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Interfacial Kinetics of the Stripping of Acetic and Citric Acids from Tri-*n*-octylamine Complexes

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ABSTRACT

A rotating diffusion cell (RDC) was used to measure the kinetics of acetic and citric acids stripping from an organic solvent phase to water. It has been proved that the carboxylic acid transfer is rate controlled by a diffusion process. The rate constant for acetic acid was found to be $(3.43 \pm 0.18) \times 10^{-5}$ m·s^{-1} at 298 ± 0.1 K. For citric acid, the rate constant determined as a function of temperature was $k = (0.043 \pm 0.002)e^{-3680/T}$ for which the activation energy is 30.6 ± 1.0 kJ·mol^{-1}. The stripping resistance depends on the number of carboxylic acid groups in the acid and is largely entropic in nature.

INTRODUCTION

The importance of carboxylic acids in the fields of food, beverage, and pharmaceutical industries is well known. Many of these acids are used as buffers, plasticizers, protective coatings, and adhesives. Some of these

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acids are produced by fermentation of different raw materials, such as sugar, molasses, cell hydrolysate, etc. A major example is the citric acid production.

The high cost of chemicals and a big waste disposal problem during the separation of carboxylic acids from the aqueous fermentation broth by conventional methods have led researchers to look for reactive extraction methods. Many authors studied the extraction of carboxylic acids using different solvents. Baniel (1), Alter (2), Wennersten (3, 4), and Qader (5) reported a number of solvents and diluents for the recovery of these acids. Kertes et al. (6) and Tamada and King (7) discussed, listed, and reviewed many solvents. Yu-Ming et al. (8) studied the extraction equilibria of citric acid. Qader (5) reported extensive results and discussed the extraction of acetic, propionic, lactic, malic, and citric acids by phosphorous- and amine-based extractants.

Because long-chain tertiary amines are known to possess desirable qualities for the extraction of carboxylic acids, they have been chosen as the main extractant in this work. The extractant transfers the solute into the solvent phase by forming a complex with the functional group of the solute acid. The complexation is reversible so that the solute can be recovered by water from the extract after phase separation. The main extractant is generally mixed with a diluent and/or an organic solvent which imparts to the organic phase the desirable physical qualities that the extractant alone may lack. The optimal mixture for citric acid extraction consists of the following:

Tri-*n*-octylamine (TOA) as an extractant, 30% vol
Decanol as a modifier, 30% vol
Decane as a diluent, 40% vol

The above mixture has been confirmed by a set of phase equilibria experiments (5). This is in agreement with Bauer (9) that the three-component mixture using a tertiary amine as extractant yields better results when the ratio of modifier and extractant is 1:1.

Though efforts by many researchers have been directed toward a study of the reactive extraction mechanism for the recovery of carboxylic acids, the nature of the interfacial reaction has not been well understood due to lack of a direct interface observation method. Carboxylic acid transfer is considered to be a hybrid of "purely diffusive" and "interfacial reaction" systems, where the total mass-transfer rate is determined not only by the interfacial kinetics but also by diffusion of the reactant to the interface and diffusion of the products away from the interface. It is essential, therefore, to develop a measurement technique which measures kinetics where the influence of diffusion can be accounted for. The apparatus should operate either in a kinetically limited regime or allow calculation of the diffusional component of the overall mass-transfer rate. Accurate determination of the interfacial area must be a feature of any effective technique. The rotating diffusion cell (RDC), originally designed by Albery et al. (10), possesses that feature and is adopted in the present study.

Details of previous work on interfacial kinetics have been summarized by Qader (5). The main purpose of this study is to prove the mechanism and rate-determining role of stripping (reextraction) process. The kinetics of stripping of acetic and citric acids from the above-mentioned solvent phases to equilibrated water were investigated for different concentrations of acid in the solvent phase.

Acetic acid kinetics were first studied mainly to verify the technique as well as to determine the rate constant and the order of complexation reaction at 298 K during its stripping from hexane solution only.

EXPERIMENTAL

Apparatus Used

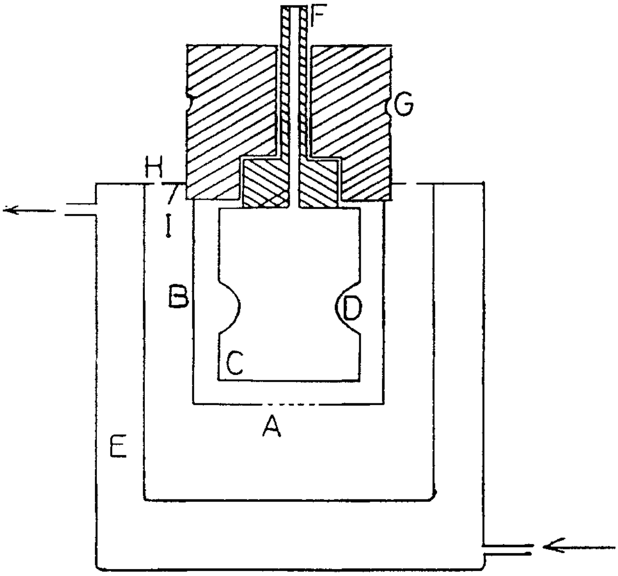
The rotating diffusion cell (RDC) is shown in Fig. 1. It consists of a rotating cylinder (B), containing one phase (organic), which is immersed in a second quiescent phase.

The most important component of the RDC is the Millipore filter (A) which divides it into two chambers. The filter is treated so that only a central area, shown as a dotted line, remains permeable. It is mounted on the cylinder. Inside the cylinder is a stationary baffle (C) made of PTFE which has three slots (D) cut in it for the correct hydrodynamic flow of the inner liquid. The baffle shields the central core from the rotation of the cylinder without impeding the flow toward the disc. The inner solution circulates toward the disc inside the baffle, is flung out centrifugally through the gap, and returns through the slots. Thus the baffle protects the organic liquid inside it from the shear of the rotating reservoir.

The rotating cell is surrounded by a thermostatted glass vessel (E) which contains the second phase (the aqueous phase). The stationary stainless steel shaft (F) for the baffle and the cylinder is hollow so that the inner compartment can be filled. The cell is rotated by a pulley system (G) driven by a Velodyne motor, which has a speed up to 16 Hz.

The apparatus for the kinetic experiments consisted of the RDC arrangement as described above in conjunction with the Radiometer pH-stat apparatus consisting of pH-meter, autotitrator, autoburette, and servograph.

Further details of the apparatus are to be found in the thesis of Patel (11).



A : Millipore filter (membrane)	B : rotating cylinder
C : stationary baffle	D : slots
E : thermostatted glass vessel	F : shaft for baffle C
G : pulley system	
H : holes for electrodes and delivery tube	
I : perspex lid	

FIG. 1 The rotating diffusion cell (RDC).

Procedure

For the experiments described here, the solvent was placed in a rotating cylinder whose end was closed with a porous filter disc. The acids diffused through the disc and into the aqueous phase. This aqueous phase was kept at a constant pH (generally 8) by a Radiometer autotitration system operating as a pH Stat, and the volume of base (NaOH) required to maintain the set pH was displayed as a function of time on an X-Y recorder.

The outer aqueous phase was contained in a thermostated water bath whose temperature was controlled to ±0.1°C. The pH of the aqueous phase was monitored using the glass electrodes.

To begin a run, the 0.22-μm filter (Millipore) was mounted on the end of the cylinder by glue and, leaving the center part permeable, the pores in the periphery were collapsed with a solution by volume of dioxane

33%, dichloroethane 33%, hexane 33%, and water 1%. The center part was about 2 cm^2 in area which was calculated from the accurately measured diameter using a traveling microscope. The filter was impregnated with the solvent overnight, and the preequilibrated aqueous phase was then added into the outer space of the assembled apparatus until it almost reached the filter. Both the organic and aqueous phases were then added simultaneously, keeping the level of the organic a little higher than that of the water. When the premeasured amounts (aqueous : organic = 7.5 by volume) were added, the filling equipment was removed, rotation was started, and the volume of standard base necessary to keep the pH constant was recorded continuously.

THE KINETIC MODEL

The RDC can be considered a type of immobilized liquid membrane cell with known hydrodynamics. This is attributed to the fact that the thin membrane (which is also called the "filter") attached to a hollow cylinder is rotated which creates rotating disc hydrodynamics on both sides of the filter, and mass transfer can occur from the inner chamber, through the membrane, and into the outer chamber. In the RDC, the concentration profiles during extraction may be looked upon as in Fig. 2. In the study of stripping, the inner side of the cell contains organic solvent with the

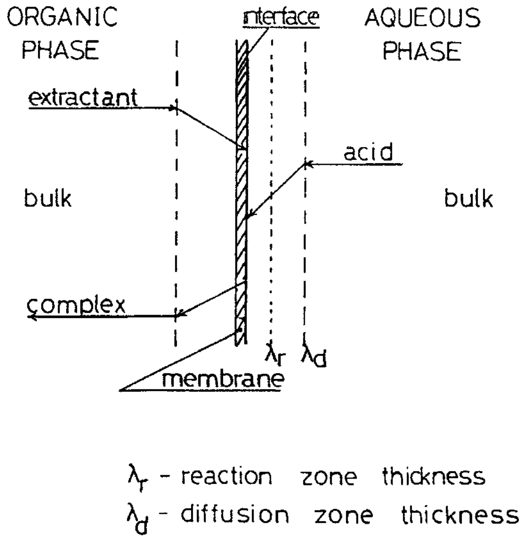


FIG. 2 Concentration profiles during extraction/stripping.

membrane impregnated by the same solvent, and the aqueous phase is contained in the outer side. Hence, there are four resistances to the overall mass-transfer. If a chemical reaction is involved, then it is assumed that the interfacial transfer is diffusional in nature with a chemical reaction contribution.

The kinetic model equations used here are the same as published by Sagert et al. (12):

$$J = kA\Delta C \tag{1}$$

$$\frac{1}{k} = \frac{l}{aD_{\beta}} + \frac{1}{ak_{\mathrm{j}}} + 0.643\left(\frac{\nu_{\beta}^{1/6}}{D_{\beta}^{2/3}} + \frac{K_{\mathrm{d}}\nu_{\alpha}^{1/6}}{D_{\alpha}^{2/3}}\right)\Omega^{\frac{1}{2}} \tag{2}$$

The rate constant for the transfer of acid to water, k, was determined by constructing well-known Levich plots using the data obtained from the RDC experiments. The slope in the Levich plot refers to the diffusion of solute to and away from the interface, and the intercept corresponds to an infinite rotation speed; that is, there are no stagnant layers on either side of the filter (membrane). Thus, by extrapolation to infinite rotation speed of the cell, the rate constant for the transfer reaction at the interface can be measured.

By determining k from the kinetic experiments using the RDC at different temperatures, the activation energy (E) may be evaluated. It is found from the slope of the Arrhenius plot of $\ln(k)$ versus $1/T$. The activation energy may indicate the nature of the process (diffusion or reaction) controlling the kinetics.

RESULTS AND DISCUSSION

Acetic Acid

Levich plots have been constructed from the experimental results to find the slope and intercept for calculating the resistances of mass transfer of stripping.

Initially, the Levich plot of acetic acid stripping from 0.1 M heptane to water was constructed to compare with the literature values of flux for the same system. Table 1 shows that the experimental results (in italics) are almost the same as those produced by Lawson (13). Having proved its reliability, other experiments were performed. The Levich plots for 0.05, 0.1, 0.2, 0.3, and 0.5 M acetic acid in hexane (which had been used as a diluent in subsequent studies) are shown in Fig. 3.

The slopes of these plots decreased with the increase of the initial acid concentration. The intercept also decreased with the increase of the acidity, indicating higher interfacial rate constants or lower interfacial resistance. The flux, on the other hand, increased with increasing acidity.

TABLE 1
Levich Plot Intercepts and Slopes for Acetic Acid

Initial acid concentration (M)	Temperature (K)	Intercept × 10^{-5} ($s \cdot m^{-1}$)	Slope × 10^{-5} ($s \cdot m^{-1}$)
		This Work	
0.05	298	6.989	2.933
0.10	*298*	*3.252*	*1.915*
0.20	298	1.626	0.861
0.30	298	0.667	0.464
0.50	298	0.420	0.552
		Lawson (1986)	
0.10	*298*	*3.368*	*1.828*

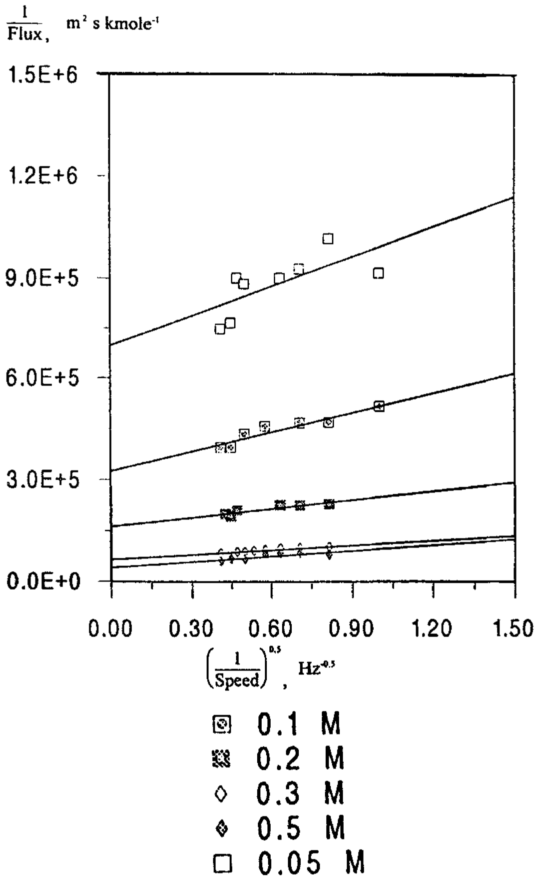


FIG. 3 Levich plots for acetic acid stripping at 298 K.

Flux versus concentration curves for particular rotational speeds were drawn to determine a pseudorate constant and a pseudo-order of reaction as the following equation:

$$\text{Flux} = k \times (\text{acid concentration})^n$$

Figure 4 illustrates such a curve constructed for the rotational speed of 4 Hz. The data were "curve fitted" by the Hewlett-Packard curve-fitting software. The average results for different speeds were

$$k = (3.43 \pm 0.18) \times 10^{-5}\ \text{m}\cdot\text{s}^{-1}$$

$$n = 1.14 \pm 0.05$$

or

$$\text{Flux} = (3.43 \pm 0.18) \times 10^{-5} \times (\text{acid concentration})^{1.14 \pm 0.05}$$

Citric Acid

Like acetic acid, the flux versus concentration relationship has been established for citric acid. The results are tabulated in Table 2. The overall

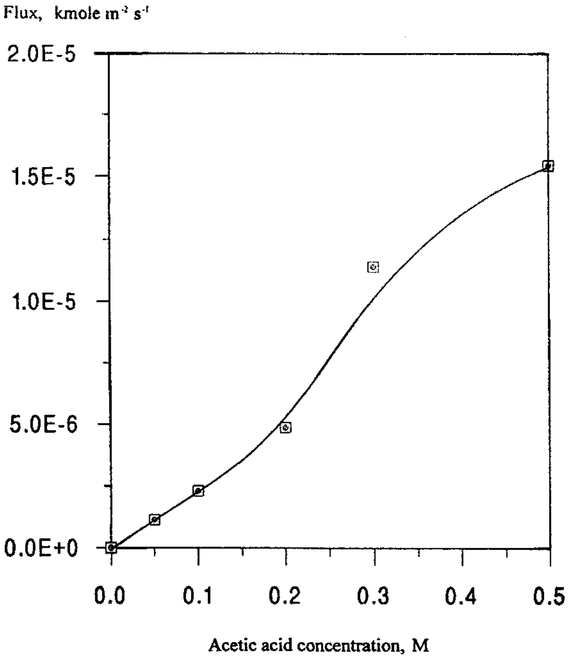


FIG. 4 Flux versus concentration for acetic acid stripping (at the speed of 4 Hz).

TABLE 2
Rate Constants and Order of Complexation for Citric Acid

Temperature (K)	Rate constant, $k \times 10^7$ (m·s^{-1})	Order of complexation (n)
294	1.60	0.80
298	1.97	0.87
301	1.90	0.75
305	2.61	0.86

relationship is

$$\text{Flux} = k \times (\text{acid concentration})^{0.82 \pm 0.03}$$

By comparing the flux equations for acetic and citric acids, it can be established that acetic acid flux is higher than citric for similar conditions, the reason of which is discussed in a later paragraph.

Levich plots have also been constructed for citric acid stripped from a solvent phase (TOA + decane + decanol) with varied acid concentrations. Unlike acetic acid, kinetic experiments with citric acid were performed at four different temperatures: 294, 298, 301, and 305 K.

Figure 5 shows the combined Levich plots for 294, 298, 301, and 305 K: at each temperature three different plots were constructed for three different concentrations. It is clear that as the acid concentration increases, the slope decreases sharply (also Table 3), showing the increase of the flux. For a particular concentration, increase of temperature affected the slopes in the same way. As it is seen from these plots and also from Table 3, the intercepts, in general, have a similar pattern, i.e., decreasing with the increase of temperature and concentration of the acid. As a result, the chemical and membrane resistances are lowered.

Comparison of the slopes and intercepts of citric acid with those of acetic acid for a particular concentration and at the same temperature (Tables 1 and 3) reveals that they are much higher for citric acid, and so acetic acid is more easily stripped from the organic to the aqueous phase compared to citric acid. This phenomenon may be explained by the complexation between the acid and the TOA molecules involving proton transfer or hydrogen bond formation. The citric acid molecule with its three carboxylic acid groups should form stronger complexes than acetic acid. Also, the affinity of an acid molecule toward a water molecule is less than that of the acid toward a TOA molecule; e.g., acid–base bonding is stronger than hydrogen bonding with water.

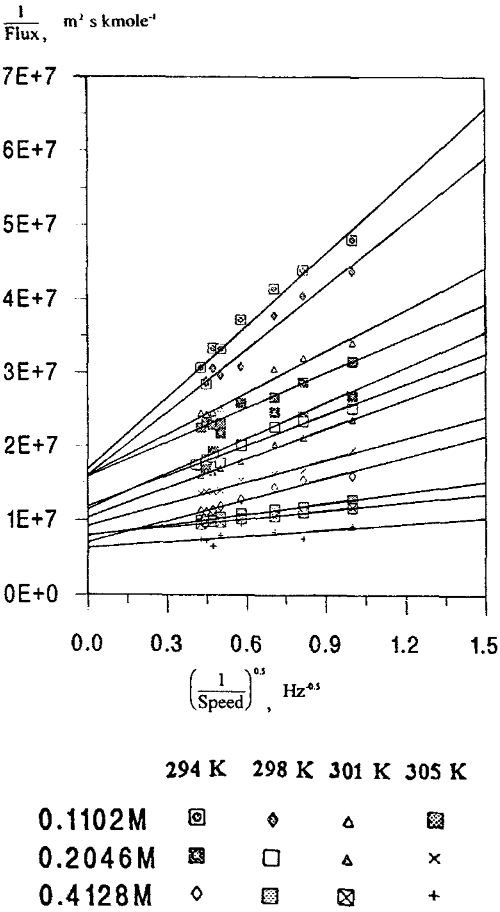


FIG. 5 Levich plots for citric acid stripping at different concentrations and temperatures.

The resultant activation energy from Fig. 6 was found to be

$$E = 30.6 \pm 1.0 \text{ kJ}\cdot\text{mol}^{-1}$$

Comparing the value of E with those obtained by Sagert et al. (12) for some other carboxylic acids, it is seen that E for citric acid is slightly higher (Table 4) but still below 40 kJ·mol^{-1}, suggesting that the stripping of citric acid is diffusion controlled.

Now, k may be written as a function of temperature:

$$k = (0.043 \pm 0.002)e^{-3680/T}$$

TABLE 3
Levich Plots Intercepts and Slopes for Citric Acid

Initial acid concentration (M)	Temperature (K)	Intercept × 10^{-7} ($s \cdot m^{-1}$)	Slope × 10^{-7} ($s \cdot m^{-1}$)
0.1102	294	1.691	3.255
0.2046	294	1.148	1.608
0.4128	294	0.712	0.955
0.1102	298	1.609	2.864
0.2046	298	1.185	1.388
0.4128	298	0.791	0.491
0.1102	301	1.601	1.886
0.2046	301	1.039	1.337
0.4128	301	0.802	0.372
0.1102	305	1.584	1.575
0.2046	305	0.926	0.991
0.4128	305	0.631	0.274

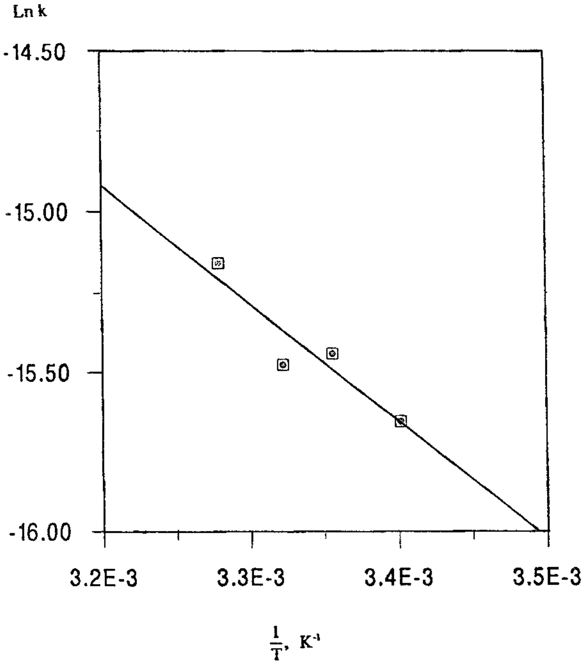


FIG. 6 Arrhenius plot for citric acid stripping.

TABLE 4
Comparison of E, ΔH, and ΔS Calculated for Citric Acid

Acid studied	E (kJ·mol^{-1})	ΔH (kJ·mol^{-1})	ΔS (J·mol^{-1}·K^{-1})
	This Work		
Citric acid	30.6 ± 0.8	29.4 ± 0.5	−68 ± 3
	Sagert et al. (1981)		
Acetic acid	10.0	8.8	−112
Butanoic acid	23.9	22.7	−69
Hexanoic acid	7.3	6.1	−120

ΔH and ΔS were calculated by the method of Sagert et al. (12) for stripping and were found to be near the range of butanoic acid (Table 4). They found the entropies of stripping of all monocarboxylic acids studied, with the exception of butanoic acid, were large and negative and more or less similar. The relatively smaller negative entropy for citric acid stripping found in the current study reconfirms their view that the effect of the carboxylic acid group is to increase the stripping resistance. The negativity of the entropic values proves that the resistance is largely entropic rather than enthalpic. Similar explanations were also cited by Kertes and King (7) in their study of extraction chemistry of carboxylic acids.

CONCLUSIONS

The known interfacial area in conjunction with the known hydrodynamic behavior of the RDC makes it a very reliable device for the study of mass transfer kinetics in a liquid–liquid system.

The RDC data were analyzed by the established method of Levich plots. Both the slope and the intercept, in all cases studied, decreased with an increase of the initial acidity in the organic phase, so the transfer resistances are lowered and the flux is increased.

Citric acid stripping from tri-*n*-octylamine in decanol and decane was chosen because of its commercial importance. The activation energy calculated for citric acid stripping was 30.6 ± 1.0 kJ·mol^{-1}. Hence, carboxylic acids stripping from the solvent phase to the aqueous phase is found to be diffusion controlled.

The overall pseudorate constant was found to be temperature-dependent and may be expressed as

$$k = (0.043 \pm 0.002)e^{-3680/T}$$

The pseudo-order of stripping for acetic acid was found to be 1.14 ± 0.05 and for citric acid 0.82 ± 0.03, and so:

$$\text{Flux} = (3.43 \pm 0.18) \times 10^{-5} \times (\text{acid concentration})^{1.14 \pm 0.05}$$

$$\text{for acetic acid at } 298 \pm 0.1 \text{ K}$$

$$\text{Flux} = (0.043 \pm 0.002)e^{-3680/T}$$

$$\times (\text{acid concentration})^{0.82 \pm 0.03} \text{ for citric acid}$$

Acetic acid is more easily transferred from the organic to the aqueous phase than is citric acid. The transfer resistance is found to be largely entropic rather than enthalpic.

NOMENCLATURE

A	area of the center of the filter over which mass transfer takes place (m^2)
a	porosity of the filter
ΔC	effective concentration difference between solvent and water (M)
D	diffusion coefficient (m^2·s^{-1})
E	activation energy (kJ·mol^{-1})
ΔH	enthalpy change (kJ·mol^{-1})
J	flux (mol·s^{-1})
K_d	distribution coefficient = ratio of the molarity of acid in the solvent to that in the aqueous phase
k	overall rate constant (m·s^{-1})
k_j	rate constant for interfacial transfer (m·s^{-1})
l	effective path length of the filter (m)
n	order of reaction
R	universal gas constant
RDC	rotating diffusion cell
ΔS	entropy change (J·mol^{-1}·K^{-1})
T	temperature (K)
TOA	tri-*n*-octylamine
Ω	rotation speed (Hz)
α, β	aqueous and organic phases
δ	thickness of the diffusion layer (m)
ν	kinematic viscosity (m^2·s^{-1})

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