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Recovery of Picolinic Acid from Aqueous Streams Using a Tertiary Amine Extractant

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ABSTRACT: Solvent extraction using an extractant/diluent system was determined for the recovery of picolinic acid. Trioctylamine (TOA) was used as the extractant and alcohols (isoamyl alcohol and 1-hexanol), esters (ethyl acetate and propyl acetate), and hydrocarbons (*n*-heptane and toluene) as the diluents. TOA gives a complex with the acid resulting in an acid−amine complex which is solvated by the diluents. On the basis of results from batch extraction experiments, a mass-action analysis was introduced for modeling extraction. The experimental results of batch extraction experiments are reported as distribution coefficients, ($K_D = (C^*_{PA}/C_{PA})$), loading factors, Z, and extraction efficiency, E. The highest synergistic extraction efficiency was found to be 96.620 for the TOA + isoamyl alcohol extractant system with a K_D value of 28.587 and Z value of 0.588.

INTRODUCTION

Aqueous streams containing organic acid chemicals are present in many industrial processes. The production of organic acids in aqueous solutions is typical when using electrochemical and biochemical synthetic methods.[1,2] Besides being valuable, desirable products which need to be recovered from the reaction broths, very often organic acids cause contamination of the environment.

Reactive extraction, as a method for the recovery of organic acids from aqueous solutions, has received increasing attention over the past decades. Up to now, there are a large number of papers mainly focusing on carboxylic acids, amino acids, and phenols by using extractants such as tertiary amine and hydrogel.[3−24] Acids and phenols are extracted mainly with different kinds of amines and ammonium salts, hydrogels, or organophosphorus extractants or their synergistic mixtures. Among these studies, Senol[4] has pointed out the distribution of picolinic acid between a mixture of tertiary aliphatic amines and water dissolved in versatile diluents such as alcohols, alkanes, cyclic alkanes, haloalkanes, ketones, and nitro diluents.

Herein, the reactive extraction of carboxyl acids is considered. Carboxyl acids are compounds very frequently processed in the chemical and pharmaceutical industry. Because of their moderate polarity, they are often found in aqueous streams from which they need to be recovered. As a typical example, benzoic acid is a widely used chemical in most industries and thus one of the major components present in the wastewater from the most industries. Because of azeotrope formation, its recovery from the aqueous solution by distillation is not very feasible, putting forward the need of developing a suitable liquid−liquid extraction system.[25] The other example is the production of ethanol by fermentation. Since it inhibits the fermenting micro-organisms, it needs to be removed from the reaction broth.[26,27]

In this research the reactive extraction of carboxyl acids with tertiary amines (TOA) is explored. When contacted, carboxyl acids and tertiary amines reversibly react to form a relatively stable complex (Figure 1). To prevent potential loss of the extractant to the water phase, an amine with a large apolar organic tail should be chosen. In the present work, the extraction capability of TOA toward picolinic acid is investigated. The influences of the process parameters such as initial concentration of amine as well as the effect of diluents on the extraction equilibrium are investigated.

THEORETICAL SECTION

The extraction of picolinic acid (HA) with trioctylamine (R_3N) can be described by the following reaction.

$$\mathrm{HA}(1) + {}^*\mathrm{R_3N}(2) \leftrightarrow {}^*(\mathrm{HA})\cdot(\mathrm{R_3N})(3) \qquad (1)$$

where HA represents the nondissociated part of the acid present in the aqueous phase and organic phase species are marked with an asterisk (*). Reaction 1 can be characterized by the overall thermodynamic extraction constant K.

The loading of the extractant, Z, is defined as the total concentration of acid in the organic phase divided by the total concentration of amine in the organic phase. The expression for Z can be written in the form

$$Z = C^*_{PA}/C^*_{TOA} \qquad (2)$$

In eq 2, C^*_{PA} is the total concentration of acid in the organic phase, $\mathrm{mol \cdot L^{-1}}$, and C^*_{TOA} is the total concentration of amine in the organic phase. The partitioning coefficients, K_D, for picolinic acid extracted from water into the organic phase were determined by eq 3 where C^*_{PA} is the total concentration of picolinic acidin organic phase and C_{PA} is the total concentration (dissociated and undissociated) of picolinic acid in aqueous phase at equilibrium.

$$K_D = C^*_{PA}/C_{PA} \qquad (3)$$

The efficiency of extraction, E, is expressed as

$$E = [1 - (C_{PA}/C_{PA0})]\cdot 100 \qquad (4)$$

where C_{PA} is the concentration of acid in the aqueous phase after

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Table 1. Results of Extraction of Picolinic Acid with Pure Solvents

			C^*_{PA0}	C^*_{PA}	C_{PA}		
	solvents	pH_{aq}	$mol \cdot L^{-1}$	$mol \cdot L^{-1}$	$mol \cdot L^{-1}$	K_D	E
alcohols	isoamyl alcohol	3.117	0.699	0.022	0.677	0.033	3.192
	1-hexanol	3.112		0.025	0.674	0.037	3.601
esters	ethyl acetate	3.163		0.042	0.658	0.063	5.914
	propyl acetate	3.103		0.021	0.678	0.032	3.056
hydrocarbons	*n*-heptane	3.129		0.012	0.687	0.017	1.690
	toluene	3.124		0.018	0.681	0.026	2.510

Table 2. Experimental Results of the Extraction of Picolinic Acid with Tertiary Amine/Solvents[a]

	C^*_{TOA}		C_{PA0}	C_{PA}			
solvents (alcohols)	$mol \cdot L^{-1}$	pH_{aq}	$mol \cdot L^{-1}$	$mol \cdot L^{-1}$	K_D	Z	E
isoamyl alcohol	0.230	3.938	0.699	0.385	0.814	1.363	44.860
	0.460	4.175		0.246	1.841	0.985	64.800
	0.690	4.497		0.135	4.161	0.817	80.624
	0.920	5.021		0.056	11.569	0.699	92.044
	1.148	5.122		0.024	28.587	0.588	96.620
1-hexanol	0.230	3.840		0.453	0.544	1.070	35.222
	0.460	4.187		0.243	1.871	0.990	65.170
	0.690	4.481		0.133	4.259	0.820	80.984
	0.920	4.919		0.041	16.125	0.715	94.160
	1.148	4.965		0.033	19.903	0.580	95.216
ethyl acetate	0.230	3.853		0.589	0.187	0.479	15.749
	0.460	4.056		0.295	1.366	0.877	57.728
	0.690	4.105		0.279	1.506	0.609	60.094
	0.920	4.111		0.266	1.629	0.471	61.956
	1.148	4.143		0.242	1.892	0.398	65.417
propyl acetate	0.230	3.673		0.553	0.265	0.636	20.940
	0.460	3.807		0.451	0.550	0.539	35.481
	0.690	3.858		0.432	0.618	0.387	38.194
	0.920	3.866		0.417	0.677	0.307	40.382
	1.148	3.888		0.397	0.761	0.263	43.201
n-heptane	0.230	3.151		0.661	0.058	0.167	5.506
	0.460	3.187		0.625	0.119	0.162	10.648
	0.690	4.243		0.623	0.123	0.111	10.918
	0.920	4.461		0.596	0.172	0.112	14.678
	1.148	4.480		0.584	0.196	0.100	16.417
toluene	0.230	3.277		0.663	0.054	0.155	5.099
	0.460	3.368		0.655	0.067	0.096	6.321
	0.690	3.460		0.627	0.114	0.104	10.244
	0.920	3.511		0.595	0.174	0.113	14.812
	1.148	3.591		0.592	0.181	0.093	15.347

[a] C^*_{TOA} is the concentration of TOA in the organic phase; pH_{aq} is the pH of the aqueous phase; C_{PA0} is the initial concentration of picolinic acid; C_{PA} is the concentration of picolinic acid in the aqueous phase after extraction; K_D is the distribution coefficient; Z is the loading factor, E is the extraction efficiency.

extraction and C_{PA0} is the initial concentration of acid in the aqueous phase.

EXPERIMENTAL SECTION

TOA ($M = 353.68\ g \cdot mol^{-1}$) (purity > 99 wt %), picolinic acid (purity > 98 wt %), and the solvents were purchased from Merck Co. (Darmstadt, Germany). All chemicals were used without further purification. Alcohols (isoamyl alcohol and 1-hexanol), esters (ethyl acetate and propyl acetate), and hydrocarbons (*n*-heptane and toluene) were supplied from Merck and Fluka.

Picolinic acid was dissolved in distilled water to prepare the solutions with initial concentrations of acid of 7.92 % (w/w) ($0.699\ mol \cdot L^{-1}$). The initial organic phases were prepared by

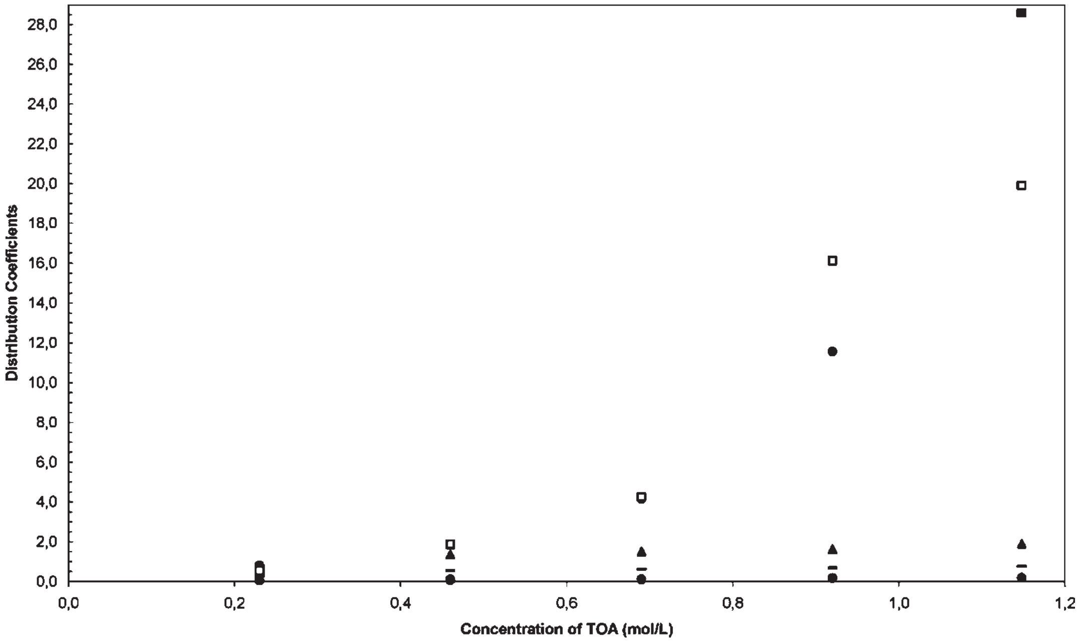

Figure 1. Variation of distribution coefficients with concentration of TOA in different individual diluting solvents: ■, isoamyl alcohol; □, 1-hexanol; ▲, ethyl acetate; —, propyl acetate; ○, *n*-heptane; ●, toluene.

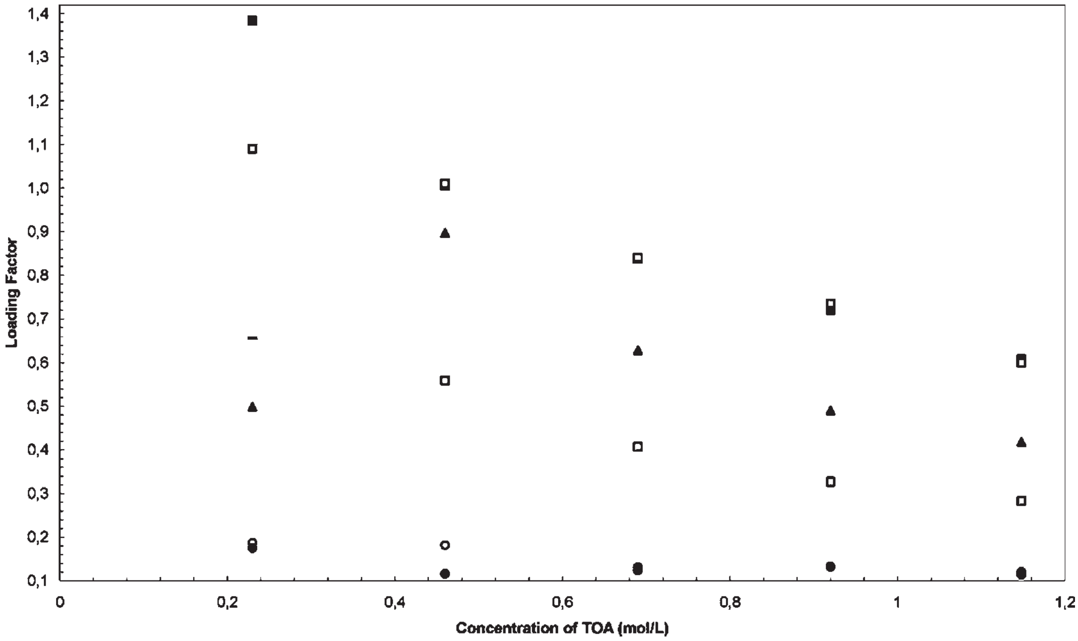

Figure 2. Variation of loading factor with the concentration of TOA in different individual diluting solvents: ■, isoamyl alcohol; □, 1-hexanol; ▲, ethyl acetate; —, propyl acetate; ○, *n*-heptane; ●, toluene.

the dissolution of TOA in the diluents to produce solutions with approximately constant concentrations. Liquid—liquid equilibrium experiments were conducted on an Erlenmeyer flask. The extraction was done in a closed 50 mL Erlenmeyer flask in which both aqueous solutions of a picolinic acid and organic phase (pure solvent or solvent enriched with TOA) were introduced. The concentration of TOA in diluents as an organic solvent was varied between (0 (pure solvent) and 1.148) $\text{mol}\cdot\text{L}^{-1}$.

After the introduction of both phases the Erlenmeyer flasks were agitated in a GFL shaker for 2 h at 25 ± 0.1 °C to ensure equilibrium. After agitation, the Erlenmeyer flasks were transferred into trays, and a settling time of at least 2 h was allowed and shown to be sufficient. After settling, samples of the aqueous phase were taken. The accuracy of the analytical method was determined to hold within 3 %.

The concentration of picolinic acid in the aqueous phase was determined by titration with aqueous 0.1 $\text{mol}\cdot\text{L}^{-1}$ sodium hydroxide (relative uncertainty 1 %) in the presence of phenolphthalein as the indicator. The organic phase was stripped from alkali solution and analyzed by checking against a material

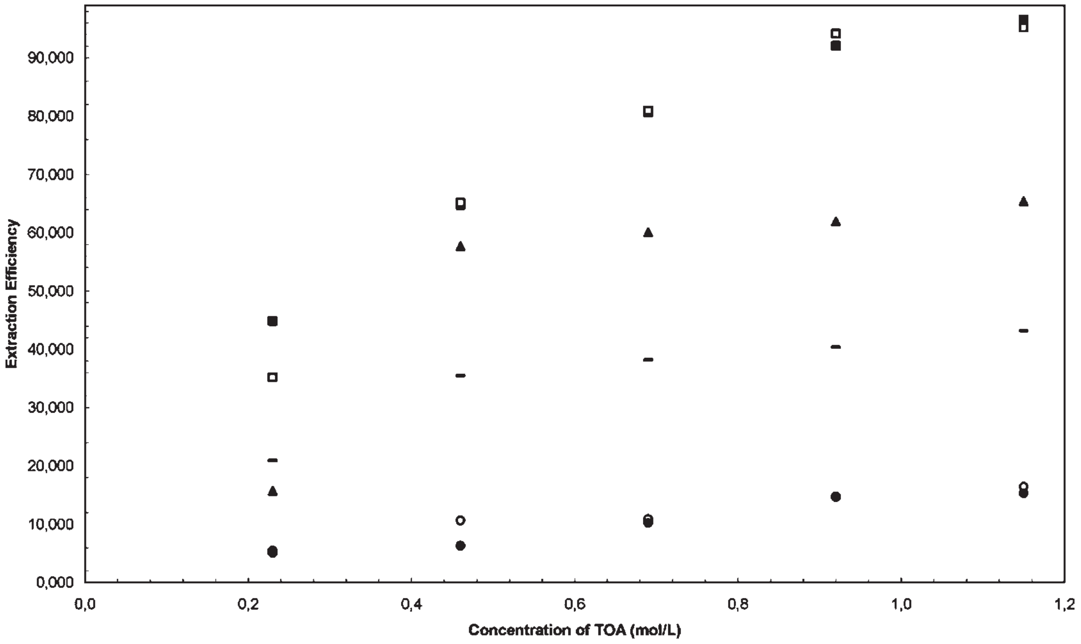

Figure 3. Variation of extraction efficiency with the concentration of TOA in different individual diluting solvents: ■, isoamyl alcohol; □, 1-hexanol; ▲, ethyl acetate; —, propyl acetate; ○, *n*-heptane; ●, toluene.

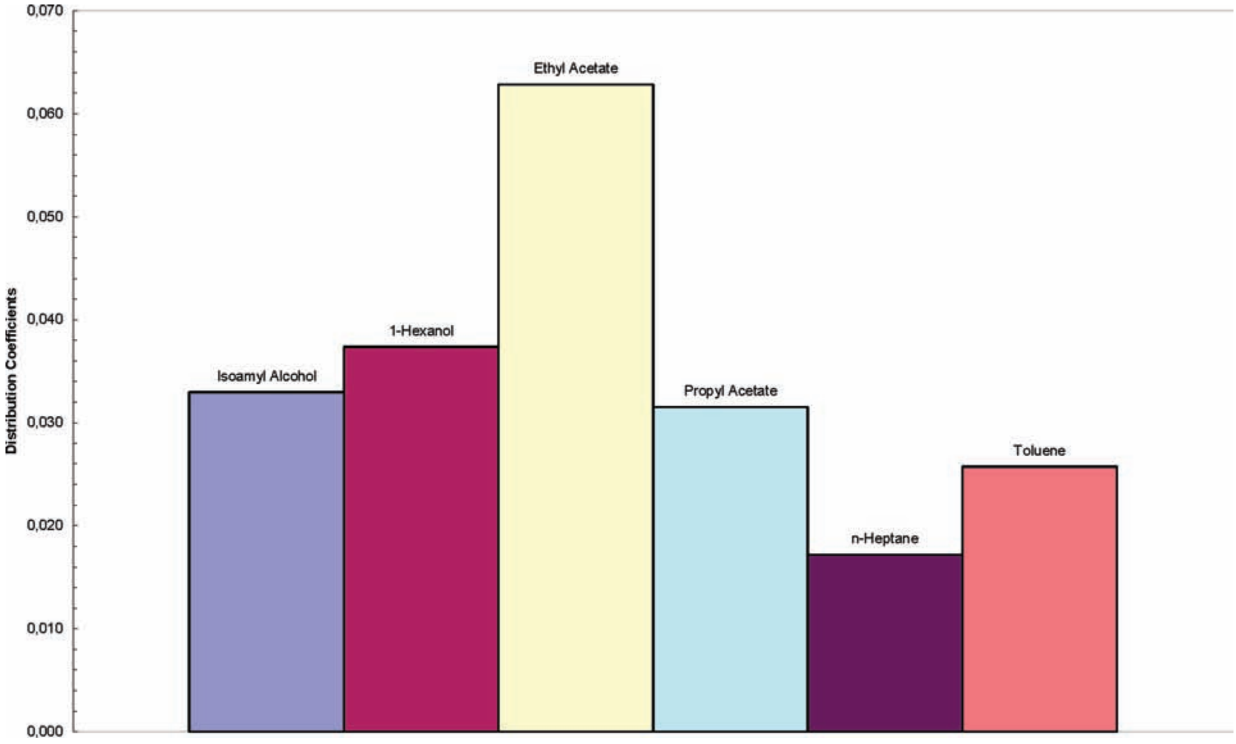

Figure 4. Distribution coefficients of picolinic acid between water and solvents used in this study.

balance. In most cases, the deviation between the amount of acid analyzed and the initial amount of acid was 3 %. In most cases, the deviation between the amount of acid analyzed and the amount of acid known by preparing the solutions by mass did not exceed 3+ %. The pH value of the aqueous phase was determined with a pH meter (Mettler Toledo pH meter) with the uncertainty of 1 %.

■ RESULTS AND DISCUSSION

The physical extraction of picolinic acid was studied for a better understanding of the amine effect on picolinic acid (reactive extraction). Table 1 presents the extraction of picolinic acid by pure solvents without TOA. In the diluent categories, alcohols more dominated than others since they have high polarity. The extraction of picolinic acid by TOA dissolved in alcohols (isoamyl alcohol and 1-hexanol), esters (ethyl acetate and propyl acetate), and hydrocarbons (*n*-heptane and toluene) were studied. Results of the equilibrium data on the reactive extraction of picolinic acid from aqueous phase to organic phase are presented in Table 2. The prepared constant concentrations of TOA in various solvents were between 0.230 $\mathrm{mol \cdot L^{-1}}$ and 1.148 $\mathrm{mol \cdot L^{-1}}$. The picolinic acid concentration in the initial aqueous phase was 0.699 $\mathrm{mol \cdot L^{-1}}$. It can be seen from Figure 1 that the extraction efficiency of the TOA−diluents mixture changes with increasing initial concentration of TOA in the organic phase. According to Table 2 and Figure 1, the distribution coefficients for picolinic acid extraction by TOA were obtained the following orders: alcohols > esters > hydrocarbons; in alcohols: isoamyl alcohol > 1-hexanol; in esters: ethyl acetate > propyl acetate; in hydrocarbons: *n*-heptane > toluene.

The highest extraction efficiency of picolinic acid has been found as 96.620 % using isoamyl alcohol at 1.148 $\mathrm{mol \cdot L^{-1}}$ initial concentration of TOA. The acid concentration in the organic phase at equilibrium C^{*}_{PA} increases from 0.012 $\mathrm{mol \cdot L^{-1}}$ to 0.675 $\mathrm{mol \cdot L^{-1}}$ with increasing concentration of TOA from 0.230 $\mathrm{mol \cdot L^{-1}}$ to 1.148 $\mathrm{mol \cdot L^{-1}}$. The distribution coefficient has increased from 0.017 to 28.587 with increasing initial TOA concentration among all of the diluents used in this study. Obviously, as can be seen from Table 2, the increase of amine concentration brings about gradual increase of extraction efficiency. At 1.148 $\mathrm{mol \cdot L^{-1}}$, the maximum values of 96.620 % and 95.216 % of the picolinic acid (for two diluents) are extracted with isoamyl alcohol and 1-hexanol, respectively.

Experimentally obtained values are presented in Figures 1 to 4. As the initial amine concentration increases, the distribution ratio increases, reaching very high values. For the lower initial concentration of amine the overall distribution ratios are lower. It can also be noticed that eq 3 gives a rather good fit of the experimental data. For esters, they are significantly lower, whereas the distribution ratios for hydrocarbons are the lowest. The distribution ratios of alcohols are the highest among the diluents.

CONCLUSIONS

The reactive extraction of picolinic acid by using TOA dissolved in three diluents was explored. The distribution coefficients, loading factors, and extraction efficiencies were obtained for this extraction system. The highest synergistic extraction efficiency was found for the TOA + isoamyl alcohol extractant system with the K_{D} value of 28.587. For the explanation of the experimental results a simple equilibrium model, taking into account both physical solubility and chemical reaction, is also explored.

A higher initial concentration of the amine results in a higher overall distribution ratio. On the other hand, for a higher initial concentration of amine, the loading factor ratio is lower. The overall extraction performance of the TOA depends highly on the molecular structure. It decreases in the following order: alcohols > esters > hydrocarbons.

In general, it can be stated that the developed reactive extraction with tertiary amines can be of a great interest especially for acids with a high affinity for water, that is, where the pure physical extraction is low.

Polar diluents have been shown to be more convenient diluents than inert ones (nonpolar), due to their higher distribution. However, active polar and proton-donating diluents such as alcohols have been shown to be the most suitable diluents for amines because they give the highest distributions resulting from the formation of solvates through specific hydrogen bonding between the proton of the diluents and the acid−amine complex.

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SYMBOLS AND ABBREVIATIONS

TOA = trioctylamine
HA = picolinic acid
K_{D} = distribution coefficient
Z = loading factor
C_{PA} = picolinic acid concentration $[\mathrm{mol \cdot L^{-1}}]$
C_{PA0} = initial concentration of picolinic acid $[\mathrm{mol \cdot L^{-1}}]$
E = extraction efficiency
aq = aqueous phase
* = organic phase

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