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SIMULATED FOAM SEPARATION OF BUTYL ACETATE FROM WASTEWATER DISCHARGED BY SOLVENT EXTRACTION OPERATION IN PENICILLIN PRODUCTION

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ABSTRACT

The recovery of solvent dissolved in wastewater from the extraction of penicillin in fermentation broth is explored using a simulating wastewater. Results show that butyl acetate can be separated partially, no matter what type of surfactant is used. The butyl acetate is evaporated from the wastewater into the gas phase, as it is highly volatile. With the concentration of surfactant at a suitable low level, the maximum separation of butyl acetate is obtained. The amount of butyl acetate volatilized to the gas phase will increase with the increase in surfactant until it reaches the maximum. The residual ratio of butyl acetate with sodium dodecyl sulfate as surfactant is higher than that with dodecylsulfonate as surfactant. Both the butyl acetate residual ratio and the enrichment

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concentration decrease with the increase in initial butyl acetate concentration when Tween80 is used as surfactant.

Key Words: Foam; Separation; Penicillin; Butyl acetate; Surfactant; Extraction

INTRODUCTION

Penicillin is a universal antiseptic medicine. Since its isolation in 1920, it has saved innumerous human lives. Penicillin is biosynthesized by a fermentation process nowadays. Usually, after 10 days of fermentation, the broth is filtered. Then, penicillin in aqueous solution is extracted by butyl acetate for purification. Finally, it is stripped of water and crystallized (1).

During the extraction process, butyl acetate dissolves into the aqueous broth up to concentration of 1% by weight. Distillation is the conventional method to recover this part of butyl acetate. After that, the wastewater must be processed to lower the chemical oxygen demand (COD) and biological oxygen demand (BOD) to satisfy the requirement of environmental protection. Both operations are costly and energy consuming.

Foam separation is a new approach for wastewater processing (2). The fermentation broth contains a large amount of soluble proteins and soluble sugars. During the foam separation process, proteins can form foam, which is in turn stabilized by soluble sugars (3,4). According to the Gibbs equation, the extractant, butyl acetate, can be co-adsorbed by the foam. Since butyl acetate is rather volatile, the butyl acetate molecules can penetrate the foam film and enter the gas phase contained in the foam (5). So, after the foam separation, butyl acetate can be recovered from the enriched gas phase and the proteins recovered from the collapsed foam liquid.

In this work, recovery of butyl acetate in the simulated wastewater from extraction of penicillin was simulated. The surfactants, such as Tween80, dodecyl sulfate, and cetyl trimethyl ammonium bromide, are added to simulate the proteins generating a stable foam.

EXPERIMENTAL

Materials

Butyl acetate of analytical grade and Tween80 of chemical grade were purchased from the Beijing Chemical factory, China. Dodecylsulfonate, dodecylsulfate, and cetyl trimethyl ammonium bromide (all analytical grade) were purchased from the Beijing Chemical Reagent Company, China. Distilled water was used in all experiments.

Methods

The schematic diagram of the foam separation apparatus is shown in Fig. 1. The separation was made in a Plexiglas cylindrical column of 50 cm height and 8 cm internal diameter. One liter of simulation wastewater containing butyl acetate and surfactant was fed into the column from the bottom. Scrubbed air was introduced into the column bottom through a sintered glass disk with the mean pore size of 0.14 mm. A sample port was located 10 cm above the column bottom and liquid phase samples (5 mL each) were taken at an interval of 5 min after starting the air bubbling for analysis of the butyl acetate content. The overflowing foam from the column was collected. The collected overflow was defoamed for analysis by freezing for 30 min followed by melting at ambient temperature. Concentration of butyl acetate was determined by gas chromatography HP6890 using HP-5 capillary column (Agilent Technologies, USA), with a flame ionization detector (FID) (6). A 0.4 μL aqueous sample was injected directly without any further processing.

RESULTS AND DISCUSSION

The enrichment ratio and residual ratio are defined, respectively, as (7):

$$\text{enrichment ratio} = \frac{\text{recovered concentration}}{\text{initial concentration}}$$

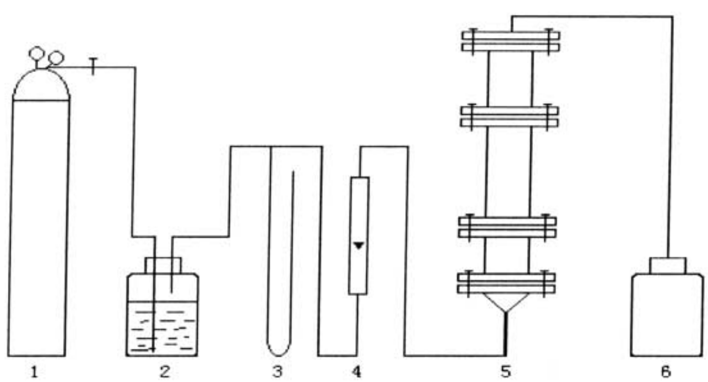

Figure 1. Schematic diagram of the experimental apparatus. 1: gas cylinder; 2: gas scrubber; 3: U-pressure gauge; 4: flow meter; 5: separation column; 6: container of separated foam.

$$\text{residual factor} = \frac{\text{bulk liquid concentration}}{\text{initial concentration}}$$

Effect of Anionic Surfactants on Separation of Butyl Acetate

The relation between the residual factor of butyl acetate and the operation time is shown in Fig. 2, with sodium dodecylsulfonate as the surfactant. In this paper, unless otherwise specified, the initial butyl acetate concentration in the bulk liquid is the saturated concentration of butyl acetate in the water at 25°C. The surfactant concentrations used are labeled in the figure and the unit is the weight ratio of added surfactant to the solution. It can be observed that the residual concentration of butyl acetate in the bulk liquid phase increases with the increase in surfactant concentration. However, the residual concentration of butyl acetate in the bulk liquid without added surfactant is generally higher than those with surfactant added. This may be explained as bubble diameter in the bulk liquid containing no surfactant is larger than those with the addition of surfactant. Therefore, the surface area for mass transfer is smaller and the residual factor of butyl acetate in bulk liquid decreases slowly with time of operation. On the other hand, when the

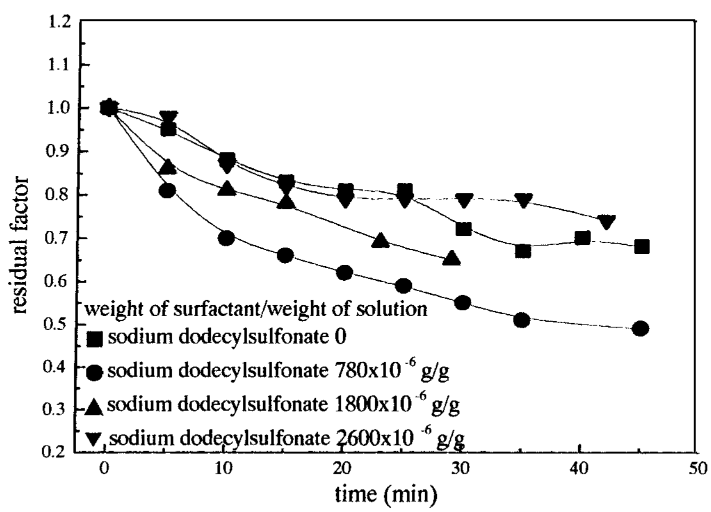

Figure 2. Effect of surfactant concentration on the residual bulk butyl acetate concentration.

surfactant is added into the bulk liquid, the bubbles in the bulk liquid become smaller, resulting in increase of the surface area for butyl acetate transfer from liquid to gas. Besides that, the foam is formed, which enhances the mass transfer rate from the bulk liquid to the gas/liquid interface. When the surfactant concentration increases further above the critical micelle concentration, the adsorption of surfactant on the gas/liquid interface is also increased (8). Meanwhile, the amount of butyl acetate adsorbed on the surface decreases, causing the transport efficiency of butyl acetate to decrease. Ososkov also observed that the volatility rate of toluene is decreased when the cetyl trimethyl ammonium bromide was added into the bulk liquid during experiments of air stripping of toluene from aqueous solution (9).

When the surfactant is present in the bulk liquid, the foam starts to overflow from the top of the column. The relation of butyl acetate concentration in the foam against the initial surfactant concentration is shown in Fig. 3. The surface tension of butyl acetate is rather low, which is 25.09 dynes/cm at 20°C. According to the Gibbs equation, the butyl acetate tends to adsorb on the gas/liquid interface. However, from Fig. 3, it can be found that the enrichment ratio of butyl acetate is less than 1, which means that butyl acetate cannot be concentrated on the bubble surface of the foam. Butyl acetate is removed from the bulk liquid mainly due to evaporation. The butyl acetate enrichment ratio reaches a maximum at a certain intermediate surfactant concentration. The reason is that the concentration of surfactant adsorbed on the bubble surface increases with the increase in initial surfactant concentration. The hydrophobic chains of the surfactant molecules adsorbed on the bubble surface can retain butyl acetate, so that the adsorption of

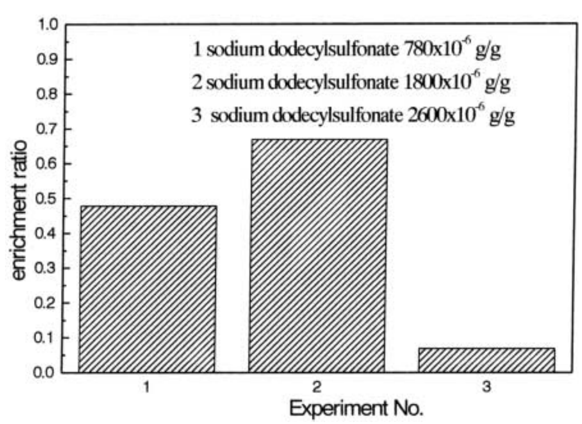

Figure 3. Effect of surfactant concentration on butyl acetate concentration in the fractionated foam.

butyl acetate on the bubble surface increases with the increase in the surfactant concentration. When the initial surfactant concentration increases further, the molecules of the surfactant probably compete for the gas/liquid interface position with the molecules of butyl acetate. Therefore, the surface concentration of butyl acetate decreases with the further increase in the initial concentration of the surfactant.

To quantify the loss of butyl acetate into the gas flow by the volatilization of butyl acetate during the foam separation, the apparent volatility

$$V\% = \frac{C_\mathrm{i} \times V_\mathrm{i} - C_\mathrm{r} \times V_\mathrm{r} - C_\mathrm{f} \times V_\mathrm{f}}{F_\mathrm{g} \times t} \cdot 100\%$$

is defined.

The relation between the volatility of butyl acetate and the surfactant concentration is shown in Fig. 4, demonstrating the same trend as shown in Fig. 3. This phenomenon probably is also related with the surfactant concentration. When the surfactant is added to the aqueous solution, the surface tension of the aqueous solution gradually decreases. Therefore, the bubble diameter is decreased, the specific surface area for adsorption grows larger, and the mass transfer of butyl acetate is increased. So the apparent volatility of butyl acetate is enhanced. When the surfactant concentration is high enough, the molecules of surfactant compete with the molecules of butyl acetate for adsorption at the gas/liquid interface. Therefore, the concentrations of butyl acetate both on the surface and in the gas decrease.

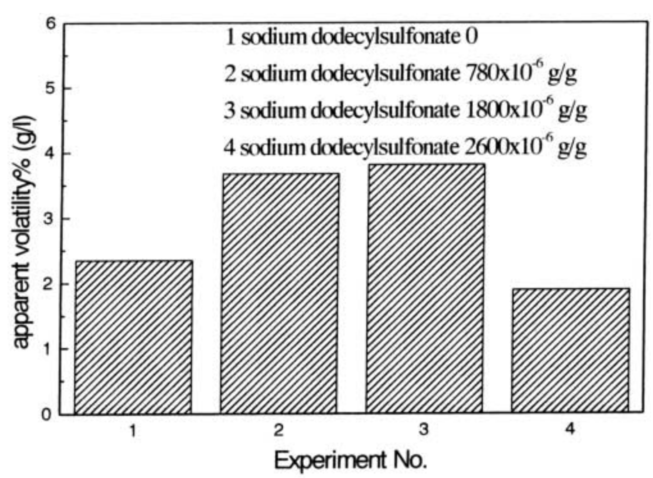

Figure 4. Effect of surfactant concentration on the apparent volatility of butyl acetate.

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Effects of Anionic Surfactants with Different Hydrophilic Head on Separation of Butyl Acetate

The effect of two kinds of anionic surfactants, which have different hydrophilic heads, on the separation of butyl acetate is shown in Fig. 5. It can be observed that when SDS is the surfactant, the residual factor of butyl acetate is significantly lower.

The comparison of butyl acetate concentrations in the collapsed foam liquid using different surfactants is shown in Fig. 6. The enrichment ratios are lower than 1 and similar in value. The amount of butyl acetate adsorption is influenced by the hydrophobic chain of the surfactant used. The hydrophilic group affects the situation of butyl acetate in water. The molecule of sodium dodecylsulfate has an oxygen atom more than the molecule of SDS. It makes the molecules of sodium dodecylsulfate more hydrophilic. This result coincides with the hydrophilic and lipophilic balance (HLB) data. Maybe the dodecylsulfate and the butyl acetate form the micelle structure, it makes the diffusion rate of butyl acetate from bulk liquid to the gas/liquid interface very slow. Therefore, the residual factor of butyl acetate is increased (10). The drainage of the liquid entrained in the foam is affected by the hydrophobic chains of surfactants. Since they are the same, the enrichment ratio is expected to be similar.

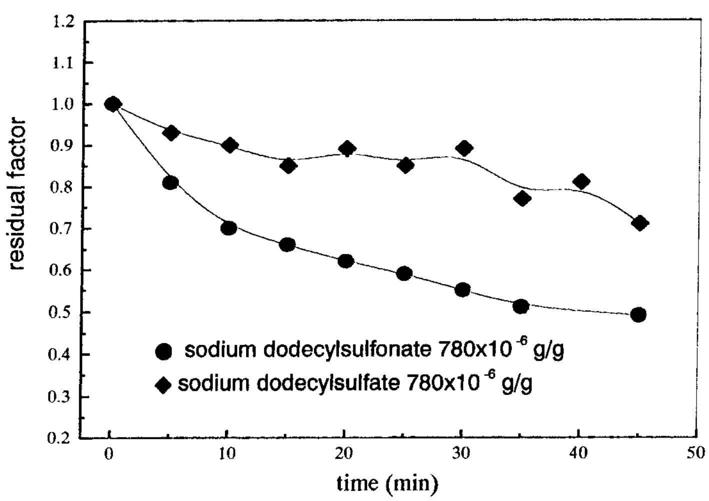

Figure 5. Effect of different hydrophilic groups on the bulk concentration of butyl acetate.

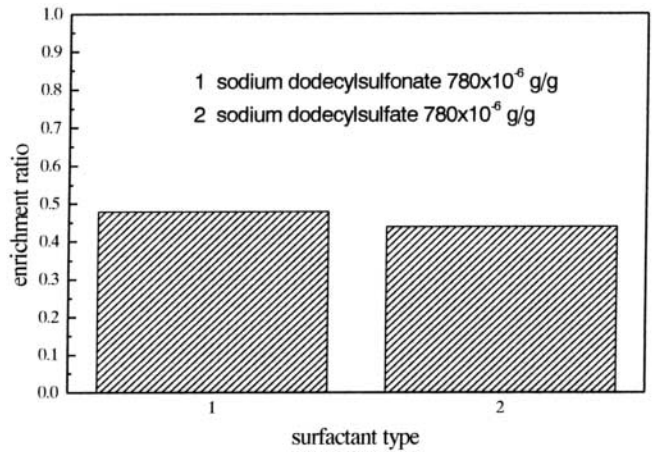

Figure 6. Effect of different hydrophilic groups of surfactants on the butyl acetate enrichment ratio.

Effect of Nonionic Surfactant on Separation of Butyl Acetate

The effect of nonionic surfactant on the residual factor of butyl acetate in bulk liquid is shown in Fig. 7. It shows the similar trend as the results obtained with anionic surfactant. The butyl acetate also cannot be concentrated in the foam. The lower the initial concentration of butyl acetate used, the higher is the

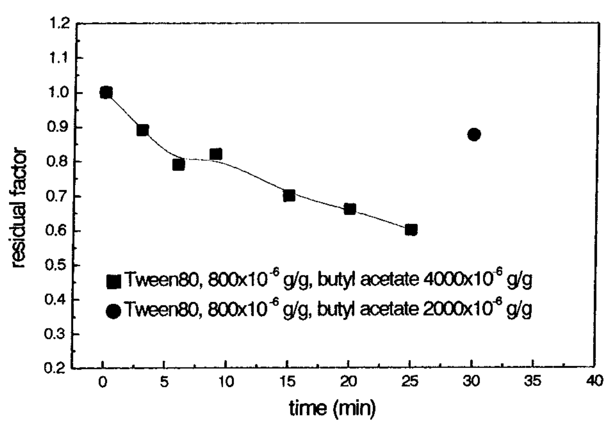

Figure 7. Effect of Tween80 on the bulk concentration of butyl acetate.

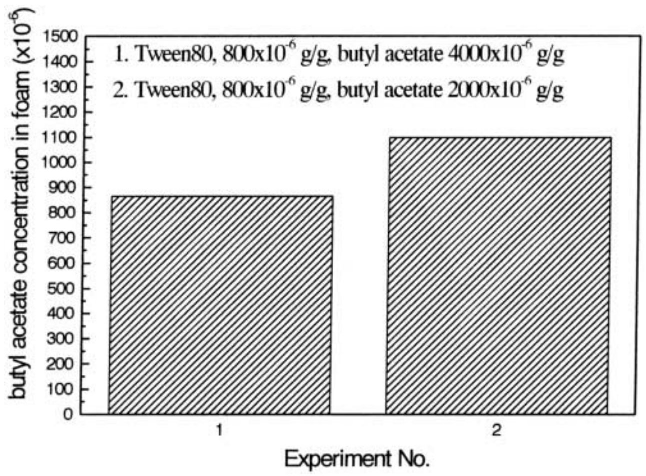

Figure 8. Effect of Tween80 on butyl acetate enrichment concentration.

residual factor of the butyl acetate in bulk liquid. The effect of nonionic surfactant on the enrichment concentration of butyl acetate is shown in Fig. 8. This phenomenon suggests that the diffusion rate of butyl acetate in water is faster than that of the surfactant in water.

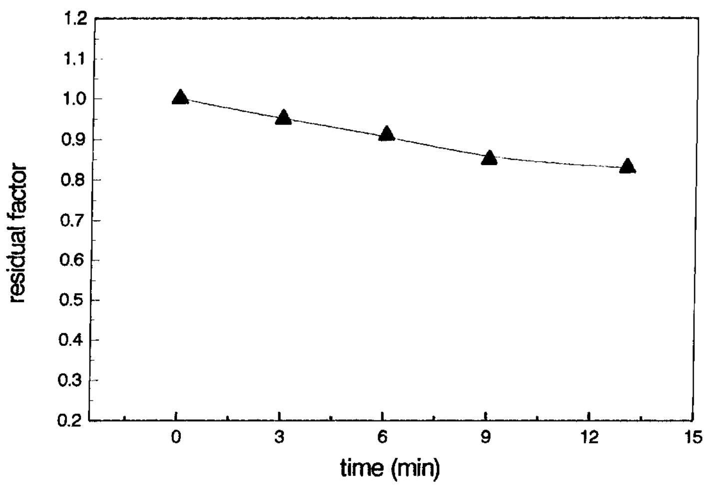

Figure 9. Effect of cetyl trimethyl ammonium bromide on the bulk concentration.

Effect of Cationic Surfactant on Separation of Butyl Acetate

The effect of a cationic surfactant, cetyl trimethyl ammonium bromide, on the separation of butyl acetate is shown in Fig. 9. The result is similar with anionic and nonionic surfactants.

CONCLUSION

Since the volatility of butyl acetate is comparatively high, it is depleted from the liquid phase mainly into the gas no matter what type of surfactant is used. Addition of surfactants can enhance the separation of butyl acetate, but excessive addition of surfactant in turn decreases the separation efficiency. Butyl acetate is not concentrated in the foam phase.

SYMBOLS

V	apparent volatility of butyl acetate (g/L)
C_i	initial concentration of butyl acetate (g/L)
V_i	initial volume of bulk liquid (L)
C_r	residual concentration of butyl acetate (g/L)
V_r	residual volume of bulk liquid (L)
C_f	concentration of butyl acetate in the broken foam liquid (g/L)
V_f	volume of liquid in collected foam (L)
F_g	gas flowrate (L/min)
t	operating time (min)

ACKNOWLEDGMENTS

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