교반조에서 유기산의 반응성 추출에 대한 물질 전달 모델간의 비교

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Reactive Extraction of degradable organic Acid in Agitated Vessels Comparison among Mass Transfer Models with Negligible Continuous-Phase Resistance

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INTRODUCTION

We suggested a right equilibrium expression for the reaction of penicillin G with Amberlite LA-2[1], we developed the mass transfer model with negligible continuous aqueous film resistance for the reactive extraction of penicillin G in a dispersed liquid-liquid extraction system, in which its extraction rate is very high [2]. In the work, justification of the mass transfer model will be proved. For this, we will present several mass transfer models which describe transport of penicillin G from continuous aqueous phase to dispersed organic drops and compare the experimental kinetic data with the calculated results from the models.

MASS TRANSFER MODELS

In a liquid-liquid dispersion extraction system, undissociated penicillin acid (HP) in the continuous aqueous phase reacts with the extractant (A), Amberlite LA-2, in the dispersed organic phase to form penicillin G-Amberlite LA-2 complex ($A_2(HP)_2$ or C) at the interface between the two phases. When a diluent of the organic phase is highly nonpolar, the interfacial reaction is given as follows [1]:

$$2A + 2HP \xleftrightarrow{K_{eq}} A_2(HP)_2 \qquad (1)$$

The complex diffuses into the dispersed organic drops. Also, the mass transfer resistance in the continuous aqueous film was neglected because stirrer speed was fast. Here, we suggested two probable mass transfer models which describe transport of penicillin G from continuous phase to organic drops having the average radius of R:

Model 1: Diffusion controlled in organic drops with very fast interfacial reaction

The mass balance of penicillin G in the continuous aqueous phase is expressed by

$$-V_{aq}\frac{dC_P}{dt}(1+10^{pK_a-pH}) = 2SD_C\frac{\partial C_C}{\partial r}\Big|_{r=R} \qquad (2)$$

The mass balances of complex and extractant within a drop are represented as follows:

$$\frac{\partial C_C}{\partial t} = D_C\frac{1}{r^2}\left(\frac{\partial}{\partial r}r^2\frac{\partial C_C}{\partial r}\right) \qquad (3)$$

$$\frac{\partial C_A}{\partial t} = D_A \frac{1}{r^2}\left(\frac{\partial}{\partial r} r^2 \frac{\partial C_A}{\partial r}\right) \tag{4}$$

When the interfacial reaction is very fast, the reaction equilibrium exists at the interface and is represented by

$$K_{eq} = \frac{C_{C,i}}{C_{A,i}^2 C_H^2 C_P^2} \tag{5}$$

The initial and the boundary conditions are expressed as follows:

I.C.: $C_P(1+10^{pK_a-pH}) = C_{P0} \quad for\ t=0$ (6)

B.C. 1: $\frac{\partial C_A}{\partial r}=0,\ \frac{\partial C_C}{\partial r}=0 \quad for\ r=0,\ all\ t$ (7)

B.C. 2: $2D_C \frac{\partial C_C}{\partial r} = -D_A \frac{\partial C_A}{\partial r} \quad for\ r=R,\ all\ t$ (8)

Model 2: Interfacial reaction and diffusion controlled in organic drops

If the interfacial reaction is elementary, the mass balance of penicillin G in the continuous phase is expressed by

$$\begin{aligned} -V_{aq}\frac{dC_P}{dt}(1+10^{pK_a-pH}) &= k_f' S(C_{A,i}^2 C_{HP}^2 - C_{C,i}/K_{eq}') \\ &= k_f S(C_{A,i}^2 C_H^2 C_P^2 - C_{C,i}/K_{eq}) \end{aligned} \tag{9}$$

is substituted to where k_f' is the forward reaction rate constant and K_a is the acid dissociation constant of penicillin G. The mass balances of complex and extractant within a drop are expressed by Eqs. (3) and (4) as given in the first mass transfer model. To solve these differential equations, one initial condition and two boundary conditions are required. Only the second boundary condition among the three conditions given in Eqs. (6)-(8) is changed as follows:

B.C. 2:
$$\begin{aligned} 2D_C \frac{\partial C_C}{\partial r} &= -D_A \frac{\partial C_A}{\partial r} \\ &= k_f\left(C_{A,i}^2 C_H^2 C_P^2 - C_{C,i}/K_{eq}\right) \quad for\ r=R,\ all\ t \end{aligned}$$

EXPERIMENTAL

The continuous aqueous phase was prepared by dissolving penicillin G potassium salt (Sigma-Aldrich Co.) in a citrate buffer solution, which maintains constant pH throughout the experiments. The dispersed organic phase was prepared by dissolving Amberlite LA-2 (Sigma-Aldrich Co.) in kerosene. A cylindrical flat-bottomed glass vessel set up in a water bath maintained at 25℃. A six flat-blade turbine impeller stirred at 250 rev/min. Samples were taken from the vessel at intervals. penicillin G concentration was analyzed by a UV spectrophotometer (UV2-100, ATI Unicam) at 258 nm. The initial concentration of Amberlite LA-2 in the dispersed organic phase was 50 mM, pH of the continuous aqueous phase was 5.0, and the initial concentration of penicillin G in the continuous aqueous phase ranged from 30 to 200 mM.

RESULTS AND DISCUSSION

Figs. 1 and 2 show the effect of initial penicillin G concentration in the continuous aqueous

phase on extraction of penicillin G for Model 1 and Model 2, respectively. According to Model 1, mass transfer of penicillin G is controlled only by the diffusion of the complex in organic drops. According to Model 2, on the other hand, the interfacial reaction as well as the diffusion functions as rate determining steps. Also, all the lines originate from the point (0,1) which is not shown in the figures. The initial extraction rate based on the normalized penicillin G concentration ($dY_P / dt|_{t=0}$) for Model 1 in Fig. 1 is higher than that for Model 2 in Fig. 2 because the interfacial reaction is at equilibrium state in the case of Model 1. Also, degrees of extraction at 300 sec for the two models were almost the same, which shows that the extractant in an organic drop was all saturated with the undissociated penicillin acid at that time. In two models, the initial extraction rates increased with the increase in the initial penicillin G concentration as long as both initial concentration ratio of penicillin G to the extractant and interfacial reaction rate were not high. This extraction behavior was observed in our previous ELM system for extraction of penicillin G [3,4], whose transport mechanism may be explained by the diffusion-controlled models with the reaction equilibrium or the elementary reaction at the interface. However, the calculated results from Model 2 fit the experimental data much better than those from Model 1. Therefore, it could be concluded that mass transfer of penicillin G was controlled by both of the diffusional resistance in organic drops and the interfacial reaction resistance.

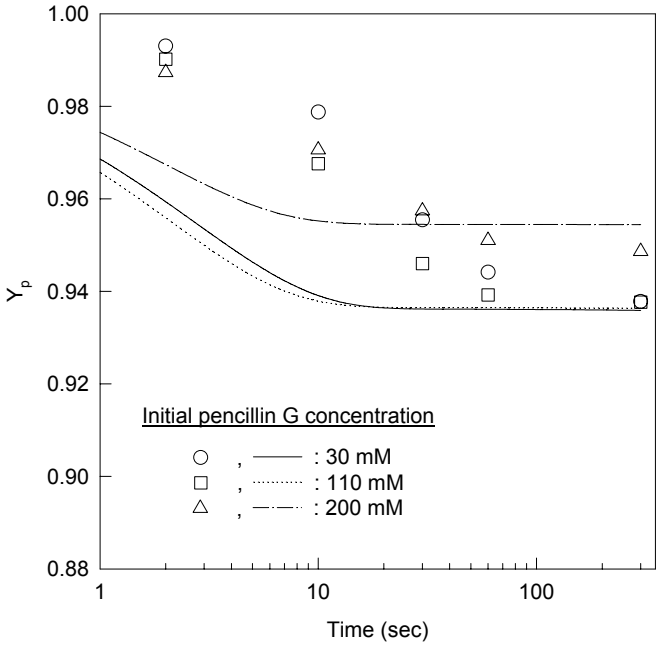

Fig. 1. Comparison between the calculated results from Model 1and the experimental data on penicillin G extraction as a function of initial concentration of penicillin G in the continuous aqueous phase

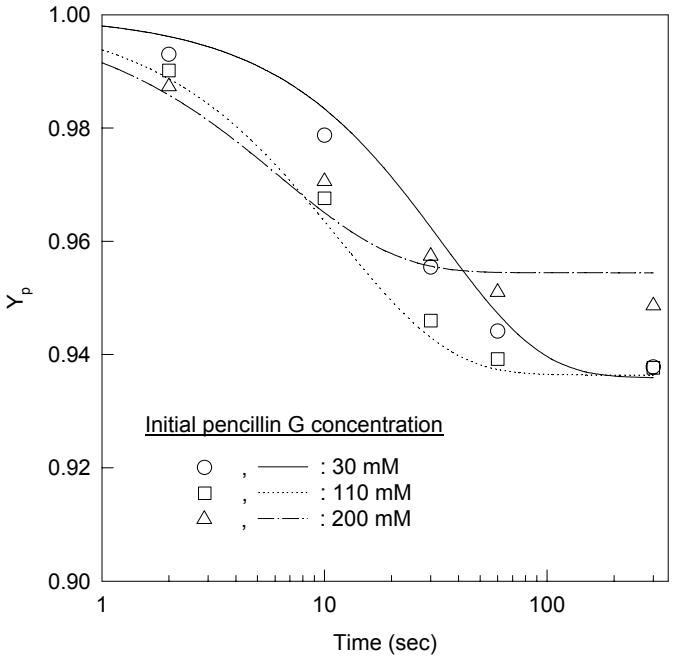

Fig. 2. Comparison between the calculated results from Model 2 and the experimental data on penicillin G extraction as a function of initial concentration of penicillin G in the continuous aqueous phase

Conclusions

Reactive extraction of penicillin G from continuous aqueous phase to dispersed organic phase in agitated vessels was simulated using two mass transfer models with negligible continuous phase resistance. The calculated results from one of the two models (Model 2), in which mass transfer of penicillin G was controlled by the diffusion in organic drops and the interfacial reaction, fit the experimental data for degree of extraction better.

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