

## SEPARATION OF FATTY ACIDS BY CRYSTALLIZATION USING TWO LIQUID PHASES

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**Abstract** – First, the phase diagrams for the water+ethanol+fatty acids system were described, and the separation method was considered. Second, the separation of lauric acid+myristic acid mixture in the ethanol aqueous solution including ethanol by liquid-liquid extraction and crystallization has been examined. The extraction of fatty acids from the organic phase to the aqueous solution has been done. Fatty acids in the aqueous solution were crystallized using the aqueous SLE surface. The solvent-free mole fraction of lauric acid in the aqueous solution was a little higher than that in the organic phase. Fine crystals made in the aqueous solution had better purity for lauric acid than the solvent-free mole fraction of lauric acid in the aqueous solution. The effects of the mole fraction of ethanol in the aqueous solution, the mole fraction of lauric acid in the organic solution, extraction temperature and crystallization temperature on the purity of the crystals were reported.

*Key words* : Crystallization, Extraction, Liquid-Liquid-Solid-Equilibria, UNIFAC, Fatty Acid

### INTRODUCTION

An anti-solvent has been used in a homogeneous solution for precipitation process [Myerson, 1993]. Once large amount of anti-solvent would be added to the solution, the solution will naturally separate and introduce two liquid phases, as crystals are produced in the two liquid phases. In the extraction process, the phase separation is easy generally. However, the separation factor of the mixed solutes between the two liquid phases are not so good. On the other hand, in the crystallization process, solid-liquid separation is difficult generally, even though the separation factor of the solutes is extremely good thermodynamically. If we can use both advantages of extraction and crystallization, an effective separation process can be expected. Partially miscible liquids have been used for extraction processes such as solvent-extraction [King, 1980]. Two liquid phases have also been applied for a few crystallization processes. The two liquid phases in crystallization process play intermediate roles of displacement of mother liquor [Sun, 1971], agitation solvent and coolant. Davey et al. recently has investigated the organic crystals in the aqueous solution with emulsified liquids.

The purpose of this study is to recognize the possibility of crystallization using two liquid phases, and to examine the separation of fatty acids by crystallization using two liquid phases.

### PHASE DIAGRAMS

Isothermal solid-liquid equilibria (SLE) and liquid-liquid equilibria (LLE) for the water+ethanol+lauric acid system were described by the UNIFAC model [Reid et al., 1987] using the LLE parameters [Magnussen et al., 1981] in Fig. 1. Water is an anti-solvent for lauric acid solute. Only the binary solution of

water+lauric acid is partially miscible. The height of the pillar shows the temperature. The LLE plotted by both an organic bi-

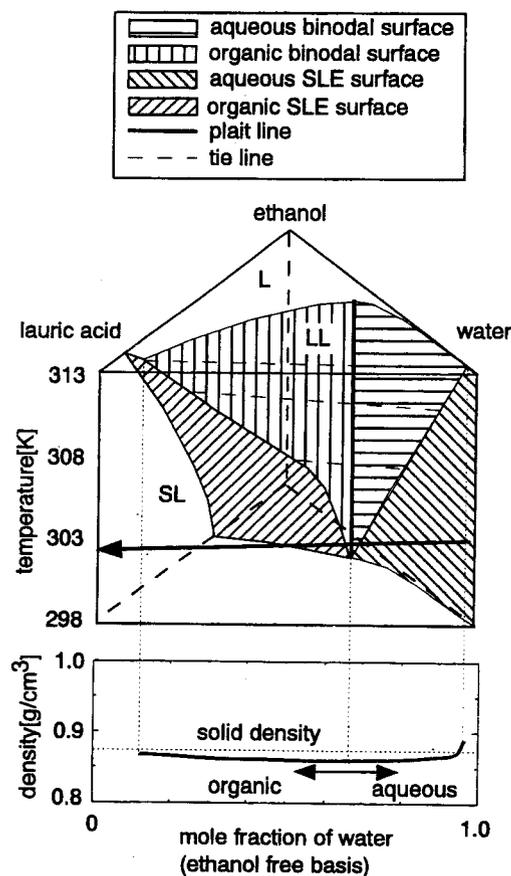


Fig. 1. Triangle pillar of liquid-liquid-solid equilibrium for the water+ethanol+lauric acid system.

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nodal surface and an aqueous binodal surface exists in large region at a high temperature, and the region of two liquid phases decreases as temperature decreases. The organic SLE surface and the aqueous SLE surface become large as temperature decreases. The aqueous SLE surface is not familiar because it exists in the aqueous solution where the solute is diluted extremely. The triangle pillar shows the four different phases. The first phase is a liquid phase (L), and the second phase indicates two liquid phases (LL). The third phase presents two phases of a liquid phase and a solid phase of lauric acid (SL). The fourth phase is the three phases of two liquid phases and a solid phase between the two SLE surfaces.

Removal of the crystals from a solution is used to be difficult by nature, therefore, the purity of the crystals is influenced by impurities in a surrounding liquid. Crystallization of hydrophobic organic solutes such as fatty acids in the aqueous solution is very attractive because the density difference between the organic crystals and the aqueous solution is very large, as shown in Fig. 1. The density was predicted by the modified Racket Equation [Reid et al., 1987]. In practical processes, the organic crystals will float on the aqueous solution. It will be easier to recover the crystals.

As considering the separation of mixed solutes, it is necessary to provide the quaternary phase diagram containing the two solutes. Fig. 2 shows the tetrahedron phase diagrams. The four apices are water, ethanol, lauric acid and myristic acid respectively. The upper diagram shows the two liquid phases at a high temperature above the melting temperatures of two fatty acids. As temperature decreases, two SLE surfaces of lauric acid and myristic acid appear in the organic phase, as shown in the lower diagram. The binary SLE for the lauric acid+myristic acid

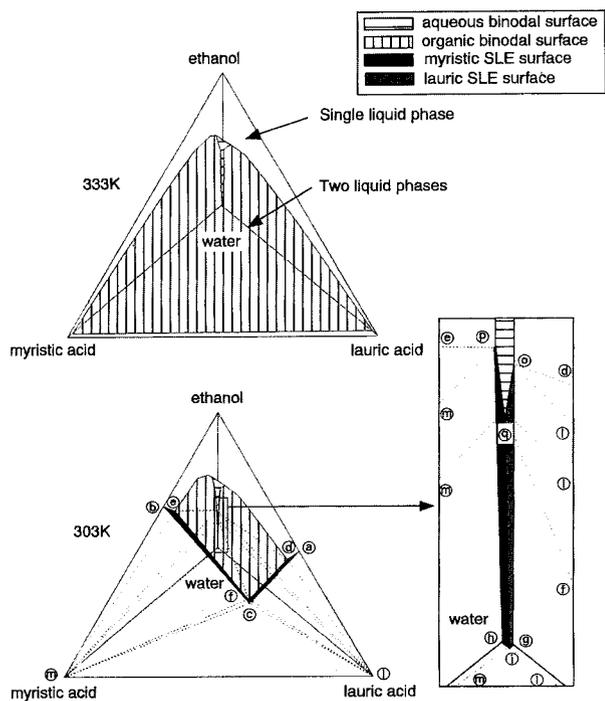


Fig. 2. Tetrahedron of liquid-liquid equilibrium and solid-liquid equilibrium for the water+lauric acid+myristic acid+ethanol system.

system is a simple eutectic system. Near the water apex, the two aqueous SLE surfaces of lauric acid and myristic acid exist, shown in detail. The space (l)-(a)-(c)-(f)-(d) produces a pure lauric acid, and the space (m)-(b)-(c)-(f)-(e) produces a pure myristic acid. Crystallization in those spaces are traditional methods. In the magnified diagram, the space (l)-(g)-(i)-(q)-(o) yields the pure lauric acid. The space (m)-(h)-(i)-(q)-(p) yields the pure myristic acid. Those SLE surfaces can distinguish a pure organic solute from the mixed organic solutes in the aqueous phase even though the solubilities of the organic solutes are very low in the aqueous phase. The crystallization process in those spaces have rarely examined.

EXPERIMENTAL

The GR grade reagents of lauric acid and myristic acid from Nacalai Tesque Co. were used as organic solute mixtures. The GR grade of ethanol from Nacalai Tesque Co. was used as a solvent. The distilled water was used as an anti-solvent. The schematic phase diagram in Fig. 3 shows illustrative procedures for extraction of fatty acids between the organic solution to the aqueous solution and for crystallization in the aqueous solution. The aqueous solution which contained ethanol in range of 0.01-0.05 mole fraction of ethanol ( $x^e$ ) was prepared with distilled water of 0.5 kg. 0.05 kg of fatty acids with known mole fraction of lauric acid ( $X^o$ ) was added to the aqueous solution. The mixture was heated to the extraction temperature ( $T_e$ , 323 K-

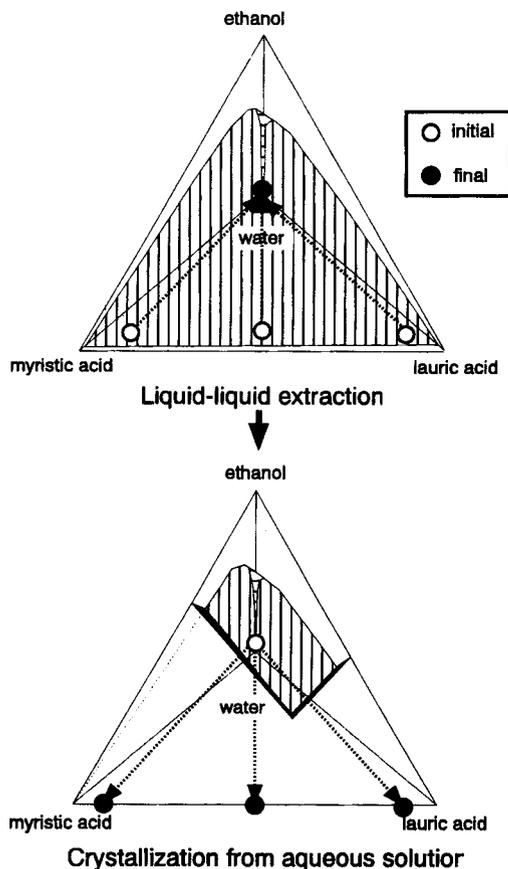


Fig. 3. Experimental procedures on the phase diagrams.

333 K), and then it was completely melted. The two liquid phases were achieved to LLE with 10 minutes agitation. The heterogeneous was left for two hours in order to separate and introduce two liquid phases again. The aqueous solution was taken out for four 0.02 L samples. One sample was used for the analysis of mole fraction of lauric acid in the aqueous solution ( $X^a$ ). The other samples were used for crystallization of the aqueous solution. The aqueous solution was cooling to the crystallization temperature ( $T_c$ , 303 K-293 K). The crystals in the aqueous solution were filtrated using an injection with filter. The remained crystals on the filter were dissolved by acetone. The mole fraction of lauric acid in the crystals ( $X^s$ ) was analyzed. The reproductivity of the mole fraction of lauric acid for three same experiments was less than 1%.

The effects of mole fraction of ethanol in the aqueous solution ( $x^e$ ), extraction temperature ( $T_e$ ) and crystallization temperature ( $T_c$ ) on the purity of the crystals were measured against three different mole fractions of lauric acid in organic phase ( $X^o$ ). The mole fractions of lauric acid in the aqueous solution ( $X^a$ ) and in the crystals ( $X^s$ ) were determined by a gas chromatography (GC8A, Shimadzu Co.). The mole fractions of lauric acid were indicated in water and ethanol free basis.

## RESULTS AND DISCUSSION

### 1. Liquid-Liquid Extraction

The mole fraction of lauric acid in the aqueous solution ( $X^a$ , water and ethanol free basis) is slightly different from the mole fraction of lauric acid in the organic phase ( $X^o$ , water and ethanol free basis). The relationship between  $X^a$  and  $X^o$  was shown in Fig. 4.  $X^a$  trended to be higher than  $X^o$ .  $X^a$  increased as the extraction temperature increased. The increase of the mole fraction of ethanol in aqueous solution made  $X^a$  increase.  $X^a$  became twice as much as  $X^o$  at  $X^o=0.11$ . This property means that lauric acid is easier to dissolve in aqueous phase than myristic acid. Here, we can conclude that the liquid-liquid extraction does not effectively separate the fatty acid mixtures.

### 2. Crystallization of Fatty Acids in Aqueous Solution

Once the homogeneous aqueous solution becomes two liquid phases of the aqueous solution and the organic solution, the fat-

ty acids are distributed in both the organic solution and the aqueous solution. The binodal surface slightly shifts to the large region as temperature decreases, and the solubility surfaces of fatty acids appear, as mentioned before. The crystals of fatty acids made in the aqueous solution were very fine. The crystals floated on the aqueous solution, because the density of fatty acid crystals was smaller than the density of the aqueous solution.

Purity of the crystals was defined as the mole fraction of lauric acid ( $X^s$ , water and ethanol free basis). When the fatty acids were crystallized in the aqueous solution at three different crystallization temperatures, the relationships between  $X^s$  and  $X^o$  at three different extraction temperatures were shown in Figs. 5-7. The increase of extraction temperature and the increase of the mole fraction of ethanol in the aqueous solution caused the purity of the crystals to increase. At  $X^o=0.89$  or 0.49,  $X^s$  became so high, as compared with  $X^a$ . At  $X^o=0.11$ ,  $X^s$  decreased from  $X^a$ . The aqueous solutions extracting fatty acids from the organic phases, which mole fraction of lauric acid were 0.89 and 0.49, crystallized lauric acid selectively. However, the aqueous solution extracting fatty acids from the organic phase, which mole fraction was about 0.11, crystallized myristic acid selectively.

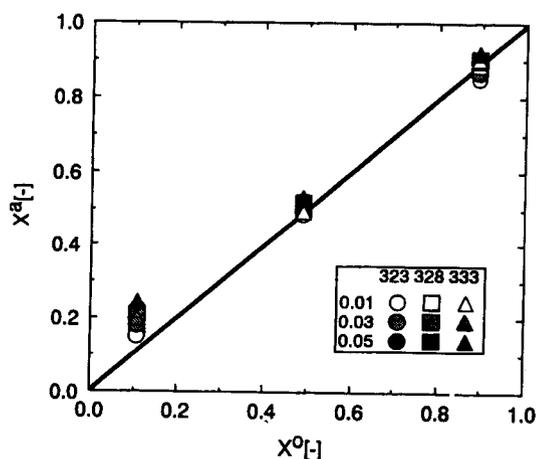


Fig. 4. Distribution of fatty acids from organic phase to aqueous phase.

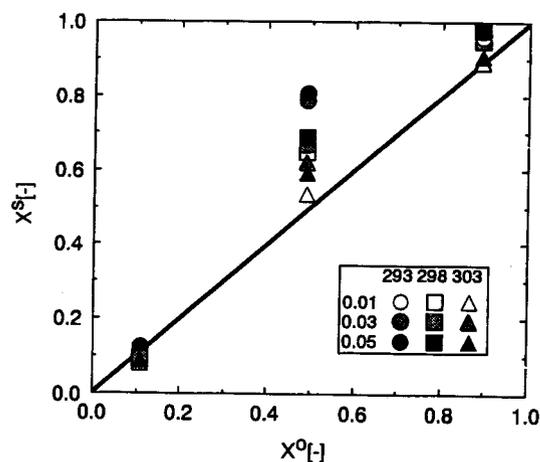


Fig. 5. Distribution of fatty acids from organic phase at 323 K to solid phase.

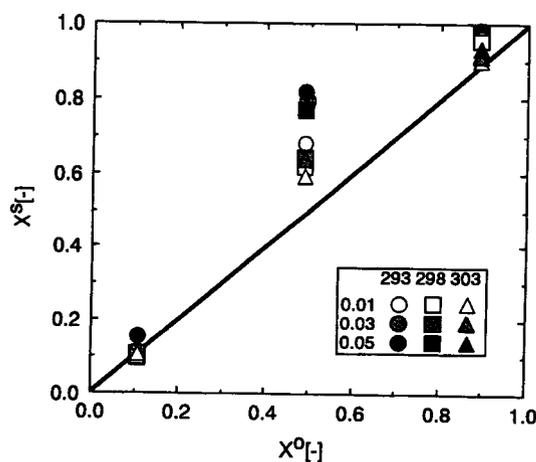


Fig. 6. Distribution of fatty acids from organic phase at 328 K to solid phase.

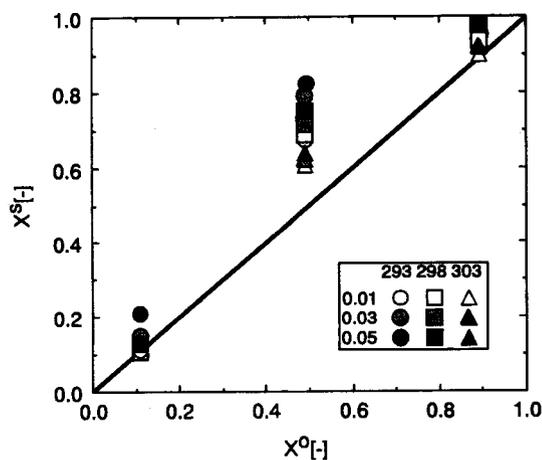


Fig. 7. Distribution of fatty acids from organic phase at 333 K to solid phase.

The crystallization temperature influenced the purity of the crystals strongly. When temperature increased, the purity of the crystals decreased considerably. As the results of the crystallization in the aqueous solution, the operating conditions (high extraction temperature, low crystallization temperature and much ethanol mole fraction in the aqueous solution), which produce more yield of the crystals, caused the purity of the crystals to be higher. It was found that the crystallization in the aqueous solution was more effective for the separation of fatty acids than only the liquid-liquid extraction.

The crystallization in the aqueous solution proposes two improvements. One improvement is that the organic crystals float on the aqueous solution. Another is that the organic hydrophobic crystals prevent the impurities in the solution from entering into the crystals.

### CONCLUSIONS

The crystallization method using two liquid phases was sug-

gested on base of the phase behavior. The crystallization of fatty acids combined with the liquid-liquid extraction was examined experimentally. It was found that the crystals of fatty acids could be produced in the aqueous solution. The crystals made in the aqueous solution were very fine, and they floated on the aqueous solution. The purity of the crystals was higher than purity of the aqueous solution which extracted fatty acids from the organic phase.

### NOMENCLATURE

- $T_e$  : extraction temperature [K]  
 $T_c$  : crystallization temperature [K]  
 $x^e$  : mole fraction of ethanol in aqueous phase [-]  
 $X^O$  : mole fraction of lauric acid in organic phase (water and ethanol free basis) [-]  
 $X^a$  : mole fraction of lauric acid in aqueous phase (water and ethanol free basis) [-]  
 $X^S$  : mole fraction of lauric acid in the crystals (water and ethanol free basis) [-]

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