Investigation of Formic Acid Separation from Aqueous Solution by Reactive Extraction: Effects of Extractant and Diluent

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This study aims to investigate the extraction of formic acid by a high molecular-weight aliphatic amine, tridodecylamine (TDA), and a phosphorus-bonded, oxygen-containing extractant, tributyl phosphate (TBP), dissolved in five different diluents (ethyl valerate, diethyl adipate, diethyl sebacate, 1-octanol, and heptane) each. The experiments were carried out at 298.15 K. Comparisons of the results were made using the distribution coefficient, loading factor, separation factor, and the percentage of extraction yield. The results demonstrated that combination of TDA and diethyl adipate had the greatest synergistic effects with a distribution value of 6. The maximum value of the extraction efficiency was found to be 87 % with a 1.09 $\text{mol}\cdot\text{L}^{-1}$ concentration of TDA in diethyl adipate.

Introduction

Carboxylic acids are used as raw materials and additives in many fields like polymer, detergent, food, and pharmaceutical industries.[1−5] Some production processes yield aqueous wastes or byproduct containing carboxylic acids. Furthermore, one of the most important production methods of carboxylic acids is the fermentation processes.[6−8] The recovery of acids from the fermentation broth is necessary in various technical fields and is of great importance from the point of economic view. By the distillation method, water has to be evaporated to recover the acid leading to the high cost of energy. In addition, a distillation column with many trays is necessary for an efficient separation causing an increase in the manufacturing cost. At high product concentrations, azeotropes are also a common problem in distillation and require additional methods like azeotropic or extractive distillation or adsorption to yield a dry product. The cost of recovering and purifying a chemical contained in a mixture can depend strongly on the concentration of that chemical in the mixture. The more dilute the chemical is in the mixture, the higher its price is. That is why the preferred method to recover the carboxylic acids comprising at most 10 wt % of fermentation broth is liquid−liquid extraction (LLE), which creates a second phase immiscible with the feed phase, in the form of a solvent that selectively dissolves some of the species in the feed mixture.[9]

Classical extractants have no ability to extract some acids from their aqueous solutions, since they have low distribution coefficients (lower than 1).[10] For an affordable process a high distribution coefficient is a must. Reactive extraction with an extractant has been gaining great attention to solve this problem. Reactive extraction is developed to intensify separation by solvent extraction and represents a connection between chemical (solute and extractant reaction) and physical phenomena (diffusion and solubilization of the system components).[11] In reactive extraction, a reaction occurs between the extractant and the solute. In this reaction a complex formation occurs. This complex is solubilized into the organic phase, and the acid is recovered from the organic phase by stripping.[8,12] The extractant must be diluted with an organic solvent to produce appropriate physical properties like extractant concentration, viscosity, and density.[13]

The reactive extraction mechanism with organophosphorus and amine-based extractants can be expressed by following interface equilibrium as given in eqs 1 and 2, respectively:

$$\text{mR}{-}\text{COOH}_{\text{aq}} + \text{nP}_{(\text{org})} = \text{R}{-}\text{COOH}_{\text{m}}\text{P}_{\text{n}(\text{org})} \tag{1}$$

$$\text{mR}{-}\text{COOH}_{\text{aq}} + \text{nNR}_{3(\text{org})} = \text{R}{-}\text{COOH}_{\text{m}}\text{NR}_{3\text{n}(\text{org})} \tag{2}$$

Formic acid (methanoic acid) is mainly used as a preservative and an antibacterial agent in livestock feed. It is applied in diverse industries. It is used as an intermediate in the production of pharmaceuticals such as caffeine, enzymes, antibiotics, artificial sweeteners, plant protection agents, dyes, flavors, and perfume ingredients.[14] In the textile industry, it is consumed either in dyeing or textile finishing. Being a volatile acid, it does not remain on the fiber on drying. In addition, formic acid is preferred for acid coagulation of rubber latex. It is also used as a catalyst in the manufacturing of phenolic resins.[15]

Extractive recovery of carboxylic acids produced by fermentation has been gaining great attention. There have been a number of searches related to reactive extraction with different acid and extractant + diluent systems to achieve the best extraction system. Wang et al.[16] investigated equilibria of aqueous solutions of several monocarboxylic acids including formic acid with trialkylphosphine oxide in kerosene. Shan et al.[17] used trioctylamine (TOA) + 1-octanol, TOA + methyl isobutyl ketone (MIBK), TOA + tetrachloromethane (CCl_4), trialkylphosphine oxide (TRPO) + 1-octanol, and TRPO + kerosene as the extractant to extract 11 monocarboxylic acids other than formic acid in their study.

The purpose of this research in this paper is to contribute to the knowledge of the extraction equilibria of formic acid from its aqueous solutions with various extractant + diluent systems.

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Two types of extractant were used: a long-chain tertiary amine, tridodecylamine (TDA), and tributyl phosphate (TBP). These extractants were diluted in three different esters, ethyl valerate, diethyl adipate, and diethyl sebacate, a long-cahin alcohol, 1-octanol, and an alkane, heptane, respectively.

Experimental Section

Materials. Formic acid, TDA, ethyl valerate, diethyl adipate, diethyl sebacate, 1-octanol, and heptane were supplied by Merck and were of > 0.98, > 0.99, > 0.98, > 0.99, > 0.95, > 0.99, and > 0.99 mass fraction purity, respectively. TBP was purchased from Fluka and was of ≥ 0.99 mass fraction purity. The melting temperature, density, and molecular mass of TDA are 16 °C, 0.82 $g\cdot cm^{-3}$, and 522.01 $g\cdot mol^{-1}$, respectively (Merck, catalog number 821160). TBP's melting temperature, density, and molecular mass are (180 to 183) °C, 0.979 $g\cdot cm^{-3}$, and 266.31 $g\cdot mol^{-1}$, respectively (Fluko, catalog number 90820).

Procedure. The initial acid mass fraction, *w*, was prepared by diluting with distilled water to $w = 0.1$. Different acid mass fractions were chosen to investigate the effects of initial mass fractions of formic acid, ranging from 4 % to 8 %.

Equal volumes of a mixture of acid and water and TDA or TBP solutions were shaken in a thermostatted shaker bath (Nüve ST402) at 298.15 K for 4 h, which is given for equilibrium in literature. After that, phase separation was achieved by centrifuging at 2000 rpm for 15 min. This equilibrium period was found in preliminary experiments. Reaching the equilibrium state, the acid concentrations of the aqueous phase were analyzed by the titration method using 0.1 $mol\cdot L^{-1}$ NaOH solution with a relative uncertainty of 1 %. A material balance with regard to acid was established to confirm the analytical results. It was seen that the deviation between the amount of acid analyzed and the amount of acid known by preparing the solutions by mass did not exceed 3 %.

Results and Discussion

Tables 1 and 2 show the results of the extraction experiments when TDA and TBP were used as an extractant, respectively. The concentrations of TDA in the diluents varied from 0.47 $mol\cdot L^{-1}$ to 1.09 $mol\cdot L^{-1}$, and the concentrations of TBP in the diluents varied from 1.10 $mol\cdot L^{-1}$ to 2.58 $mol\cdot L^{-1}$. The initial formic acid concentration was 2.18 $mol\cdot L^{-1}$.

The distribution coefficient (*D*) is defined as the ratio of the concentration of organic acid in the organic phase to the concentration of organic acid in the aqueous phase,

$$D = \frac{C_{A,org}}{C_{A,aq}} \tag{3}$$

The loading factor (*Z*) of the extractant is defined as the total concentration of acid in the organic phase, $C_{A,org}$, divided by the total concentration of amine in the organic phase, C_B,

$$Z_t = \frac{C_{A,org}}{C_{B,org}} \tag{4}$$

The influences of TDA and TBP mass fractions in different diluent systems on distribution coefficients (*D*) and loading factors (*Z*) were illustrated in Figures 1, 2, 3, and 4, respectively. The related data were given in Tables 1 and 2. According to Figures 1 and 3, distribution coefficient *D* increases with the increase of the amount of the extractant. Distribution coefficients decrease in the order of diethyl adipate > diethyl sebacate > ethyl valerate > 1-octanol > heptane at the same TDA mass fraction. The influence of diluents on the formation of acid−amine complexes, and therefore on the values of the extraction constants, includes the interaction of value type (dipole−dipole and/or dipole-induced−dipole interactions, hydrogen bonding, etc.) according to the nature of the diluent.[18] In this manner, the formation of an acid−amine complex is promoted by the dipole−dipole interactions between diluent and complex and, in the case of proton-donating diluents, by the formation of a complex-diluent hydrogen bond. In regards to TBP, this order decreases as diethyl adipate > diethyl sebacate > 1-octanol > ethyl valerate > heptane. As the polarity of the diluent increases,

Table 1. Extraction Results of Formic Acid with TDA + Diluent Systems, at the Initial Acid Mass Fraction of 10.06 % at 298.15 K[a]

diluent	C_{Ao}	C_{Araf}	C_{Aorg}	C_{eorg}	*D*	*D*	100 *E*
		$mol\cdot L^{-1}$					
ethyl valerate	2.18	0.34	1.84	1.09	5.37	1.69	84.29
	2.18	0.45	1.73	0.94	3.80	1.84	79.17
	2.18	0.61	1.57	0.79	2.61	2.01	72.26
	2.18	0.81	1.37	0.63	1.72	2.19	63.17
	2.18	1.05	1.13	0.47	1.07	2.41	51.84
heptane	2.18	0.50	1.68	1.09	3.41	1.54	77.34
	2.18	0.67	1.51	0.94	2.24	1.60	69.09
	2.18	0.89	1.29	0.79	1.45	1.65	59.15
	2.18	1.11	1.07	0.63	0.96	1.71	49.15
	2.18	1.33	0.85	0.47	0.64	1.81	39.02
1-octanol	2.18	0.44	1.74	1.09	3.94	1.58	79.77
	2.18	0.62	1.56	0.94	2.53	1.66	71.67
	2.18	0.78	1.40	0.79	1.81	1.79	64.41
	2.18	1.00	1.18	0.63	1.17	1.88	54.07
	2.18	1.15	1.03	0.47	0.91	2.21	47.52
diethyl adipate	2.18	0.28	1.90	1.09	6.59	1.73	86.83
	2.18	0.46	1.72	0.94	3.73	1.83	78.87
	2.18	0.59	1.59	0.79	2.67	2.03	72.76
	2.18	0.75	1.43	0.63	1.89	2.28	65.46
	2.18	0.98	1.20	0.47	1.21	2.54	54.82
diethyl sebacate	2.18	0.31	1.87	1.09	6.01	1.71	85.74
	2.18	0.42	1.76	0.94	4.17	1.87	80.66
	2.18	0.53	1.65	0.79	3.12	2.11	75.69
	2.18	0.78	1.40	0.63	1.78	2.23	63.96
	2.18	1.05	1.13	0.47	1.08	2.42	52.04

[a] C_{Ao}, initial acid concentration; C_{Araf}, the acid concentration in the aqueous phase; C_{Aorg}, the acid concentration in the organic phase; C_{eorg}, the amine concentration in organic phase.

Table 2. Extraction Results of Formic Acid with TBP + Diluent Systems, at the Initial Acid Mass Fraction of 10.06 % at 298.15 K[a]

diluent	C_{Ao}	C_{Araf}	C_{Aorg}	C_{eorg}	*D*	*Z*	100 *E*
		$mol\cdot L^{-1}$					
ethyl valerate	2.18	1.15	1.03	2.58	0.91	0.40	47.61
	2.18	1.17	1.01	2.21	0.86	0.46	46.32
	2.18	1.31	0.87	1.84	0.67	0.47	40.06
	2.18	1.41	0.77	1.47	0.55	0.53	35.58
	2.18	1.52	0.66	1.10	0.44	0.61	30.62
heptane	2.18	1.22	0.96	2.58	0.79	0.37	44.43
	2.18	1.35	0.83	2.21	0.62	0.37	38.07
	2.18	1.50	0.68	1.84	0.46	0.37	31.41
	2.18	1.59	0.59	1.47	0.37	0.41	27.24
	2.18	1.71	0.47	1.10	0.28	0.43	21.92
1-octanol	2.18	1.12	1.06	2.58	0.96	0.42	49.01
	2.18	1.29	0.89	2.21	0.69	0.40	40.85
	2.18	1.41	0.77	1.84	0.55	0.42	35.48
	2.18	1.52	0.66	1.47	0.44	0.46	30.72
	2.18	1.56	0.62	1.10	0.39	0.56	28.53
diethyl adipate	2.18	1.07	1.11	2.58	1.04	0.43	51.09
	2.18	1.13	1.05	2.21	0.94	0.48	48.36
	2.18	1.25	0.93	1.84	0.74	0.51	42.64
	2.18	1.31	0.87	1.47	0.67	0.59	40.11
	2.18	1.39	0.79	1.10	0.56	0.71	36.03
diethyl sebacate	2.18	1.11	1.69	2.58	0.96	0.42	49.15
	2.18	1.18	1.00	2.21	0.86	0.46	46.27
	2.18	1.30	0.88	1.84	0.67	0.48	40.36
	2.18	1.39	0.79	1.47	0.57	0.54	36.43
	2.18	1.48	0.70	1.10	0.47	0.64	32.26

[a] C_{Ao}, initial acid concentration; C_{Araf}, the acid concentration in the aqueous phase; C_{Aorg}, the acid concentration in the organic phase; C_{eorg}, the amine concentration in the organic phase.

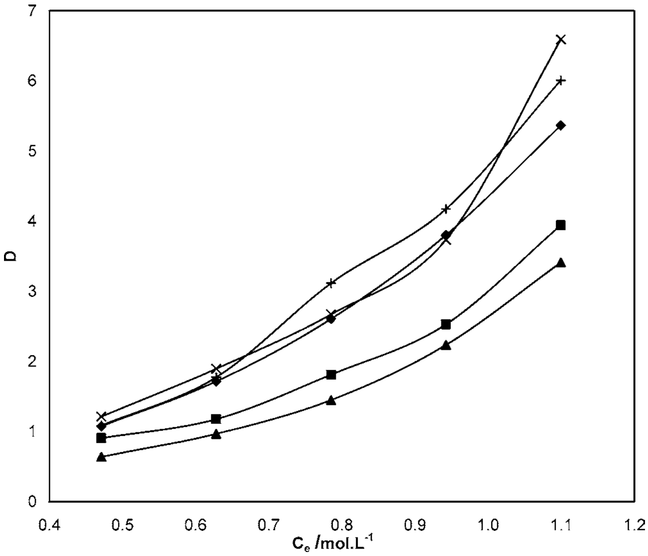

Figure 1. Effect of TDA concentration in different diluents on distribution coefficients (*D*) of formic acid. ◆, ethyl pentanoate; ■, 1-octanol; ▲, heptane; ×, diethyl adipate; +, diethyl sebacate.

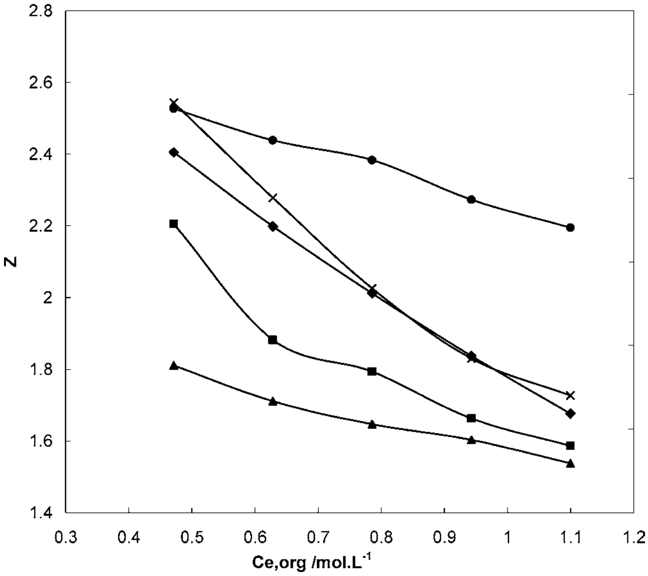

Figure 2. Effect of TDA concentration in different diluents on loading factors (*Z*) of formic acid. ◆, ethyl pentanoate; ■, 1-octanol; ▲, heptane; ×, diethyl adipate; ●, diethyl sebacate.

the solubility of the acid + extractant complex increases. Diethyl adipate, which has two carbonyl groups, is the most polar solvent of all. Therefore, it has the maximum ability to solve the acid–extractant complex. It gave distribution coefficient values ranging from 1.21 to 6.59 with TDA and from 0.56 to 1.04 with TBP in each diluent, respectively. Its performance was slightly better than diethyl sebacate, the chain length of which is longer than diethyl adipate. Consequently, the longer the chain, the lower the polarity is. An apolar diluent, heptane, gave the lowest distribution coefficients changing between 0.64 and 3.41 with TDA and 0.28 and 0.79 with TBP, respectively. Because it affects the complex slightly it is called an inert diluent.[8]

Extraction yield (*E*) is determined as the fraction of extracted acid,

$$E = \left(1 - \frac{(C_{\mathrm{A,aq}})}{C_{\mathrm{Ao}}}\right) \qquad (5)$$

In eq 5, $C_{\mathrm{A,aq}}$ is the concentration of acid in aqueous phase after extraction: C_{Ao} is the initial acid concentration in the aqueous phase. Tables 1 and 2 show that TDA is the most effective extractant in terms of extraction yield, *E*. Extraction yield with TDA changes between 77 % and 86 % at the maximum extractant concentration quantity. It becomes between 44 % and 51 % when TBP is used at the same conditions.

As shown in Figures 2 and 4, loading factors decrease while amine concentrations in different diluents increase. The loading values decrease in the order of diethyl adipate > diethyl sebacate > ethyl valerate > 1-octanol > heptane at the maximum amount of TDA and TBP concentrations, respectively.

To observe the influence of the extractant, the physical extraction of formic acid was studied. The results of the extraction of formic acid by diluents without TDA or TBP are presented in Table 3 and illustrated in Figure 5. All of them gave comparatively very low values.

In addition, initial acid concentration was also investigated to present an important parameter for the extraction of acids. The results of extraction of formic acid by TDA at different initial acid concentrations is given in Table 4. As it is seen in Figure 6, the distribution coefficient decreases while the initial acid concentration increases.

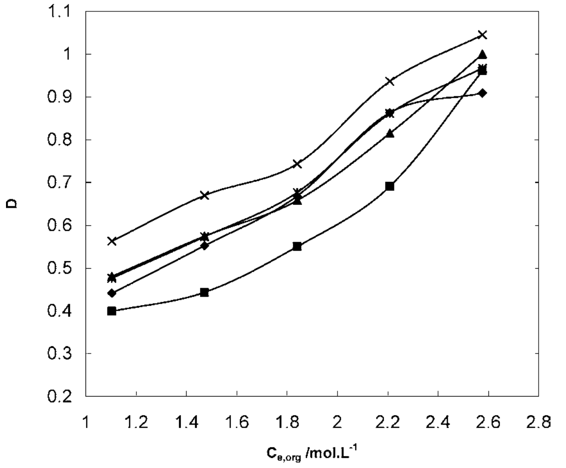

Figure 3. Effect of TBP concentration in different diluents on distribution coefficients (*D*) of formic acid. ◆, ethyl pentanoate; ■, 1-octanol; ▲, heptane; ×, diethyl adipate; ●, diethyl sebacate.

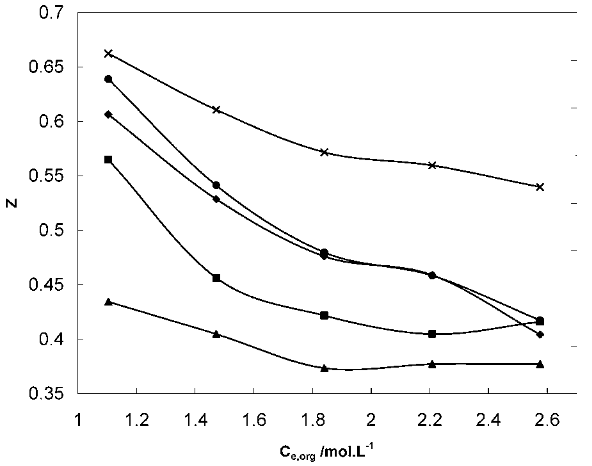

Figure 4. Effect of TBP concentration in different diluents on loading factors (*Z*) of formic acid. ◆, ethyl pentanoate; ■, 1-octanol; ▲, heptane; ×, diethyl adipate; ●, diethyl sebacate.

Table 3. Results of Physical Extraction of Formic Acid at the Initial Acid Mass Fraction of 10.06 % at 298.15 K[a]

diluent	C_{Ao}	C_{Araf}	C_{Aorg}	D	100 E
	mol·L^{-1}				
ethyl valerate	2.18	1.98	0.20	0.10	9.25
diethyl adipate	2.18	1.75	0.43	0.25	19.93
diethyl sebacate	2.18	1.94	0.24	0.13	11.48
heptane	2.18	2.16	0.02	0.01	0.99
1-octanol	2.18	1.72	0.46	0.27	21.32

[a] C_{Ao}, initial acid concentration; C_{Araf}, the acid concentration in the aqueous phase; C_{Aorg}, the acid concentration in the organic phase.

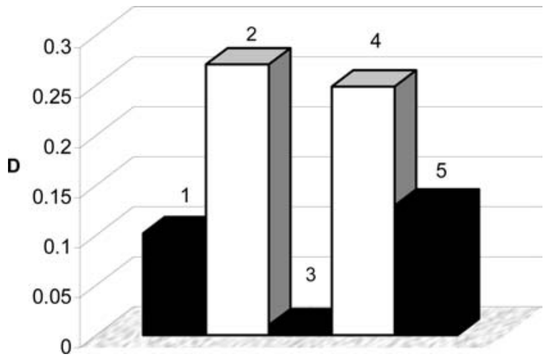

Figure 5. Distribution coefficients (D) of formic acid between water and pure diluents. 1, Ethyl pentanoate; 2, 1-octanol; 3, heptane; 4, diethyl adipate; 5, diethyl sebacate.

Table 4. Results of Extraction of Formic Acid by TDA at Different Initial Acid Mass Fractions at 298.15 K[a]

diluent	100 C_{Ao}	C_{Ao}	C_{Araf}	C_{Aorg}	C_{eorg}	D	Z	100 E
		mol·L^{-1}						
diethyladipate	4.18	0.91	0.09	0.82	1.09	8.50	0.74	89.47
	6.38	1.38	0.15	1.23	1.09	8.25	1.13	89.18
	8.21	1.78	0.22	1.56	1.09	7.08	1.42	87.64
	10.06	2.18	0.28	1.90	1.09	6.59	1.73	86.83

[a] C_{Ao}, initial acid concentration; C_{Araf}, the acid concentration in the aqueous phase; C_{Aorg}, the acid concentration in the organic phase; C_{eorg}, the amine concentration in the organic phase.

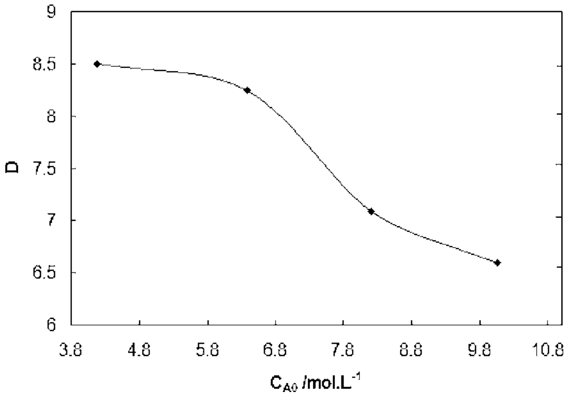

Figure 6. Change distribution coefficient (D) in 1.09 mol·L^{-1} of TDA in diethyl adipate with different initial formic acid concentrations.

Conclusion

In this study, TDA and TBP in five different diluent systems (ethyl valerate, diethyl adipate, diethyl sebacate, 1-octanol, and *n*-heptane) were used to increase the performance of the extraction of formic acid. Of all of the diluents used, a dibasic ester, diethyl adipate, alone showed the maximum extraction yield (20 %) and distribution coefficient (0.25). An apolar, inert diluent, heptane showed the minumum value of the extraction yield (0.99 %) and distribution coefficient (0.01).

These calculated values in pure diluent systems led to reactive extraction for obtaining formic acid. In the case of the TDA + diethyl adipate system, the extraction efficiency was found to be between 55 % and 87 % in terms of extraction yield. It is the consequence of acid−amine complex formation and the solvation power of polar diethyl adipate. It means that the performance of the tertiary amine depends on the nature of the diluent. Extraction yield values changed between 36 % and 51 % with the TBP + diethyl adipate system. Consequently, the long-chain tertiary amine TDA is more effective than the phosphorus-bonded, oxygen-containing extractant, TBP. The highest distribution coefficient, 6.59, was attained by TDA in diethyl adipate. The maximum extracted formic acid was 87 % with TDA dissolved in diethyl adipate. The TDA + diethyl adipate solvent system is nearly six times higher than that of TBP with its distribution coefficient value and almost twice better in terms of extraction yield. Judging from the findings of this research, TDA + diethyl adipate is the best solvent system to recover formic acid from its aqueous solutions of all of the systems here.

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