

# Extraction Equilibria of Formic and Acetic Acids from Aqueous Solution by Phosphate-Containing Extractants

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The purpose of this work is to study the feasibility of extraction and recovery of formic acid and acetic acid in the industry synthesis of these two acids. In this work, extraction equilibria of formic and acetic acid with kerosene solutions of such phosphate-containing extractants as trialkylphosphine oxide (TRPO) and tributyl phosphate (TBP) were studied. The solutions of formic and acetic acid in aqueous phase at equilibria ranged from 0.4 mol·L<sup>-1</sup> to 8 mol·L<sup>-1</sup>. The influences of temperature on extraction equilibria were also studied. A model was proposed to describe the equilibria by postulating the structure of the complexes. The parameters in the model were obtained by fitting the experimental data, and the values predicted by this model are very close to the measured results.

## Introduction

Formic acid and acetic acid are fundamental chemical industry materials. Formic acid is widely used in the textile industry, tanning industry, rubber processing industry, and pharmaceutical industry. Acetic acid is used in the synthesis of acetyl cellulose and plastics and in the food industry, printing and dyeing industry, and medicinal chemistry. In the industrial synthesis of formic acid, for example, by the reaction of methanol and carbon monoxide and hydrolysis of the methyl formate formed, aqueous solutions containing 20–50% acid are always obtained. When concentrated by distillation, these solutions give an azeotrope, so that the formic acid cannot be obtained from them directly in an anhydrous form. Distillation under pressure, extractive distillation, and azeotropic distillation are used to concentrate the solutions. These processes are of high energy consumption. The synthesis of acetic acid is similar to that of formic acid as extractive distillation and azeotropic distillation are used, and they are also of high energy consumption.

To reduce the cost of concentrating acid solutions, extraction can be applied. The extraction equilibria of formic and acetic acid at low acid concentration have been studied by many researchers.<sup>1–3</sup> In 1974, a process of acetic acid recovery using solvent extraction from aqueous waste was developed by Dow Chemical Co.<sup>4</sup> In this process, tri-*n*-octylphosphine oxide (TOPO) was employed as extractant because of its excellent chemical stability, high boiling point, and low solubility in water. In this work, extraction of formic and acetic acid by phosphate-containing extractants such as trialkylphosphine oxide (TRPO) and tributyl phosphate (TBP) is studied.

## Experimental Section

**Chemicals.** Formic acid and acetic acid, >99.5%, were provided by Yi Li Co., Beijing, China; TBP, >98.5%, and TRPO, 93% (mass percent), diluted in kerosene, were provided by Chemical Engineering Co., Beijing, China.

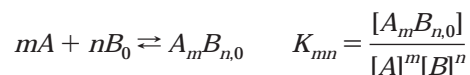
**Experimental Procedure.** Amounts of 30 cm<sup>3</sup> of the solvent (extractant + kerosene) containing different percentages of the extractant were equilibrated with 30 cm<sup>3</sup>

acid solutions of different concentrations in a shaker for 1 h. Previous study showed that this time is sufficient to attain equilibrium. The solution was then left to settle in a thermostat at the same temperature for 8 h. After phase separation, the concentration of aqueous phase was titrated with standard sodium hydroxide (0.1 mol·L<sup>-1</sup> and 1 mol·L<sup>-1</sup>). The acid concentration in the organic phase was determined by adding ethyl alcohol and water before titration.

Studies were mainly carried out at a temperature of 25 °C. As part of a sensitivity study the temperature range was extended to 20–50 °C.

## Extraction Equilibrium

The extraction equilibrium behavior can be described by the law of mass action, as a set of reactions of *m* acid, *A*, molecules, and *n* extractant, *B*, molecules to form various (*m*, *n*) acid–extractant complexes, with corresponding equilibrium constants, *K<sub>mn</sub>*:



Different authors have proposed different stoichiometries of acid–extractant complexes and different proposals to explain their data. For example, Hano<sup>5</sup> thought that for an acid of H<sub>*n*</sub>A (*n* is the number of hydrogen ions that can ionize in one acid molecule), the stoichiometries of the complex formed would be 1:*m* (acid–extractant), where *m* = *n* and the acid dimerizes in the organic phase; Fahim<sup>6</sup> tried different stoichiometries of (*m*, *n*) for the description of the equilibrium data and recommended some complex structures. For acetic acid and TBP, a (1:1) acid–extractant complex was proposed, and for acetic acid and TOPO, a (0.7:0.5) acid–extractant complex was proposed, but complexes with fractional *m* and *n* values are very difficult to explain. Different complexes may combine to yield fractional values. A hybrid model of this phenomenon is developed in a separate study.<sup>7</sup> Chen<sup>8</sup> considered both association and physical distribution, and the physical distribution of acid includes the distribution of acid between the aqueous phase and the free extractant, different complexes. This model can explain the data very well. Tamada<sup>9</sup> gave a comprehensive description of complexes

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formed between the acids and amine. In this paper, (2:1) and even (3:1) acid-amine complexes were proposed. For phosphate-containing extractants, previous researchers have not considered a (2:1) acid-extractant complex. However, in this work, (1:1) and (2:1) complexes were considered, and the model can be explained very well.

For acid-solvent complexes, the reaction and corresponding equilibrium constants are written as



where the  $A$  represents the acid in the aqueous phase, subscript  $o$  represents the organic phase,  $B_o$  is the free extractant in the organic phase, and  $K_1$  and  $K_2$  are the corresponding equilibrium constants.

For practical application, the activities of the organic phase species are assumed to be proportional to the concentrations of the species, and the activity of the acid is assumed to be proportional to the concentration of undissociated acid in the equilibrium aqueous phase. Thus, the constants of proportionality (the nonidealities) are taken into the equilibrium constant. The apparent equilibrium constant for the overall reaction can be written as

$$K_1 = \frac{C_{AB,o}}{C_{A,aq} C_{B,o}} \quad (3)$$

$$K_2 = \frac{C_{A_2B,o}}{C_{A,aq}^2 C_{B,o}} \quad (4)$$

The total concentrations of extractants,  $C_{B,tot}$ , and acid,  $C_{Ao,tot}$ , in the organic phase can be written as

$$C_{B,tot} = C_{B,o} + C_{AB,o} + C_{A_2B,o} \quad (5)$$

$$C_{Ao,tot} = C_{AB,o} + 2C_{A_2B,o} \quad (6)$$

Thus, the total acid concentration in the organic phase can be acquired by the equation:

$$C_{Ao,tot} = C_{AB,o} + 2C_{A_2B,o} \\ = \frac{(K_1 C_{A,aq} + 2K_2 C_{A,aq}^2) C_{B,tot}}{1 + K_1 C_{A,aq} + K_2 C_{A,aq}^2} \quad (7)$$

The distribution ratio  $D$  is defined as the total concentration of acid (all forms) in the organic phase,  $C_{Ao,tot}$ , divided by the total concentration of acid in the aqueous phase,  $C_{A,tot}$

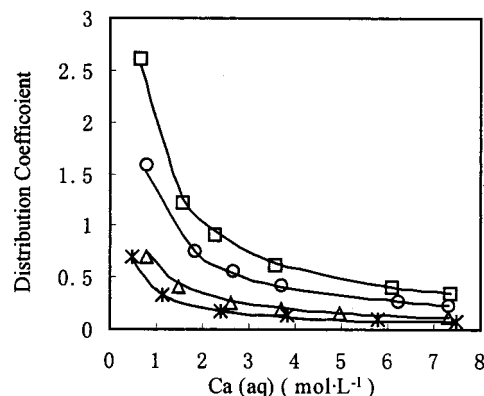
$$D = C_{Ao,tot} / C_{A,tot} \quad (8)$$

In this calculation, the computer searches for the best set of equilibrium constants for the given model that would minimize the error square sum defined by

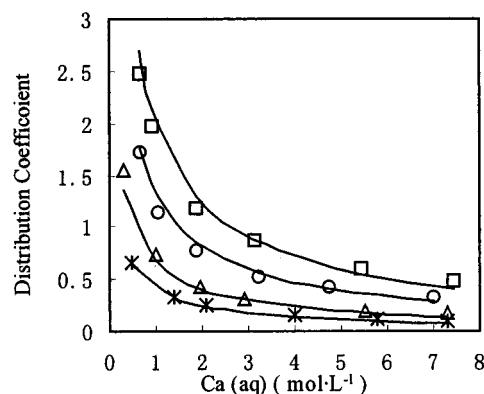
$$J = \min \sum_{\text{all\_data\_points}} (1 - C_{o,pred} / C_{o,exptl})^2 \quad (9)$$

$C_{o,pred}$  is the calculated value according to eq 7, and  $C_{o,exptl}$  is the experimental value,  $C_{o,exptl} = C_{Ao,tot}$ .

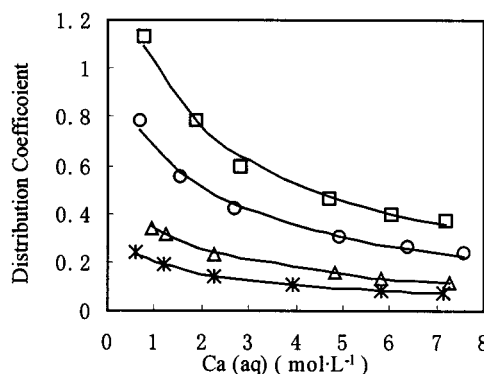
The deviation involved in such a prediction is calculated by



**Figure 1.** Distribution coefficients of formic acid from water at 25 °C to TRPO in kerosene: □, 75 vol % TRPO; ○, 50 vol % TRPO; △, 25 vol % TRPO; \*, 15 vol % TRPO.



**Figure 2.** Distribution coefficients of acetic acid from water at 25 °C to TRPO in kerosene: □, 75 vol % TRPO; ○, 50 vol % TRPO; △, 25 vol % TRPO; \*, 15 vol % TRPO.



**Figure 3.** Distribution coefficients of formic acid from water at 25 °C to TBP in kerosene: □, 75 vol % TBP; ○, 50 vol % TBP; △, 25 vol % TBP; \*, 15 vol % TBP.

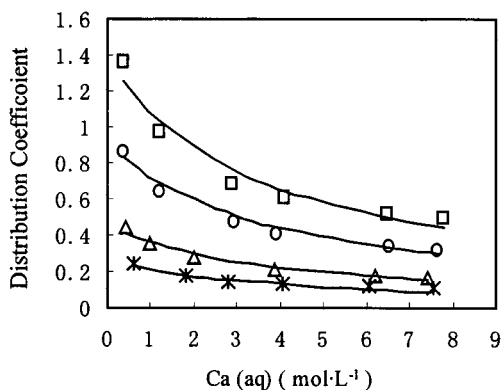
$$\text{error \%} = \frac{1}{n} \sum_{i=1}^n \frac{|C_{o,exptl} - C_{o,pred}|}{C_{o,exptl}} \times 100 \quad (10)$$

where  $n$  is the number of data points.

The effect of the dissociation of acids is found to be negligible. The deviation is no more than 2%.

## Results and Discussion

The experiment curves of distribution coefficients versus concentration of formic and acetic acid in the aqueous phase  $C_{a,aq}$  are shown in Figures 1–4. Every symbol represents an experimental data point. The curves are calculated lines according to the given model, which will



**Figure 4.** Distribution coefficients of acetic acid from water at 25 °C to TBP in kerosene: □, 75 vol % TBP; ○, 50 vol % TBP; △, 25 vol % TBP; \*, 15 vol % TBP.

**Table 1. Equilibrium Constant and Average Deviation**

	$K_1$	$K_2$	error (%)
TRPO + formic acid	14.48	2.07	3.46
TRPO + acetic acid	5.03	2.44	7.71
TBP + formic acid	0.56	0.01	2.48
TBP + acetic acid	0.51	0.05	6.18

**Table 2. Distribution Coefficients for Formic and Acetic Acid**

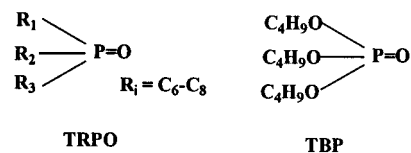
extractant (vol)	Ca(aq), mol·L <sup>-1</sup>	distribution coefficient	
		formic acid	acetic acid
<b>TRPO</b>			
75%	0.6	2.76	2.47
25%	0.6	0.83	1.03
75%	6	0.41	0.56
25%	6	0.16	0.18
<b>TBP</b>			
75%	0.6	1.19	1.23
25%	0.6	0.37	0.40
75%	6	0.40	0.55
25%	6	0.13	0.19

be discussed later. As can be seen from the figures, the distribution coefficients are relatively high in the low concentration of acid and decrease quickly with increasing acid concentration. In the region of higher acid concentration, they become much smaller.

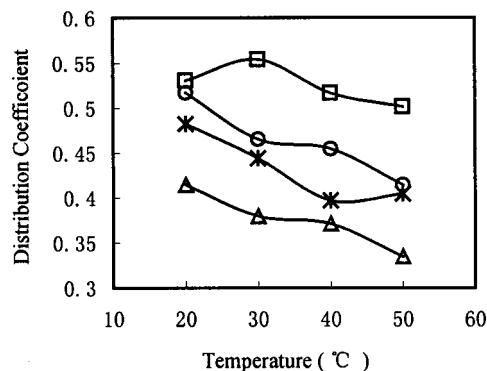
From the data shown in Figures 1–4 the equilibrium constants  $K_1$  and  $K_2$  can be evaluated, as given in Table 1. According to the proposed model, the distribution coefficients predicted are in well accordance with the experimental data. As shown in Figures 1–4, most of the symbols (the experimental data points) are very close to the curves. The average deviations are shown in Table 1.

Table 2 gives the distribution coefficients of formic and acetic acid with TBP and TRPO at extraction equilibrium. In the region of low acid concentration (0.6 mol·L<sup>-1</sup>) it is evident that for both formic acid and acetic acid, TRPO gives higher distribution coefficients than TBP does. This can be explained by the extraction efficiency of the two extractants.

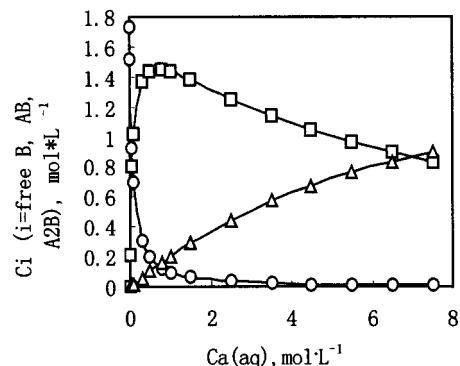
The molecular structures of TRPO and TBP are shown in Figure 5. In TBP and TRPO the phosphoryl bond (>P=O) serves as a Lewis base for its high polarity. The extraction efficiency depends on the Lewis basicity of the phosphoryl bond. If the alkoxy groups in TBP are substituted by alkyl groups, then the Lewis basicity is increased through inductive effects. This is the case with TRPO. With the removal of oxygen from the other linkages to the phosphorus atom, the phosphoryl becomes a still stronger electron donor. Due to its higher basicity, it should give



**Figure 5.** Molecular structures of TRPO and TBP.



**Figure 6.** Influence of temperature on acid extraction, the acid concentration in aqueous phase being 3 mol·L<sup>-1</sup> at equilibrium: □, TRPO + acetic acid; ○, TRPO + formic acid; \*, TBP + acetic acid; △, TBP + formic acid.



**Figure 7.** Relations among free [B], [AB], [A<sub>2</sub>B], and Ca(aq) for formic acid/TRPO system: ○, free B; □, AB; △, A<sub>2</sub>B.

higher distribution coefficients.

However, with increasing acid concentration, the distribution coefficient of acid by TRPO drops more quickly than that by TBP. As can be seen from Table 1, when the acid concentration is 6 mol·L<sup>-1</sup>, the distribution coefficients for TBP and TRPO are nearly equivalent. This is because the molecular weight of TRPO is 340–350, whereas that of TBP is 266. When the mass percents of the two solvents containing TBP and TRPO, respectively, are equal, the mole concentration of TBP is higher than that of TRPO. With increasing acid concentration in aqueous phase at equilibrium, there is less free TRPO (unassociated TRPO) in the solvent than TBP.

Figure 6 shows the influence of temperature on the extraction of formic and acetic acid. The TRPO and TBP used are 50 vol % TRPO–kerosene and 50 vol % TBP–kerosene, and the acid concentration at equilibrium was 3 mol·L<sup>-1</sup>. The influences of temperature in the range of 20–50 °C on the extraction equilibria are found to be very small. With increasing temperature, the distribution coefficients drop a little.

By using the equilibrium constants  $K_1$  and  $K_2$  the relationships among  $C_B$ ,  $C_{AB}$ , and  $C_{A_2B}$  can be calculated. Figure 7 shows such relationships. The acid is formic acid, and the solvent is 75 vol % TRPO–kerosene, corresponding to 1.74 mol·L<sup>-1</sup> TRPO. When the concentration of formic

acid is low, most of the extractant (TRPO) is free, that is, unassociated. As the acid increases in the aqueous phase, the amount of free extractant drops sharply. The complex AB increases quickly at first, but then it begins to drop, whereas the complex A<sub>2</sub>B keeps increasing.

### Recovery of Formic and Acetic Acid

It is not easy to recover formic and acetic acid from the extraction mixture, when distilling it, the temperature needed is very high. However, if reduced pressure distillation is applied, the temperature needed drops a lot. The acetic and TBP–kerosene system is the easiest of the four systems. At 0.003 MPa and 120 °C, the acetic acid acquired can be >90% (w/w), and the concentration of acetic acid in the extraction mixture after distillation is <0.04 mol·L<sup>-1</sup>. The recovery of formic and acetic acid from the other three systems is similar to the recovery of acetic from TBP–kerosene. When distilled at the pressure of 0.003 MPa, the temperature needed ranged from 120 °C to 140 °C.

When formic or acetic acid is extracted to the organic phase, some amount of water is also extracted. Therefore, in the recovery of formic and acetic acid from the extraction mixture, pure acid cannot be obtained; rather, solutions of the two acids are obtained. The concentrations of the solutions acquired are much higher than those of the solutions before extraction.

### Conclusion

Extraction equilibria of formic and acetic acid by TRPO and TBP in kerosene are studied. For dilute acids, TRPO gives higher distribution coefficients than TBP, whereas for high acid concentration, the differences become very small. The influences of temperature in the range 20–50 °C on extraction equilibria are found to be very small.

A mathematic model considering both (2:1) and (1:1) acid–extractant complexes was proposed. The equilibrium constants were evaluated according to the experimental data.

Formic and acetic acid can be recovered from the extraction mixture. Solutions are concentrated after recovery.

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