LIQUID-LIQUID EQUILIBRIUM FOR SEPARATION OF ACETONITRILE FROM PHARMACEUTICAL WASTEWATER BY EXTRACTION WITH HYDROCABON SOLVENT

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1. Introduction

Acetonitrile is one of the important compounds in the chemical industry, produced by the Sohio process as a byproduct of acrylonitrile production, but contains only 3% of acrylonitrile. Especially in pharmaceutical industry, acetonitrile needs to concentrate more than 99.9% for feed of chemical products or solvent of chemical analysis. While the demand for acetonitrile is increasing, the production of acetonitrile is largely dependent on the production of acrylonitrile, so the supply is shortage on the demand. Therefore, the recovery of acetonitrile from pharmaceutical wastewater has attracted attention. In other hand, it is difficult to separate by ordinary distillation because acetonitrile and water form azeotropic mixture. Then, some separation method have been studied, such as extractive distillation, pressure-swing distillation [1], solvent extraction by hydrocarbons [2] and so on. However the solvent extraction using hydrocarbon solvents has not been sufficiently studied and needs to be studied.

The objective of this study was to recover of acetonitrile from pharmaceutical wastewater by solvent extraction using hydrocarbons based on liquid-liquid equilibrium. So liquid-liquid equilibrium using hydrocarbons solvent was measured and estimated with an activity coefficient estimation model. And acetonitrile recovery process using hydrocarbons solvent was studied.

2. Experimental and calculations
2.1. Materials

Acetonitrile aqueous solution as a model wastewater was used as an aqueous phase, and hydrocarbon solvents, toluene and heptane, as an oil phase. Toluene and heptane were selected as a typical aromatic carbon and alkane, respectively. The physical properties of these materials are shown in Table1.

Table1 Physical properties of materials

Component	Molecular formula	Boiling point[K]	Density [kg/L]
Acetonitrile(AN)	CH_3CN	354.75	0.786
Toluene(Tl)	$C_6H_5CH_3$	383.78	0.867
Heptane(Hp)	C_7H_{16}	371.15	0.680

2.2. Experiment

Table2 shows the experimental conditions for liquid-liquid equilibrium. The aqueous phase and the oil phase components were brought into contact in the same Erlenmeyer flask and shaken for 2 days in a thermostatic shaking bath. After shaking, the phases were separated in a separating funnel. The components of each liquid phase were analyzed by gas chromatography (GC-2010) and by a Karl Fischer titrator.

Table2 Conditions of experiment of liquid-liquid equilibrium

Feed		Aqueous solution of AN
Mass of feed	[g]	20
Mass fraction of acetonitrile in feed	[-]	0.00-1.00
Solvent		Mixture solution of Tl and Hp
Mass fraction of toluent in solvent	[-]	0.00-1.00
Mass of ratio of solvent to feed	[-]	1
Temperature, T	[K]	298-308
Shaking time	[h]	48
Setlling time	[h]	1

2.3. Calculations

To estimate each liquid-liquid equilibrium, UNIFAC model, one of the activity coefficient estimation model was used [3]. UNIFAC model is a theory that considers a molecule as a set of functional groups and functional group interaction instead of molecular interaction. Unlike other activity coefficient models, it is possible to estimate many activity coefficients with a small number of parameters. The logarithmic value of the activity coefficient of component i in the mixture γ_i is shown as

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \qquad (1)$$

γ_i^C is combinatorial part, a term in which the size and shape of the component i take into account the contribution to the activity coefficient and γ_i^R is residual part, is a term that the interaction between functional groups contributed to the activity coefficient. These were shown simply by function as

$$\ln \gamma_i^C = f(\nu_k, R_k, Q_k, X_i) \qquad (2)$$
$$\ln \gamma_i^R = g(Q_k, X_i, a_{m,n}, T) \qquad (3)$$

where ν_k ,always an integer, is the number of group of type k. R_k and Q_k are group volume parameter and group area parameter of type k, respectively. X_i is liquid phase group fraction in molecule i. $a_{m,n}$ is group-interaction parameters between groups m and n. Table3 showed the functional groups in the components used in this study and their numbers. Table4 showed R_k and Q_k. X_i and T were decided by experimental conditions. So only determination of group-interaction parameters $a_{m,n}$ enables estimation by UNIFAC model.

Table3 Number of functional groups in studied components

Component	Used functional group
Acetonitrile(AN)	$CH_3CN \times 1$
Water(W)	$H_2O \times 1$
Toluene(Tl)	$ACH \times 5$, $ACCH_3 \times 1$
Heptane(Hp)	$CH_3 \times 2$, $CH_2 \times 5$

Table4 Volume and area parameters

k	R_k	Q_k
CH_3	0.9011	0.8480
CH_2	0.6744	0.5400
ACH	0.5313	0.4000
$ACCH_3$	1.2663	0.9680
H_2O	0.9200	1.4000
CH_3CN	1.8701	1.7240

3. Results and discussion

3.1. Relationships

The distribution ratio of components i, m_i, was defined as,

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

where x_i and y_i denote the mass fractions of component i in the raffinate phase and extract phase at equilibrium, respectively. The separation selectivity of acetonitrile relative to water, $\beta_{AN,W}$, was defined as,

$$\beta_{AN,W} = \frac{m_{AN}}{m_W} \qquad (5)$$

Group-interaction parameters $a_{m,n}$ was determined to minimize difference between experimental data and an estimation of UNIFAC model.

3.2. Binary system

Acetonitrile and toluene formed 1 liquid phase for all compositions under experimental conditions. Figure1 showed mutual solubility of acetonitrile-heptane with temperature. Circle plots and blue dotted line showed experimental data and an estimation by UNIAC model, respectively. The mutual solubility of the acetonitrile-heptane was increased with increasing temperature. Acetonitrile and heptane formed 2 heterogeneous liquid phases under experimental conditions. Table5 showed mutual solubility of water-hydrocarbons. Mutual solubility was higher used toluene as solvent than heptane. Mass fraction of water in solvent were lower than mass fraction of solvent in water. A red part in Table6 showed a summary of group-interaction parameters can be determined by mutual solubility.

3.3. Ternary system

Figure2 and 3 showed acetonitrile-water-toluene or heptane system at 298K, respectively. Circle and square plots showed experimental data in this and previous study, respectively, and red line showed estimation by UNIFAC model. Dotted line showed tie line, black is experimental
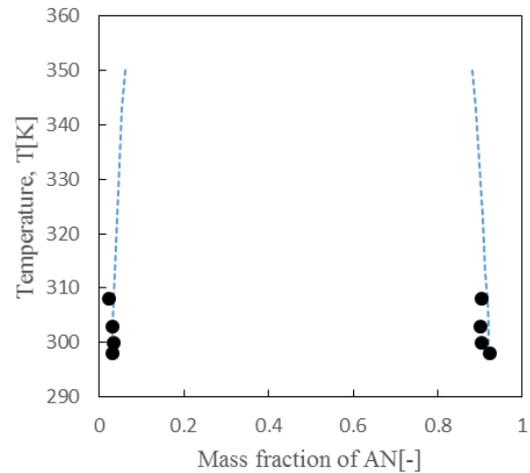

Fig.1 Mutual solubility between Hp and AN

Table5 Mutual solubility between W and solvent at 298K

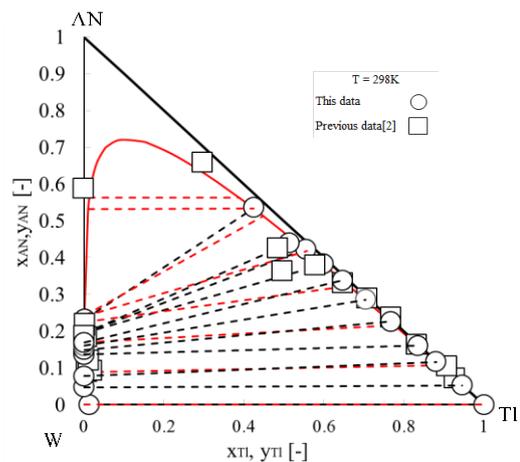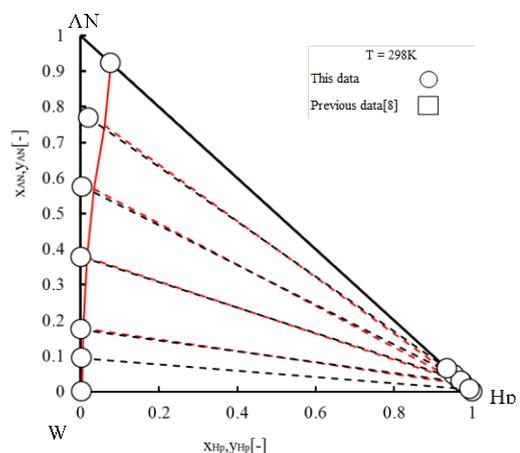| Solvent	Mass fraction of W in solvent[-]	Mass fraction of solvent in W[-]
Hp	0.00010	0.00311
Tl	0.00016	0.01394

Fig.2 Phase diagram of AN-W-Tl

Fig.3 Phase diagram of AN-W-Hp

data and red is estimation by UNIFAC model. Toluene and feed where the mass fraction of acetonitrile was over 0.90 formed 1 liquid phase and it is difficult to operate solvent extraction using toluene solvent. Compared to previous data, the tendency was similar to the experimental data in this study and matched the estimation by UNIFAC model. A blue part group-interaction parameters in Table6 was determined by this experimental data in Fig.2. On the other hand heptane and feed formed 2 heterogeneous liquid phases within experimental condition. So it enables to operate solvent extraction using heptane solvent.

3.4. Quaternary system

Figure4, 5 and 6 showed relation of mass fraction of acetonitrile in raffinate phase with mass fraction of acetonitrile in extract phase, distribution ratio of acetonitrile and the separation selectivity of acetonitrile to water. Circle and square plots showed experimental data in this study and previous, respectively and dotted lines showed the estimation by UNIFAC model. Difference of color showed difference of mass fraction of toluene in hydrocarbons solvent. Above mass fraction of toluene in solvents was 0.75, it become one phase liquid with high concentration of acetonitrile solution. When mass fraction of toluene in solvents was 0.5 and 0.25, it become three phase liquid because acetonitrile phase probably formed between water and oil phases. So that components of three phase cannot be analyzed. The acetonitrile in feed moved to the extraction phase and the distribution ratio of acetonitrile increased and the separation selectivity of acetonitrile to water was increased as increasing mass fraction of toluene in solvent. That' because a polarity was increased as the mass fraction of toluene increased in the solvent. However part of the separation selectivity were dispersed. This is probably because the concentration of heptane in the solvent increased, and it became difficult to measure the water in the solvent. Except used heptane as solvent, the separation selectivity was almost no change in estimation by UNIFAC model. Group-interaction parameter of green part in Table6 were determined by these data.

Table6 Group-interaction parameter

a_{mn}		n				
		CH$_3$	ACH	ACCH$_3$	H$_2$O	CH$_3$CN
m	CH$_3$	0	-180	-140	1505	550.5
	ACH	500	0	700	930	200
	ACCH$_3$	555	100	0	875	500
	H$_2$O	100	470	450	0	225
	CH$_3$CN	47.65	400	-75	125	0

3.5. Process

Figure7 shows general solvent extraction process for recovery of acetonitrile from pharmaceutical wastewater. Feed is aqueous solution of acetonitrile This process consisted an extractor and a distillation column for solvent recovery. The solvent must form heterogeneous 2 liquid phases with pure acetonitrile in enriching section between feed entry point and the top of extractor. On the other hand, the solvent had better has high solubility of acetonitrile in
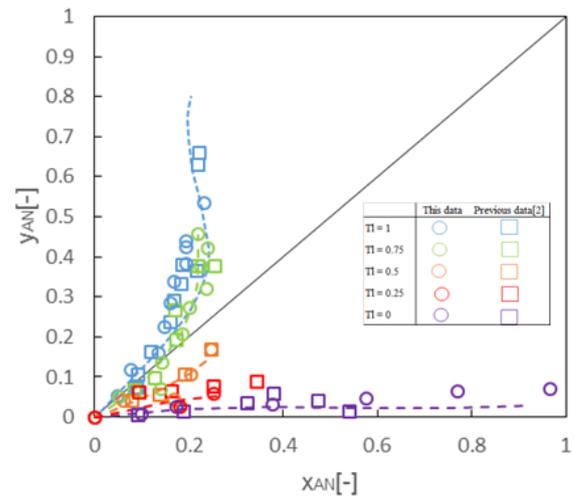

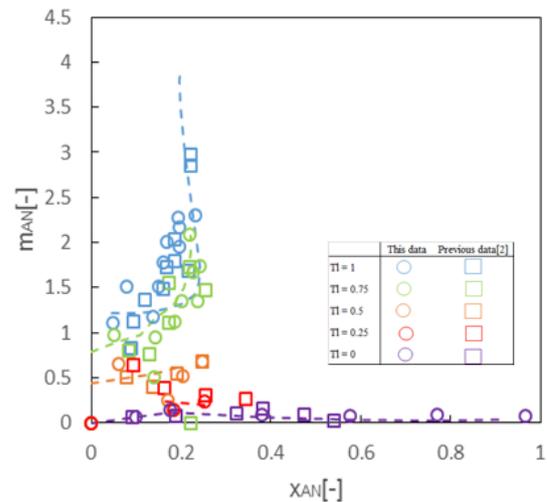Fig.4 Relation of mass fraction of AN between raffinate and extract phase

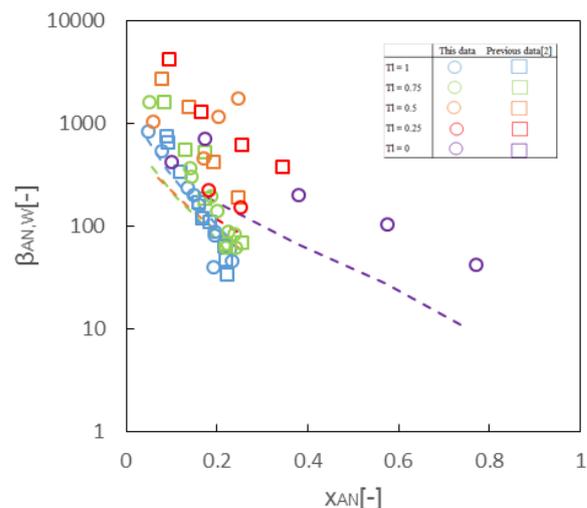Fig.5 Relation of mass fraction of AN in raffinate phase with AN distribution ratio

Fig.6 The separation selectivity of AN to W

the stripping section than feed entry to reduce acetonitrile flowing out as a raffinate product. However if the solvent has a high mass fraction of toluene, it may become 1 liquid phase in the concentration section. Conversely if the solvent has a high mass fraction of heptane, it requires much solvent. For these reasons, figure8 shows solvent extraction process using 2 hydrocarbon solvents for recovery of acetonitrile. This process consisted of 2 extractors for stripping (Extraction1) and enriching (Extraction2), and 2distillation columns for solvent recovery. 2 extractors brought feed and solvent into contact with countercurrent. It is better to use a solvent in Extraction1 with a high mass fraction of toluene, which has a high distribution ratio of acetonitrile. On the other hand, it is better to use a solvent in Extraction2 with a high mass fraction of heptane, which has a high separation selectivity of acetonitrile to water and form heterogeneous 2 liquid phases with pure acetonitrile. Therefore, it is expected to be process efficiency by using 2 hydrocarbon solvents.

4. Conclusions

To recovery acetonitrile by from pharmaceutical wastewater by extraction using hydrocarbons solvent in this study, and the following conclusions were drawn from the results.

Acetonitrile and heptane formed 2 heterogeneous liquid phases. And the distribution ratio of acetonitrile m_{AN} was increased and the separation selectivity of acetonitrile to water $\beta_{AN,W}$ was decreased as the mass fraction of toluene in solvent was increasing.

UNIFAC model enabled to estimate for liquid-liquid equilibrium roughly.

It was expected to be performance efficiency by using 2 hydrocarbons solvent process.

Nomenclature
AN = acetonitrile, W = water, Tl = toluene, Hp = Heptane, γ = activity coefficient, γ^C = combinatorial part, γ^R = residual part, ν = the number of group, R = group volume parameter, Q = group area parameter, X = liquid phase group fraction, T = temperature, a = group-interaction parameter, x = mass fraction of raffinate phase, y = mass fraction of extract phase, m = distribution ratio, β = selectivity,

Subscript
k = group of type, i = component, m = functional group, n= functional group

Reference
[1] Xu Jierui, Bachelor Theses, "Recovery of Acetonitrile from Pharmacy Factory Wastewater by Distillation Process", Tokyo Institute of Technology (March, 2018)
[2] Kaito, Sawada, Bachelor Theses, "Separation of Acetonitrile from Pharmaceutical Wastewater Using Solvent Extraction", Tokyo Institute of Technology, (March, 2019) .

[3] Fredenslund Aage "Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures", AIChE Journal vol.21 p1086-1099(1975).
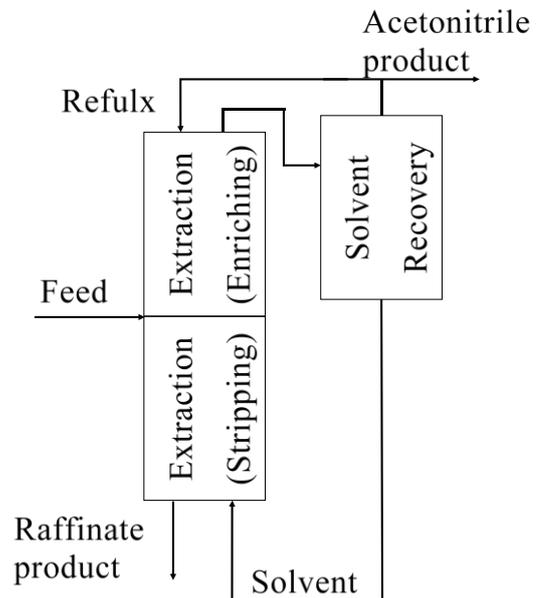
Fig.7 Recovery of acetonitrile process
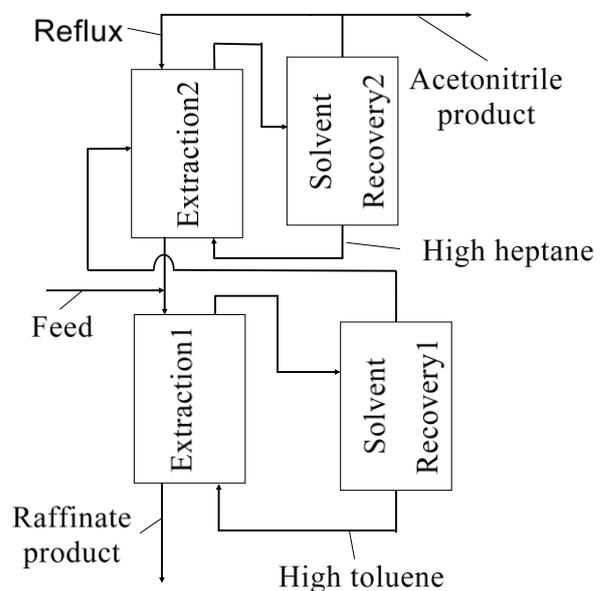using a hydrocarbons solvent

Fig.8 Recovery of acetonitrile process
using 2 hydrocarbons solvents