initial NaOH concentration in aqueous solution on extent of regeneration

mol·dm⁻³ TOA/*n*-dodecane solution in each case. Perfect stripping, as shown in Fig. 7, was achieved at β larger than unity. Here, β represents the initial molar ratio of NaOH to the extracted HPr.

From the results mentioned above, the stripping equilibrium with aqueous NaOH solution may be expressed by the following formula.

For initial concentrations of NaOH larger than those of HPr,

For initial concentrations of NaOH less than those of HPr, the following reaction is assumed to occur.

The distribution of residual HPr between two immiscible liquids is the same as described in the system with distilled water.

2) Regeneration of microcapsules with aqueous NaOH solution

Fig. 10 Regeneration results of microcapsules with 0.144 mol·dm⁻³ aqueous NaOH solution

Figure 8 shows the distribution of NaOH between microcapsules and the aqueous NaOH solution. The open circles represent the results obtained from the concentration difference of NaOH in the aqueous solution, while the solid circles show the predicted values using the distribution relationship of NaOH in the liquid-liquid system mentioned above. It is clearly implied by Fig. 8 that the distribution coefficient in microcapsules is larger than that in the organic solution. This intrinsic distribution may be due to adsorption of NaOH in the microcapsule membrane. Therefore, adsorption of NaOH in the microcapsule is considered in the following discussion.

Figure 9 represents the effect of the initial concentration of NaOH on the regeneration of microcapsules at various concentrations of extracted HPr. The microcapsule concentration was kept at 20 kg·dm⁻³ for all runs. From the results in Fig. 9, the perfect regenerations were obtained when $\beta \geq 1$, which implies that the regeneration follows Eq. (5).

Furthermore, it is clearly demonstrated that the regeneration ratio of microcapsules increases with increasing NaOH concentration in the aqueous solution in the region of $\beta < 1.0$. When β is smaller than 1.0, perfect regeneration were not realized. This means that not all extracted HPr is stripped, and that all NaOH in the aqueous solution is consumed. The concentration of residual HPr in microcapsules decreases with an increase in the initial concentration of NaOH. Therefore, a higher regeneration ratio could be obtained when a higher concentration of NaOH was used, because the distribution of residual HPr between the microcapsule and the aqueous solution proceeded after the consumption of NaOH. Judging from the results shown in Fig. 9, concentrated NaOH solution must be used to achieve the perfect regeneration.

However, the rupturing of microcapsules was observed at NaOH concentrations higher than 2 mol·dm⁻³ in aqueous solution.

Figure 10 represents the effect of stripping solution volume on the regeneration ratio when using dilute aqueous NaOH solution. Perfect regeneration was obviously realized at stripping solution volumes larger than 0.040 dm³, which corresponds satisfactorily to the calcu-

Fig. 11 Extraction performance of microcapsules in repeated use

lated volume (0.037 dm^3). In this run, moreover, no rupturing of microcapsules was observed.

2.3 Extraction characteristics in repeated use

Figure 11 shows the results of the apparent associated order, Z , in repeated use. The HPr concentration in the aqueous solution was $2.0 \text{ mol} \cdot \text{dm}^{-3}$ and the stripping solution was $0.6 \text{ mol} \cdot \text{dm}^{-3}$ aqueous NaOH solution.

It is clearly shown that microcapsules containing TOA show the same extraction capacities through repeated runs, suggesting that the extractant loss from microcapsules is negligibly small.

Conclusions

Stripping of HPr in a liquid-liquid system and regeneration of microcapsules were carried out using distilled water and aqueous NaOH solution. Furthermore the extraction characteristics of microcapsules on repeated uses was investigated. The following results were obtained.

1. Stripping equilibria of HPr with distilled water and aqueous NaOH solution are described by Eqs. (1) and (5), (6), respectively. In particular, the stripping ratio was quantitatively evaluated, taking into account of the distribution of NaOH between aqueous and organic solutions.
2. Microcapsules were perfectly regenerated with aqueous solutions containing more NaOH than extracted HPr. However, rupturing of microcapsules was observed in the concentrated NaOH aqueous solutions.
3. The extraction capacity of microcapsules remained the same through the repeated use.

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Nomenclature

C_A	= concentration of HPr	$[\text{mol} \cdot \text{dm}^{-3}]$
$C_{A,0}$	= initial concentration of HPr	$[\text{mol} \cdot \text{dm}^{-3}]$
C_B	= concentration of TOA	$[\text{mol} \cdot \text{dm}^{-3}]$
$C_{B,0}$	= initial concentration of TOA	$[\text{mol} \cdot \text{dm}^{-3}]$
C_{NaOH}	= concentration of NaOH	$[\text{mol} \cdot \text{dm}^{-3}]$
$C_{\text{NaOH},0}$	= initial concentration of NaOH	$[\text{mol} \cdot \text{dm}^{-3}]$
E'	= stripping ratio	$[-]$
K'	= equilibrium constant of HPr-TOA complex in stripping	$[-]$
m	= stoichiometric number	$[-]$
n	= stoichiometric number	$[-]$
N	= cyclic number	$[-]$
$V_{\text{aq.}}$	= volume of aqueous solution	$[\text{m}^3]$
$V_{\text{org.}}$	= volume of organic solution	$[\text{m}^3]$
Z	= apparent association order of HPr-TOA complex in extraction process	$[-]$
Z'	= apparent association order of HPr-TOA complex defined by Eq. (4)	$[-]$
β	= molar ratio of initial NaOH in aqueous solution to extracted HPr	$[-]$

upper bar = organic phase or microcapsule

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