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A study on reactive extraction equilibrium between acetic acid and bis-succinimide of C9232

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Abstract−C9232 is a typical emulsifier of emulsion liquid membrane and its main component, bis-succinimide, has amine functional groups which react with carboxylic acids. The average numbers of secondary amine groups and isobutylene units in the bis-succinimide were determined through elemental analysis. Acetic acid was extracted by emulsion liquid membrane with use of C9232, and we verified that C9232 was suitable for its extractant in the emulsion liquid membrane systems. Equilibrium experiments for reactive extraction of acetic acid by C9232 were carried out by varying the overall acetic acid concentration and overall C9232 concentration in liquid-liquid extraction systems. Also, an equilibrium model for the reactive extraction of acetic acid was investigated for the purpose of analyzing the emulsion liquid membrane systems for separation of acetic acid from other carboxylic acids or sugars in the future. The calculated results from the equilibrium model were in good agreement with the experimental data.

Key words: Acetic Acid, C9232, Bis-succinimide, Reactive Extraction, Equilibrium Model, Emulsion Liquid Membrane

INTRODUCTION

C9232, which is a trade name of polyisobutylene succinimide in highly refined mineral oil, has been commercially supplied for the purpose of lubricating oil additives [1,2]. Lately, it has been widely used as an emulsifier in emulsion liquid membrane processes because it has a surface-active property and helps prepare a stable emulsion [3-7]. Especially, C9232 can function as an extractant of acetic acid as well as an emulsifier, because the polyisobutylene succinimide of C9232 has the functional groups, secondary and tertiary amines. In our previous emulsion liquid membrane works where only C9232 was used as an extractant, acetic acid in the feed phase could be very selectively removed from succinic acid [5] or a lignocellulosic biomass hydrolysate [8] and highly concentrated into the stripping phase. Although the emulsion liquid membrane processes seem very economical for removal of acetic acid, there are no equilibrium data for reactive extraction of acetic acid by C9232 at all, which makes it very difficult for us not only to analyze the transport mechanism of acetic acid in the emulsion liquid membranes but also to develop another emulsion liquid membrane process to require removal of acetic acid. In the work, therefore, we will get the equilibrium expression for the reaction of acetic acid with a reactive component of C9232 in a liquid-liquid extraction system.

EXPERIMENTAL

1. Emulsion Liquid Membrane

In emulsion liquid membrane experiments, acetic acid (GR grade, Junsei Chemical Co.) was added into deionized water (18.2 MΩ, Simplicity, Millipore) to prepare a feed solution. A stripping solution was prepared by dissolving sodium hydroxide (First grade, Showa Chemical Co.) in deionized water. An organic membrane solution was prepared by dissolving pure C9232 in kerosene. Water-in-oil (w/o) type emulsion was made by slowly adding the stripping solution to the organic membrane solution with intensive mixing provided by a homogenizer (high speed generator, T25, IKA Lab.). For each emulsion liquid membrane experiment, 70 cm^3 of the w/o emulsion was dispersed in 420 cm^3 of the feed solution. The feed solution and the emulsion were mixed by a turbine impeller of 4.5 cm diameter in the same batch-type glass cell that we used in the previous works [5-7]. All of the extraction runs were conducted at 25 °C and a stirrer speed of 6 Hz. Samples were taken from the stirred cell periodically during the course of a run. The feed phase of the samples was separated from the emulsion phase by filtration using a filter paper. The emulsion was demulsified by the freezing and thawing method [9] so as to get the aqueous stripping phase. Unless otherwise stated, the concentration of C9232 in the membrane phase was 2 wt%, and w/o ratio (i.e., volume ratio of the stripping phase to the membrane phase) was 1. The emulsification speed and time were 200 Hz and 10 min, respectively. The stripping solution was 1.0 mol/dm^3 NaOH solution. The concentrations of acetic acid in the feed and the stripping phases from the batch emulsion liquid membrane experiment were analyzed using an HPLC apparatus equipped with a 7.8×300 mm Supelcogel 610-H column (Supelco). The degassed and filtered eluent with a 0.45 μm membrane filter (Supor(PES), Waters) contained 0.1 vol% phosphoric acid, and passed through the column at the flow rate of 0.5 ml/min by a Waters 515 pump. Detection was achieved with a PDA detector (Waters 996) at 210 nm. The typical retention time of acetic acid was about 21 min.

2. Reactive Extraction

Liquid-liquid extraction experiments were carried out to investigate the reactive extraction equilibrium between acetic acid in deionized water and a reactive component of C9232 in kerosene. The concentration of acetic acid in the aqueous solution was between 2 and 80 mmol/dm^3, and the concentration of C9232 in the organic

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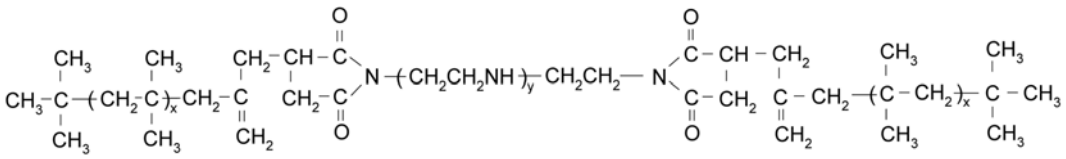

Fig. 1. Structural formula of bis-succinimide of C9232.

solution was between 0.5 and 8 wt%. Equal volumes (35 mL) of the organic and the aqueous solutions in a 250-mL flask were vigorously mixed by a shaker maintained at 25 °C for at least 2 hour. After separation of the two immiscible solutions, the concentration of acetic acid in the aqueous solution was measured by HPLC in the same way as referred above.

RESULTS AND DISCUSSION

1. Determination of Numbers of Isobutylene Units and Secondary Amine Groups in Bis-succinimide of C9232

C9232 is known as bis-succinimide in highly refined mineral oil. The bis-succinimide is a dispersant based on polyisobutylene and an amine which is suitable for oil-based dispersions [1]. The highly refined mineral oil does not have any unsaturated structures, with all aromatics removed, because a paraffinic type (C_nH_{2n+2}) exhibiting its relatively good properties is most common in lubricants [10]. Average molecular weight of the highly refined mineral oil is 320 g/mol [11]. Therefore, the average number of carbons in the mineral oil could be estimated as 22.7. Fig. 1 shows the structural formula of bis-succinimide of C9232 [12]. To obtain a mass ratio of carbon, hydrogen, nitrogen and oxygen in C9232, elemental analyses of C9232 (Infineum UK Ltd.) were performed by using two elemental analyzers, EA1110 for C, H, N, and S, and Flash EA1112 for O from CE Instruments. Their mass ratio was 2.0 : 45.5 : 6.5 : 1.7. When a known mass ratio of the bis-succinimide and the mineral oil was applied, x (number of isobutylene units) and y (number of secondary amine groups) in Fig. 1 were calculated as 12.6 and 3.42, respectively. Finally, the average molecular weight of C9232 was estimated at about 2009.1.

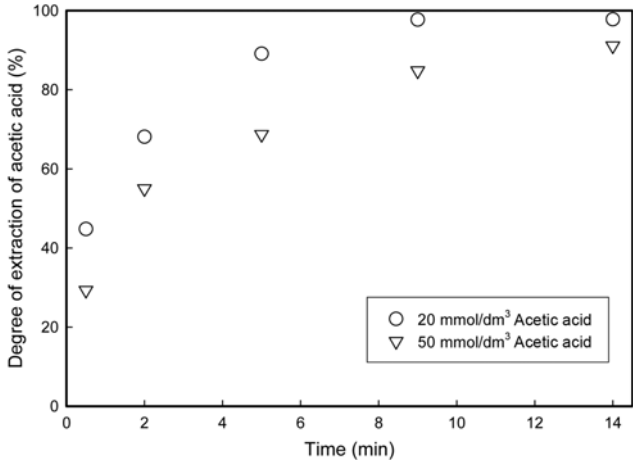

Fig. 2. The effect of initial concentration of acetic acid in the feed phase on degree extraction of acetic acid by emulsion liquid membrane.

2. Emulsion Liquid Membrane

The effect of initial concentration of acetic acid in the feed phase on degree extraction of acetic acid by ELM is shown in Fig. 2. When the initial concentration of acetic acid was higher, its degree of extraction was lower because the stripping agent, NaOH could be exhausted with acetic acid transported into the stripping phase earlier [5]. Even though C9232 (actually bis-succinimide) played the role of extractant of acetic acid in the current emulsion liquid membrane system without a commercial extractant, the degrees of extraction of acetic acid were higher than 90% in 15 minutes without optimization of operating variables. Also, the concentrations of acetic acid accumulated in the stripping phase at 9 and 14 minutes for the two ELM runs were higher than the quadruple of its initial concentration, as listed in Table 1. The high enrichment ratios in Table 1 represent that most of the complex in the organic membrane phase is dissociated to acetic acid and bi-succinimide at the internal interface and then acetic acid is released into the stripping phase, though part of the complex can remain in the organic membrane phase. Since simultaneous extraction and stripping in the emulsion liquid membrane process could remove equilibrium limitations between aqueous and organic phases [13], the concentration of acetic acid in the feed phase could be reduced to very low levels and it could be highly concentrated in the stripping phase. In conclusion, the use of C9232 will facilitate development of economical emulsion liquid membrane processes without an expensive extractant, as far as a high selectivity of acetic acid over other carboxylic acids or sugars in a feed solution can be obtained [5-8].

3. Reactive Extraction Equilibrium

As referred above, bis-succinimide of C9232 is not a single component. When that kind of amine mixture is used as an extractant of carboxylic acid, the reactive extraction equilibrium expression is given by [14],

$$p\,HA + q\,B \xleftrightarrow{K_{eq}} (HA)_pB_q,\quad K_{eq} = \frac{C_{(HA)_pB_q}}{C_{HA}^{p} C_{B}^{q}} \tag{1}$$

where HA is undissociated acetic acid, B is bis-succinimide, and

Table 1. Time-dependent degree of extraction of acetic acid and its enrichment ratio in the emulsion liquid membrane system (2 wt% C9232, 1.0 mol/dm^3 NaOH)

Initial concentration of acetic acid	Degree of extraction		Enrichment ratio*	
	9 min	14 min	9 min	14 min
20 mmol/dm^3	97.7	97.8	6.2	6.9
50 mmol/dm^3	84.8	91.1	5.4	4.4

*Enrichment ratio: ratio of acetic acid concentration accumulated in the stripping phase at any time to its initial concentration in the feed phase

K_{eq} is equilibrium constant. The mass balance equations of acetic acid and bis-succinimide are written by

$$C_{AG} = C_A + pC_{(HA)_pB_q} = C_A + pK_{eq}C_{HA}^p C_B^q \quad (2)$$

$$C_{BG} = C_B + qC_{(HA)_pB_q} = C_B + qK_{eq}C_{HA}^p C_B^q \quad (3)$$

where C_{AG} and C_{BG} are the overall concentrations of acetic acid and bis-succinimide, respectively. Also, the acid dissociation constant of acetic acid (K_a) is described as follows:

$$HA \xleftrightarrow{K_a} H^+ + A^-, \quad K_a = \frac{C_H C_A}{C_{HA}} \quad (4)$$

Its pK_a value is 4.76 [15]. Since only the undissociated acetic acid in the aqueous phase is extracted into the organic phase, the concentration of hydrogen ion in the aqueous phase is always equal to that of dissociated acetic acid. In other words, C_{HA} is C_A^2/K_a from Eq. (4). Thus, Eqs. (2) and (3) can be expressed as functions of the unknown variables, C_A and C_B. Finally, the two equations were solved with the help of the IMSL FORTRAN subroutines, BCLSF and ZPORC. The degree of reactive extraction of acetic acid (E) is given by

$$E = \left(\frac{C_{AG} - C_A}{C_{AG}}\right) \times 100 \quad (5)$$

The experimental data for its degree of extraction were obtained through the reactive extraction equilibrium experiments, and the average deviation (Dev) between the calculated and the experimental results was introduced so as to optimize the reactive extraction equilibrium constant and the stoichiometric coefficients (p and q) in Eq. (1) as follows:

$$Dev = \sum_{i=1}^{N} \frac{|E_{exp,i} - E_{cal,i}|}{E_{exp,i}} \times 100 \quad (6)$$

where $E_{exp,i}$ and $E_{cal,i}$ are the experimental data and the calculated results for degree of reactive extraction of acetic acid, respectively. The optimized values of K_{eq}, p and q were 1.15, 0.91, and 1123, respectively, and gave a good fit to the experimental data with an absolute mean deviation of 11.03%.

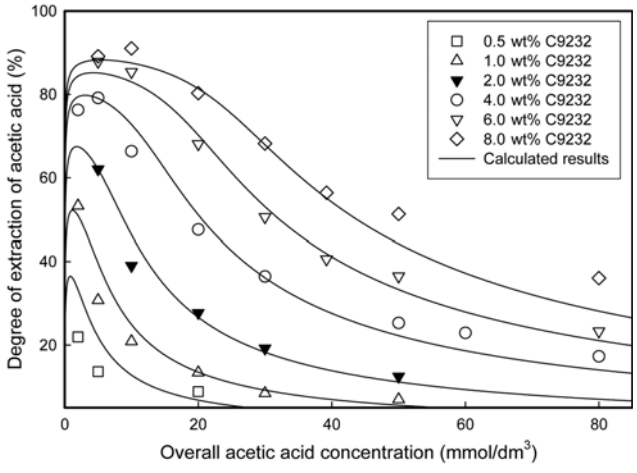

Fig. 3. Comparison of experimental data for degree of reactive extraction of acetic acid with calculated results from equilibrium model as a function of overall acetic acid concentration at different C9232 concentrations.

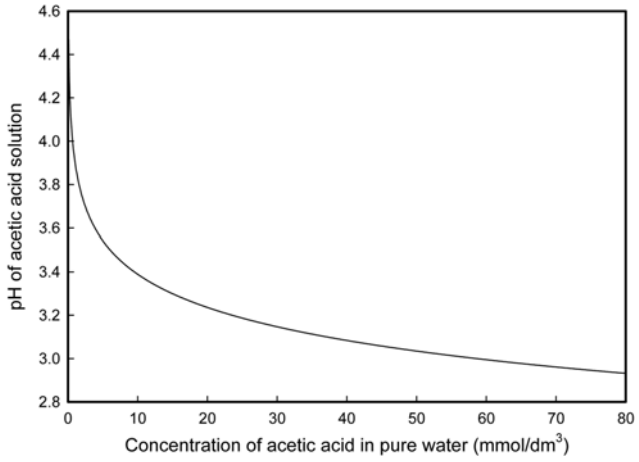

Fig. 4. Relationship between acetic acid concentration and pH of its aqueous solution.

Fig. 3 shows the effect of overall acetic acid concentration on degree of reactive extraction of acetic acid at different overall C9232 concentrations. The calculated results from the reactive extraction equilibrium model (solid lines) were plotted on the figure for the comparison with the experimental data (symbols). The degree of extraction of acetic acid increased with an increase in the overall C9232 concentration at a given overall acetic acid concentration because of an increase in reaction capacity of C9232 with acetic acid. Also, the maximum degree of extraction of acetic acid at a given overall C9232 concentration was obtained at an overall acetic acid concentration ($C_{AG,max}$) lower than 10mM, regardless of the overall C9232 concentration. This can be explained as follows. Fig. 4 shows the relationship between acetic acid concentration and pH of its aqueous solution, which was obtained using Eq. (4). As displayed in the figure, the pH value of the aqueous solution in the overall acetic acid concentration range lower than $C_{AG,max}$ is more sensitive to acetic acid concentration than that in the overall acetic acid concentration higher than $C_{AG,max}$. When the overall acetic acid concentration is lower than $C_{AG,max}$, the pH of the aqueous solution at equilibrium becomes quite high compared to its initial pH though a small quantity of acetic acid is transported to the organic solution. According to Le Chatelier's principle, the chemical reaction in Eq. (1) will favor the side opposing the subtraction of the undissociated acetic acid. Consequently, its degree of extraction at equilibrium was not high because a high pH of the aqueous solution enhances the backward reaction in Eq. (1). When the overall acetic acid concentration is higher than $C_{AG,max}$, the reaction capacity of C9232 with acetic acid is finite as far as the concentration of C9232 in the organic solution is fixed. Thus, its degree of extraction was lower at a higher overall acetic acid concentration.

CONCLUSIONS

Elemental analysis showed that the average molecular weight of C9232 was 2009.1. Through the equilibrium experiments for reactive extraction of acetic acid and modeling of the extraction equilibrium, the equilibrium expression for reaction of acetic acid with bis-succinimide was obtained as follows:

$$1.15HA + 0.91B \xleftrightarrow{K_{eq}} (HA)_{1.15}B_{0.91}$$

The equilibrium model was thought to be very helpful for analyzing the transport mechanism of acetic acid in emulsion liquid membrane systems for removal of acetic acid from other carboxylic acids in fermentation broths or sugars in lignocellulosic biomass hydrolysates in the near future.

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