EQUILIBRIUM STUDIES ON REACTIVE EXTRACTION OF A WEAK ACID BY AN AMINE EXTRACTANT IN KEROSENE

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We have experimentally and theoretically studied the extraction equilibrium between penicillin G, one of monocarboxylic organic acids, and a secondary amine extractant, Amberlite LA-2, dissolved in kerosene. Based on the previous works about extraction equilibria of monocarboxylic acids by some secondary amines in low polar organic solvents, we have first suggested four equilibrium models, which may describe the extraction equilibrium of penicillin G in the reactive extraction system. The calculated results from the four models were compared with the experimental data, and only two equilibrium models seemed to be probable. Finally, the most reasonable extraction equilibrium model was determined through spectroscopic studies on organic solutions obtained by five specific extraction equilibrium experiments.

1 Introduction

Although recovery of penicillin G, a monocarboxylic acid (pK_a=2.75), has been successfully carried out using Amberlite LA-2 in kerosene by emulsion liquid membrane (ELM) processes [1,2], a detailed transport mechanism of penicillin G in the ELM system has not yet been illuminated exactly for lack of the equilibrium and kinetics data of penicillin G in a reactive extraction system. In this work, therefore, we will find the equilibrium expression for the reaction of penicillin G in a liquid-liquid extraction system, which is a primary study prior to getting reaction kinetics in the penicillin G extraction system.

2 Development of equilibrium models

The previous results [3-6] about the reaction equilibrium between an aqueous monocarboxylic acid solution and a secondary amine in a low polar organic solvent have helped us suggest four reaction equilibrium models described in Table 1. The nth-order equations for C_{HP} and/or C_A are derived

using the overall material balances of penicillin G and amine for each model. The equations were solved by the FORTRAN subroutine ZPORC or NEQNF available from IMSL MATH/LIBRARY (Problem-solving Software Systems) in order to get C_{HP} satisfying the constraint $0 < (1 + 10^{pH-pKa})C_{HP} < C_{PG}$.

3 Experimental

The organic solution was prepared by dissolving Amberlite LA-2 in kerosene. The aqueous solution was prepared by dissolving penicillin G potassium salt in citrate buffer solutions. Equal volumes ($30cm^3$) of the prepared organic and aqueous solutions in a flask were vigorously mixed by a shaker maintained at 25 °C for about one hour, and the penicillin G concentration in the aqueous phase was measured by UV spectrophotometer (UV2-100, ATI Unicam) at 258nm after separation of two phases. Also, IR spectra for penicillin G in a solid state, and unreacted Amberlite LA-2 and penicillin-Amberlite LA-2 complex in kerosene were recorded at room temperature with a Thermo Nicolet Model MAGNA-IR 560 double beam FTIR spectrophotometer with a KBr window.

Table 1. Equilibrium models for reactive extraction of penicillin G

Model	Equilibrium expression
1	$A + HP \xleftrightarrow{K_{eq}} AHP, \quad K_{eq} = \dfrac{C_{AHP}}{C_A C_{AHP}}$
2	$A(HP)_{i-1} + HP \xleftrightarrow{K_{eq,i}} A(HP)_i, K_{eq,i} = \dfrac{C_{A(HP)_i}}{C_{A(HP)_{i-1}} C_{HP}}, i = 1,2,\cdots,n$
3	$A + HP \xleftrightarrow{K_{eq,1}} AHP, \quad K_{eq,1} = \dfrac{C_{AHP}}{C_A C_{HP}}$ $AHP + HP \xleftrightarrow{K_{eq,2}} A(HP)_2, K_{eq,2} = \dfrac{C_{A(HP)_2}}{C_{AHP} C_{HP}}$ $A(HP)_2 + A \xleftrightarrow{K_{eq,3}} A_2(HP)_2, K_{eq,3} = \dfrac{C_{A_2(HP)_2}}{C_{A(HP)_2} C_A}$
4	$2A + 2HP \xleftrightarrow{K_{eq}} A_2(HP)_2, \quad K_{eq} = \dfrac{C_{A_2(HP)_2}}{C_A^2 C_{HP}^2}$

4 Results and discussion

The experimental data of 96 runs were obtained through the equilibrium experiments, and an objective function was introduced so as to optimize reaction equilibrium constants of each equilibrium model as follows:

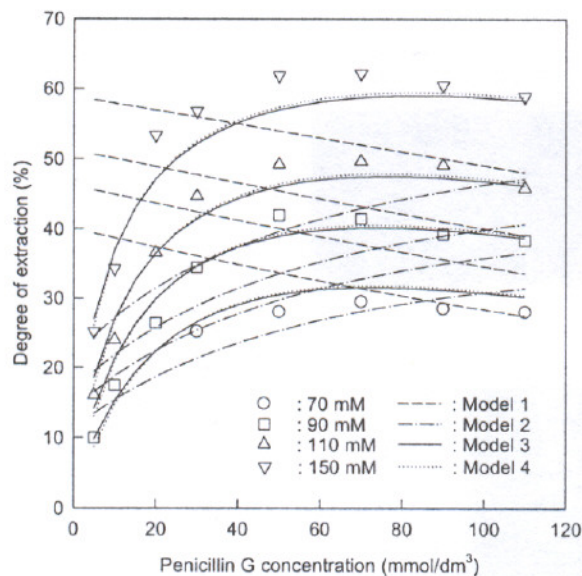$$f = \sum_{i=1}^{N} \sqrt{\left(1 - E_{exp,i} / E_{cal,i}\right)^2}$$

Fig. 1 Comparison of experimental data with calculated results for degree of extraction as a function of overall penicillin G concentation at different overall amine concentations.
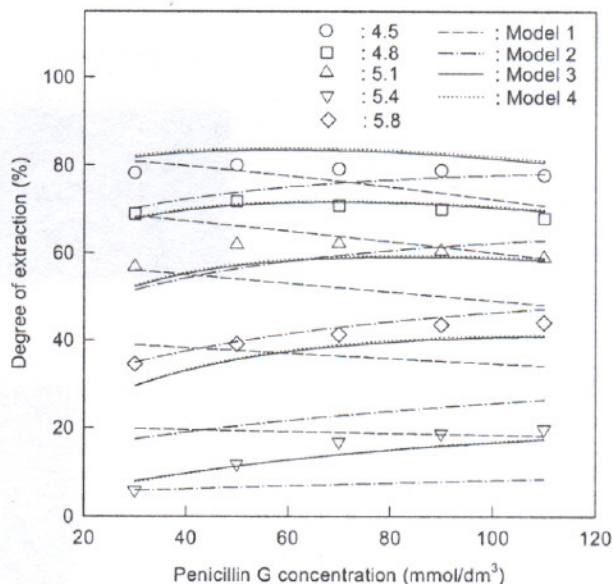

Fig. 2 Comparison of experimental data with calculated results for degree of extraction as a function of overall penicillin G concentation at different pH values of aqueous solution.

where $E_{exp,i}$ and $E_{cal,i}$ are experimental data and calculated results for degree of extraction, respectively. Figs. 1 and 2 show the effect of overall penicillin G concentration on degree of extraction of penicillin G at several overall amine concentrations and pH values of aqueous solutions, respectively. The results calculated from models 3 and 4 agreed with the experimental data much better than those from models 1 and 2. Accordingly, we could consider that model 3 or 4 was more probable than models 1 or 2 as an equilibrium model. To investigate whether model 3 is appropriate as extraction equilibrium model and thus existence of the three complexes in an organic solution depends on overall penicillin G and Amberlite LA-2 concentrations, infrared spectroscopic studies were therefore performed on organic solutions obtained by five extraction equilibrium experiments with different overall penicillin G and Amberlite LA-2 concentrations (see Table 2).
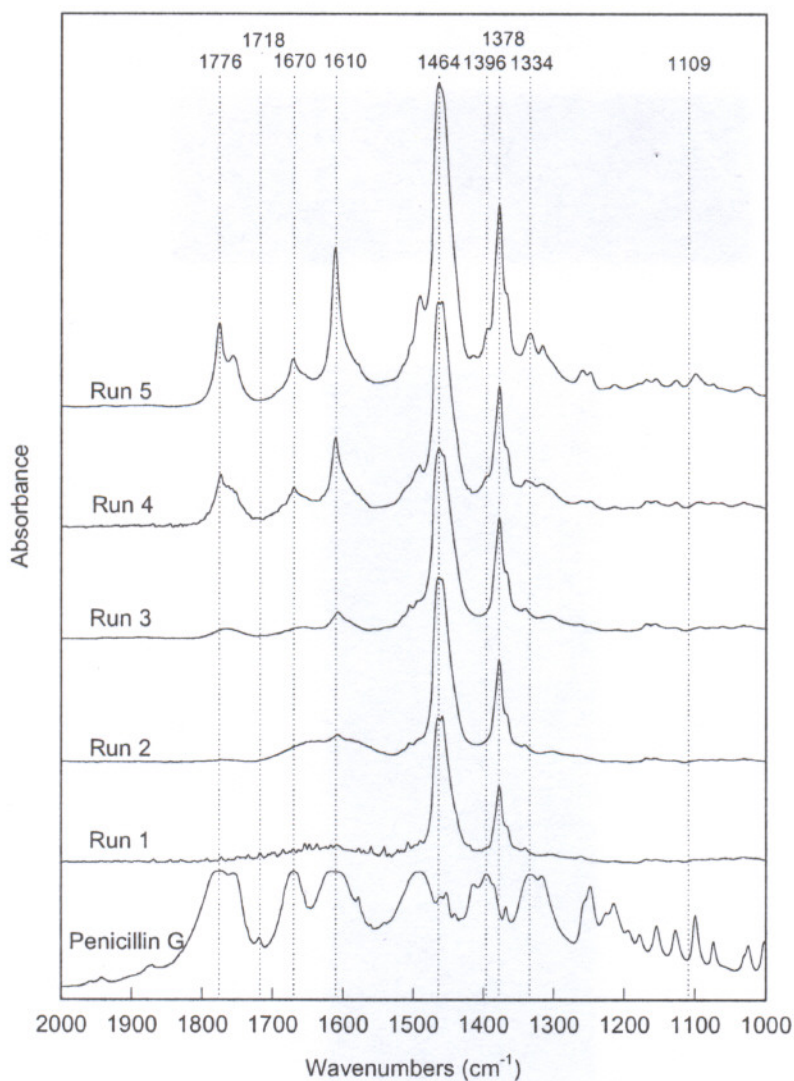
Fig. 3 Infrared spectra for penicillin G in a solid state and organic
solutions of runs 1-5.

According to the work of Tamada about carboxylic acid–amine complex [7], it has been known that an equilibrium between carboxylate and carbonyl forms of a (1,1) complex exists in organic solution. For strong acids the equilibrium is shifted towards the carboxylate form (1600cm⁻¹). For weak acids in inert diluents, the equilibrium is shifted toward the carbonyl form (1720 cm⁻¹) in structure of the (1,1) complex. However, we could not find a carbonyl peak near the band in IR spectra for organic solutions obtained in Runs 1 to 5 (see Fig. 3) while a small carbonyl peak (1718 cm⁻¹) exits in IR spectra for penicillin G in a solid state. Nonexistence of the carbonyl peak for the runs means that formation of the (1,1) complex is difficult in such a nonpolar solvent. The fact supports that only (2,2) complex exists in the organic phase. Accordingly, model 4 including the sole complex is likely to be more appropriate than model 3 as an equilibrium model of penicillin G extraction.

Table 2. Each experimental condition of extraction equilibrium for IR

spectroscopic

study, and degree of extraction calculated from Model 3.

	C_{PG} (M)	C_{AG} (M)	Degree of extraction (%)
Run 1	0.005	0.005	0.2
Run 2	0.005	0.03	3.0
Run 3	0.02	0.03	8.0
Run 4	0.1	0.15	61.3
Run 5	0.2	0.5	90.7

5 Conclusions

Extraction equilibrium experiments for penicillin G were performed using kerosene and Amberlite LA-2. Four probable equilibrium models were suggested and the calculated results from models 3 and 4 fit the experimental data better than those from models 1 and 2. In order to find the most reasonable model, the infrared absorption spectra of five organic solutions of Runs 1 to 5 have been recorded. From the facts that no bands attributable to C=O stretching of carboxylic group near 1718 cm^{-1} are detectable and there is not any shifting in main peaks with the increase in degree of extraction, model 4 including the sole complex, $A_2(HP)_2$, appears to be the most suitable as an equilibrium model of penicillin G extraction.

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