

Separation of acetonitrile from pharmaceutical wastewater using solvent extraction

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1. Introduction

Acetonitrile is an important compound in the chemical industry, especially used in the pharmaceutical industry, and is generally produced as a by-product of acrylonitrile. Since the price of acetonitrile is unstable due to demand fluctuation of acrylonitrile and most of acetonitrile used in the pharmaceutical industry has been discharged, the recovery and recycle of acetonitrile is recently attracting much attentions. On the other hand, acetonitrile forms an azeotropic mixture with water [1] and it is impossible to separate the mixture by the ordinary distillation. Then, some separation methods have been studied, such as pressure swing distillation [2], extractive distillation, solvent extraction [3], and so on.

In this study, the application of the solvent extraction to recovery of acetonitrile from pharmaceutical wastewater was studied. Then, the liquid-liquid equilibrium was experimentally measured with hydrocarbons as solvent and the recovery of acetonitrile was investigated.

2. Experimental

Heptane and toluene were selected from alkane and aromatic compounds, respectively, and used as solvents. The experimental conditions of liquid-liquid equilibrium measurements were listed in **Table 1**. In advance, the aqueous solution at the specified mass fraction of acetonitrile and the mixture of heptane and toluene at the specified ratio were prepared, and they were contacted in the conical flask at 298 K in the isothermal bath for 48 hours to be equilibrated. The mass ratio of the feed and solvent was fixed at unity. After equilibration, both phases were analyzed by gas chromatograph GC2010 and Karl Fischer titrator 758 KFD Titrimo to determine the compositions of both phases. In cases of analysis of the aqueous solution by Karl Fischer titrator, it was occasionally difficult to determine the mass fraction of water, and then it was calculated using the mass balance relationship.

Table 1 experimental conditions

Shaking	[h]	48
Settling	[h]	1
Shaking temperature	[K]	298
Acetonitrile aq.	[-] (mass fraction)	0.1~0.9
Solvent (Heptane: Toluene)		1:0, 3:1, 1:1, 1:3, 0:1
Solvent/Feed ratio	[-]	1
Mass (respectively)	[kg]	2.0×10^{-2}

3. Results and Discussion

In Water-Acetonitrile-Heptane-Toluene ternary and quaternary system, basically it forms liquid-liquid 2 phases. But three liquid phases are formed when solvent is heptane 50, 75 %, feed is higher than acetonitrile mass fraction 40 %. Since it is said that industrial operation is difficult if it becomes three phases, these samples in three phases are not measured in this study. In addition, these didn't form emulsion, therefore it is easy to separate them. From these results, it was found that separation operation is possible.

Component i, j contains Water, Acetonitrile, Heptane and Toluene as W, A, Hp and T respectively. material balance is given by

$$\sum_i^N x_i = 1 \quad (1) \quad \sum_i^N y_i = 1 \quad (2)$$

$$R_0 x_{i,0} + E_0 y_{i,0} = R x_i + E y_i \quad (3)$$

where, E, R is each mass of extract phase and raffinate phase after extraction. E_0, R_0 is mass of feed solution and solvent. x_i is mass fraction in raffinate phase. y_i is mass fraction in extract phase. $x_{i,0}$ is initial mass fraction in feed, about component i .

Water in raffinate phase is calculated by equation (1). Regarding the extract phases, the mass fraction of acetonitrile are adjusted so that the total is 1, using equation (2). Using equation (3), Data is out of this equation a lot is removed.

Distribution coefficient m_i about component i , Separation selectivity $\beta_{i,j}$ of component i relative to component j is given by

$$m_i = \frac{y_i}{x_i} \quad (4)$$

$$\beta_{i,j} = \frac{m_i}{m_j} \quad (5)$$

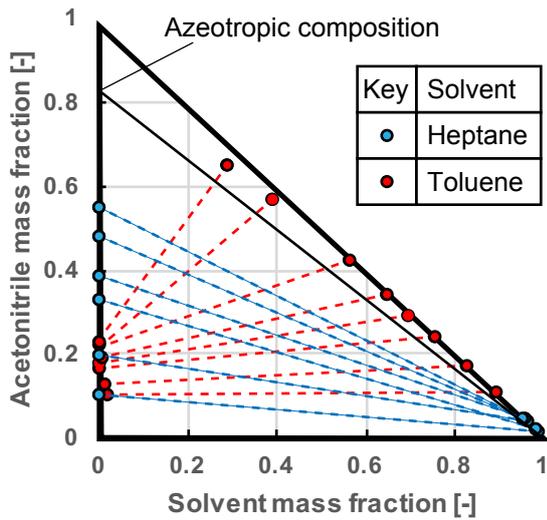


Fig. 1 Phase Diagram of Liquid-liquid equilibrium ternary system

Fig. 1 is phase diagram of Water-Acetonitrile-Solvent liquid-liquid equilibrium. In Water-Acetonitrile-Heptane ternary system, it is found that it has solubility for heptane and acetonitrile, heptane and water. In Water-Acetonitrile-Toluene ternary system, It is found that only toluene and water have solubility. In addition, the azeotropic composition in the case of removing the solvent is indicated by a black solid line in the figure. It was suggested that it is possible to exceed the azeotropic composition after the extraction operation with any solvent.

Fig. 2 shows effects of Initial feed mass fraction of acetonitrile to the distribution coefficient of acetonitrile with solvent of mixture heptane and toluene. The more Toluene mass fraction is in solvent, the higher m_A is. It is thought that the reason for this is that toluene has a higher polarity than heptane, acetonitrile also relatively high polarity, so more acetonitrile moves extract phase. And, effect of x_A was not clear.

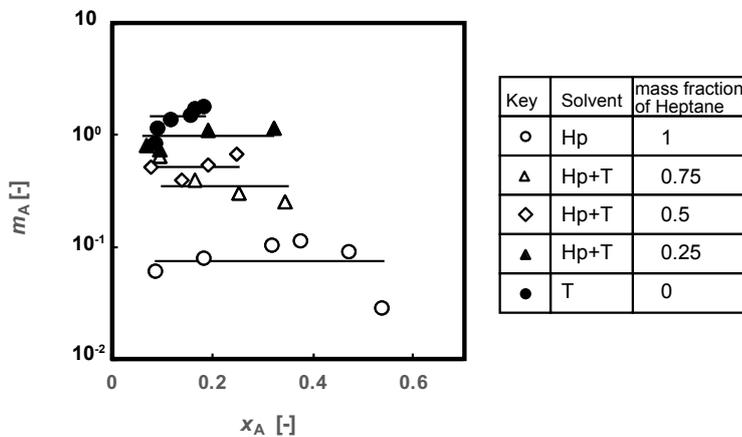


Fig. 2 Distribution coefficient of acetonitrile with solvent of mixture heptane and toluene

Fig. 3 shows separation selectivity of acetonitrile compare to water with solvent of mixture heptane and toluene. For heptane 100% solvent, when $x_{A,0}$ is 0.1 and 0.2, the mass fraction of water reached 10 ppm order, so it cannot measured.

The more Heptane mass fraction is in solvent, the higher $\beta_{A,W}$ is. Moreover, Any solvent $\beta_{A,W}$ decrease as $x_{A,0}$ rises. It is thought that the reason for those features is the large effect of the distribution coefficient of water.

4. Conclusion

From the results, it was found that acetonitrile could be separated from water using solvent extraction.

The distribution coefficient of acetonitrile increased as the polarity of solvent increased.

On the other hand, the selectivity of separation of acetonitrile against water decreased as the polarity of solvent increased.

5. Reference

- [1] J. Gmehling, J. Menke, et al. Azeotropic Data for Binary Mixtures, (1994).
- [2] Repke J U, Klein A, et al. Pressure swing batch distillation for homogeneous azeotropic separation[J]. Chemical Engineering Research and Design,85(4):492-501, (2007).
- [3] Acosta J, Rodríguez I, et al. Recovery of acetonitrile from aqueous waste by a combined process: Solvent extraction and batch distillation Sep. Purif. Technol. 2006, 52, 95– 101, (2006)

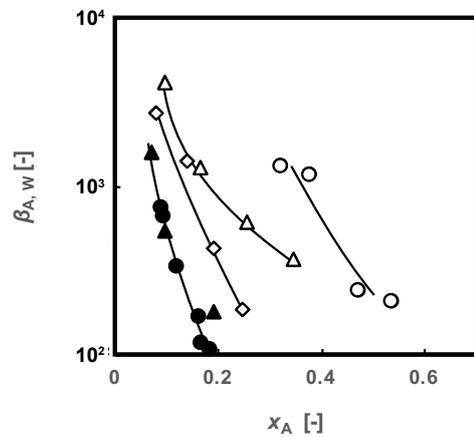


Fig. 3 Separation selectivity of acetonitrile compare to water with solvent of mixture heptane and toluene