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Development of a more efficient emulsion liquid membrane system with a dilute polymer solution for extraction of penicillin G

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Abstract

So as to find a more efficient emulsion liquid membrane (ELM) system for extraction of penicillin G from simulated media, further study was done on batch and continuous ELM systems with a dilute polymer solution in addition to our previous ELM work examined in more detail in this work. The study was carried out in the batch ELM system varying membrane composition and Na_2CO_3 concentration in the internal phase. Compared to the previous work, the polymer-dissolved ELM system with higher concentrations of Na_2CO_3 in the internal phase and lower concentrations of surfactant in the membrane phase produced much higher extraction efficiency. Also, an optimized emulsion composition from the batch system was applied to continuous extraction of penicillin G in the extraction column of Oldshue–Rushton type, and in view of the fact that high enrichment ratio of penicillin G was still obtained, development of a practical ELM system for penicillin G extraction seemed feasible.

Keywords: Penicillin; Liquid membranes; Mass transfer; Dilute polymer solution; Extraction efficiency; Continuous extraction

1. Introduction

Since Reschke and Schügerl [1] first introduced a basic concept for reactive extraction by various secondary amines into recovery of penicillin G from aqueous feed solutions near neutral pH, various works on its extraction combined with chemical reaction have been persistently tried with different organic solvents, carriers, and extraction contactors for the purpose of development of a practical system for recovery of penicillin G [2–10]. In most works, the chemical reaction is based on an acid–base reaction between penicillin G ($pK_a = 2.75$) and hydrophobic amines. One of the most promising penicillin extraction processes combined with the acid–base reaction is ELM processes because of very high mass transfer rates, simultaneous extraction/stripping in one stage and requirement of expensive carrier in small quantities, compared to liquid–liquid extraction processes. We also proved that ELM processes were applicable to recovery of penicillin G using Amberlite LA-2 in kerosene as organic membrane phase in a batch reactor and a continuous extraction column [11,12]. However, emulsion swelling and membrane breakage have faded the intrinsic advantages of the ELM processes like high degree of extraction and enrichment ratio. A few remedies for the emulsion instabilities are known to add a stabilizing surfactant or a viscous Newtonian liquid to membrane phase, but they increase mass transfer resistances within emulsion, thereby nullifying their own advantage of a high permeability.

To minimize the emulsion instabilities, Skelland and Meng [13,14] considered addition of a small quantity of viscoelastic polymers to membrane phase in ELM systems without a carrier for removal of phenol and ammonia. They found that optimized conversion of the membrane phase into a non-Newtonian form brought about increase in emulsion stability without any substantial reduction in diffusivity and permeability. In the same way as referred above, Park et al. [15] very efficiently removed phenol and substituted phenol at very high concentrations in a Taylor vortex column with emulsion containing polyisobutylene as a viscoelastic polymer.

We have also performed extraction of penicillin G using the dilute polymer solution in batch ELM systems varying surfactant concentration, polymer concentration and w/o ratio (i.e. volume ratio of internal aqueous phase to organic membrane phase) [16,17]. Good extraction efficiency was obtained with a few combinations of membrane composition and w/o ratio in the previous work. However, emulsion swelling easily diluted penicillin G accumulated in the internal phase at high surfactant concentration despite high degree of extraction,

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while the degree of extraction was quite low at low surfactant concentration despite low emulsion swelling. Therefore, an optimal value of emulsion composition such as surfactant concentration, polymer concentration, and internal reagent concentration as well as w/o ratio was required to develop a more efficient ELM system. For this, the current work on extraction efficiency of penicillin G at different emulsion compositions will be compared with a part of the previous work referred here. Ultimately, the optimal emulsion composition will be applied to the continuous column of Oldshue–Rushton type so as to confirm practicability of the current ELM system.

2. Experimental

2.1. Reagents preparation

A citrate buffer solution was used as external aqueous phase in order to reduce emulsion swelling and keep pH of the external phase constant throughout ELM experiments. The buffer solution was composed of a mixture of citric acid and trisodium citrate (EP grade, Junsei Chemical Co.), and its concentration and pH were 0.408 mol/dm^3 and 5.0, respectively. Penicillin G potassium salt with an activity of about 1600 units/mg (Sigma Co.) was added to the external phase to prepare a simulated medium as a feed solution. Internal aqueous phase was prepared by dissolving sodium carbonate (EP grade, Junsei Chemical Co.) in deionized water. Organic membrane phase was prepared by dissolving pure PARANOX 147 (Nonionic polyamine surfactant; Infinium Singapore Pte. Ltd.) as 2 or 5 vol.% emulsifier or a 90:10 mixture of PARANOX 147 and Span 80 (Sorbitan monooleate, Sigama Co.) as 8 vol.% emulsifier, Amberlite LA-2 (*N*-lauryl-*N*-trialkymethylamine, Sigma Co.) as a carrier, and a small quantity of polymer in kerosene (GR grade, Junsei Chemical Co., viscosity at 25 °C: 1.3 cp). The polymer used was an 1:1 mixture of styrene/butadiene block copolymer ($M_w \approx 140{,}000$, 30% styrene, Scientific Polymer Co.) and styrene/isoprene block copolymer ($M_w \approx 150{,}000$, 14% styrene, Scientific Polymer Co.).

2.2. Experimental apparatus and procedure

Batch experiments for extraction of penicillin G were carried out in the same stirred glass reactor that we used in the previous works [11,17–20]. A water-in-oil (w/o) type emulsion was made by slowly adding the internal phase to the organic membrane phase with intensive mixing provided by a homogenizer (high speed generator, T25, IKA Lab.). Seventy cubic centimetres of the w/o emulsion was dispersed in the batch reactor containing 420 cm^3 of the feed solution, where the concentration of penicillin G was 20 mmol/dm^3. The two phases in the batch reactor fitted with four vertical baffles were mixed by a turbine impeller of 5.5 cm in diameter and were maintained at 25 °C by water passing through a built-in water-jacket of the batch reactor. All of the batch extraction runs were conducted at the stirrer speed of 330 rev/min. Samples were taken from the stirred reactor periodically during the course of a run. The external phase of the samples was separated from the emulsion phase by filtration using a filter paper and then analyzed for penicillin G by a UV spectrophotometer (UV2-100, ATI Unicam) at the peak wavelength of 258 nm. The concentration of penicillin G in the internal phase was also analyzed after the emulsion was demulsified by the freezing and thawing method [21] at the end of the ELM runs. The ELM experiments were carried out varying the polymer and surfactant composition of the membrane phase at two different w/o ratios, 1/3 and 1/1. In all of the experiments, the initial concentration of Amberlite LA-2 in the membrane phase was 20 mmol/dm^3. The emulsification speed and time were 12,000 rev/min and 10 min, respectively. The initial mass of Na_2CO_3 in the internal phase was fixed as 3.5×10^{-3} or 6.125×10^{-3} mol.

A fourteen-stage extractor of the Oldshue–Rushton type was used for continuous extraction of penicillin G. A detailed specification of the column is described in our previous work [2]. Stirring was carried out at 330 rev/min using four-flat blade turbine impellers located centrally in each stage. A continuous aqueous phase (feed solution) was fed to the top of the extraction column, and a dispersed emulsion phase was countercurrently injected through a nozzle attached to the bottom of the column. Samples were taken from the bottom of the column and four sampling ports installed on the side wall of the column at steady state. In addition, water content in the emulsion phase effluent from the top of the column was measured by a Karl Fisher titrator (AF7, Orion) so as to obtain degree of emulsion swelling. The degree of emulsion swelling (E_S) is defined as the ratio of the volume increment of the effluent emulsion to the volume of the influent emulsion phase and is expressed by

$$E_S\,(\%) = \frac{(V_e)_{eff} - (V_e)_{inf}}{(V_e)_{inf}} \times 100 \quad (1)$$

where V_e is the volume of emulsion, and the subscripts inf and eff represent influent and effluent streams, respectively.

3. Results and discussion

Carrier-facilitated transport of penicillin G through the liquid membrane is schematically represented in Fig. 1. Amine extractants such as Amberlite LA-2 and polyamine surfactants such as PARANOX 147 function as a carrier of weak acid such as penicillin G in ELM systems. The reaction of the amines with undissociated penicillin acids at the external and the internal interfaces is known by

$$m\mathrm{A(org.)} + n\mathrm{(HP)(aq.)} \leftrightarrow \mathrm{A}_m\mathrm{(HP)}_n\mathrm{(org.)} \quad (2)$$

n moles of undissociated penicillin acid (HP) reacts with m moles of carrier (A) at the external interface between the aqueous feed and the membrane phases to form 1 mol of complex $[A_m(HP)_n]$. The complex then diffuses through the membrane phase to the internal interface between the membrane and the aqueous receiving phases, where the undissociated penicillin acid is released into the internal phase by the