

## Study of the Effect of Some Parameters Governing the Recovery Process of Formic Acid from its Aqueous Solution by Alcohols

Hadj Seyd Abdelkader <sup>1 +</sup>, Lanez Touhami <sup>2</sup>, Belfar Mohamed Lakhdar <sup>2</sup>, Kemassi Abdellah <sup>3</sup>,  
Gharib Toufik <sup>3</sup> and Ben Brahim Fouzi <sup>3</sup>.

<sup>1</sup> University Mohamed Khider-Biskra. B.P. 145, Biskra 07000, Algeria.

<sup>2</sup> VTRS Laboratory, El-Oued –University. B.P. 789, 39000 El-Oued, Algeria.

<sup>3</sup> University Centre of Ghardaia, 47000 Ghardaia, Algeria.

**Abstract.** Optimization of experimental conditions of formic acid recovery from its aqueous solution by a liquid-liquid extraction, with alcohols, was carried out in this study. The effect of each parameter governing the process such as: pH of aqueous solution, partition coefficient and initial concentration on acid, volume ratio between phases and temperature, was studied. Variation of distribution coefficient and yield of extraction of formic acid, depending on these parameters, was investigated to determine the favorable conditions to recover this acid from its aqueous solution.

Results show that, in comparison to the other alcohols used, butan-1-ol gives the higher values of yield and distribution coefficient, the optimal conditions of extraction are obtained at low pH values (lesser to its pKa), a yield of 46.15 % was obtained at pH:2.29. A departure solution concentrated on acid and a high volume ratio of organic solvent favor the extraction (69.45 % of the acid were extracted for  $V_{org}/V_{aq}=3:1$ ). Finally, we noted that the yield and the distribution coefficient increase with increasing temperature, nearly 53.23 % of formic acid were extracted at 318.15 K.

The study will be useful in the design of liquid-liquid extraction process by alcohols for formic acid recovery.

**Keywords:** liquid extraction, distribution coefficient, yield, solvent, solute.

### 1. Introduction

Liquid-liquid extraction is a method of separation of one or more components from a mixture; it is based on the distribution of the solute between two liquids practically immiscible.

The yield and the distribution coefficient are the most critical factors in liquid-liquid extraction and influenced by other parameters such as solutes concentration, nature of solvent, pH of the solution, temperature, hydrophobicity of extracted substances [1].

Formic acid is one of the simplest carboxylic acid used as a preservative and antibacterial in foods [1]. It is also used in many other industries and manufactures. It is the main product of combustion of fuels such as ethanol and methanol. It is also used as a solvent for removing paint and rust from metal surfaces [2]. It is used in the pharmaceutical industry as pH adjuster. Its salts are used as a deicing agent of first quality and valuable auxiliary in the production of oil [3,4]. Formic acid is used for the production of coagulated natural rubber destined for the production of tires and also used in textile and in chemical industries [2,5].

Various technologies have been reported for the separation of organic acids, especially formic acid from complexes mixtures. The work toward developing removal and recovery of waste stream components is started in 1974. The separation of organic acids from waste water has been important and essential from the points of view of pollution control and industrially for more than a century [6,7]. Several separation

---

<sup>+</sup> Corresponding author. Tel.: +213771551899.  
E-mail address: seydtg@gmail.com.

techniques such as liquid extraction, ultra filtration, reverse osmosis, electro-dialysis, distillation, liquid surfactant membrane extraction, anion exchange, precipitation and adsorption have been employed to remove carboxylic acids from aqueous solution, but liquid extraction can be considered as an effect way for recovery of these component, due to its simplicity and its low cost [8,9].

The distribution of constituent between two liquids phases is affected by several factors, primarily the nature of the substances used in the extraction, including volumes of phases, pH of the medium, temperature, concentrations and partition coefficients of substances to be extracted [10-11].

The effect of each parameter governing the extraction process of formic acid, by butan-1-ol, was studied and carried out in this work.

## 2. Experimental Section

### 2.1. Materials

Formic acid (99 %) was purchased from Riedel-de-Haën (Germany), butan-1-ol (99 %) was purchased from Biochem Chemopharma Co (Canada), water used in experimental was double distilled water. UV-Visible spectrophotometer (Spectrophotometer: SpectroScan 80D/80DV Biotech Engineering Management Co. Ltd.), mechanical shaker (Edmund Buhler GmbH, 420 stroke by min), pH meter (HI255 pH/mV/°C).

### 2.2. General Procedure

20 mL of formic acid solution was shaken at room temperature with a similar amount of the extractive organic solvent butan-1-ol in glass flasks of 100 mL using a mechanical shaker, after phase separation, the concentration of the acid in the aqueous layer is determined by UV-visible spectrophotometer and in the organic layer is deduced by mass balance. The distribution coefficient and the yield of extraction are then deduced. Studied solutions: 20 mL of 0.1 N aqueous formic acid solution.

In order to see the effect of the pH on extraction, this parameter is varied from 1.5-8.0 by adding 2 N aqueous HCl or NaOH solutions using a pH meter with temperature compensation, the distribution coefficient and the yield are then determined at different pH.

The influence of initial concentration of acid in water, volume ratio between aqueous and organic phases, partition coefficient and temperature, was also studied; in each case formic acid was extracted by the organic solvent and the distribution coefficient and the yield were determined.

The values of distribution coefficient  $D$  and the yield of extraction  $R$  were obtained by using the equilibrium mass balance of distribution of the carboxylic acid between aqueous and an organic solvent as given by the following equations:

$$D = \frac{[HA]_{org}^T}{[HA]_{aq}^T} \quad (1)$$

$$R = \frac{100.D}{D + V_{aq} / V_{org}} \quad (2)$$

Where  $[HA]_{org}^T$  and  $[HA]_{aq}^T$  are, respectively the total concentration of the acid in the aqueous and the organic phases,  $V_{aq}$  and  $V_{org}$  are the volumes of the aqueous and the organic phases, respectively.

## 3. Results and Discussion

### 3.1. Effect of the pH on the Extraction

The results obtained for the extraction of formic acid from an aqueous solution at a concentration of 0.1 M are summarized in Table-1. The highest yield of the extraction of the acid is 46.15 % at pH 2.29, less than pKa value (i.e., 3.75), beyond this value; the acid can not be extracted. Figure 1 represents the variations of the distribution coefficient and the yield of extraction as function of pH values. We recommend carrying out the calculations in four decimals, with the final value of coefficient distribution and yield of the extraction rounded to two decimals.

Table 1: VALUES OF DISTRIBUTION COEFFICIENT AND THE YIELD FOR THE EXTRACTION OF FORMIC ACID EXTRACTION AS A FUNCTION OF Ph (SOLVENT: BUTAN-1-OL;  $V_{aq}/V_{org} = 1:1$ ;  $T = 20\text{ }^\circ\text{C}$ )

pH	$[HA]_{aq}^T$	$[HA]_{org}^T$	D	R %
1.48	0.0541	0.0459	0.85	45.88
2.29	0.0538	0.0462	0.86	46.15
2.85	0.0578	0.0422	0.73	42.18
3.5	0.0712	0.0288	0.40	28.79
4.2	0.0922	0.0078	0.08	7.77
5	0.0962	0.0038	0.04	3.83
5.6	0.0985	0.0015	0	1.47

### 3.2. Effect of Partition Coefficient

Table 2 below includes the results of experimental values of the overall distribution coefficient for formic acid 0.1 M extracted in a ratio of  $V_{org} : V_{aq} = 1:1$  in three studied solvents: pentan-1-ol, butan-1-ol and cyclohex-1-ol which have a partition coefficient with formic acid value respectively: 0.90, 0.89 and 0.35. The results show that butan-1-ol gives the highest distribution ( $D=0,86$ ;  $R=46.15\%$ ). The distribution coefficient is even larger than partition coefficient is large ( $D_{butan-1-ol} > D_{pentan-1-ol}$ ) except in the case when the solute polymerise in the organic phase (case of cyclohexan-1-ol, partition coefficient: 0.35 and demirization coefficient: 0.83;  $D_{cyclohexan-1-ol} = 0.75$ ).

Table 2: VALUES OF DISTRIBUTION COEFFICIENT AND THE YIELD FOR THE EXTRACTION OF FORMIC ACID WITH DIFFERENT SOLVENTS ( $[C_i]=0.1\text{ mol/l}$ ;  $V_{aq}/V_{org} = 1:1$ ;  $T = 20\text{ }^\circ\text{C}$ )

Solvent	$[HA]_{aq}^T$	$[HA]_{org}^T$	D	R %
butan-1-ol	0.0538	0.0462	0.86	46.15
pentan-1-ol	0.0582	0.0418	0.72	41.79
cyclohex-1-ol	0.0573	0.0427	0.75	42.70

### 3.3. Effect of Volume Phases Ratio

The values of measured distribution coefficient and degree of extraction, in dependence on volume phase ratio, are given in table 3. The extraction is better when the volume ratio of solvent is higher than the volume of aqueous solution ( $D=0,76$  and  $R=69.45\%$  for  $V_{org}/V_{aq}=3:1$ ). The results are in agreement to that obtained by Kanungnit C. *et al* [7] for the lactic acid recovery by n-butanol, where nearly 97 % of the organic acid was extracted for  $V_{org}/V_{aq}=4:1$ . Fig. 2 shows the variations of distribution coefficient depending on volume phases ratio.

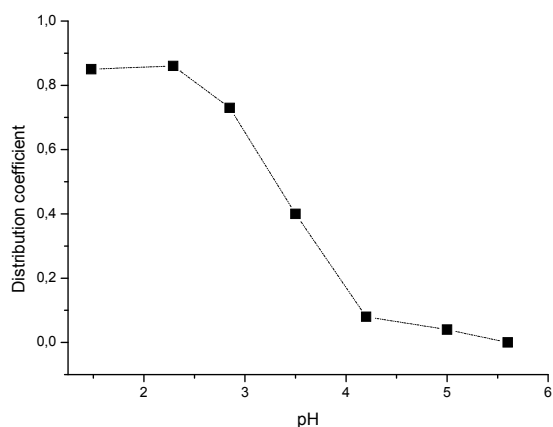


Fig. 1: Distribution coefficient as a function of pH for formic acid in butan-1-ol ( $C_i = 0.1\text{ mol/L}$ ;  $V_{org}/V_{aq} = 1:1$ ;  $T = 20\text{ }^\circ\text{C}$ )

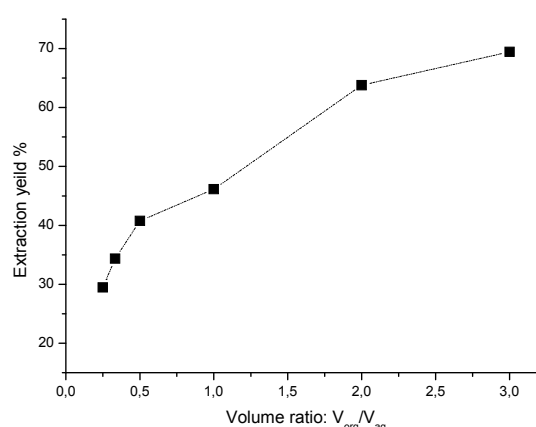


Fig. 2: Yield of extraction as a function of volume ratio formic acid in butan-1-ol ( $C_i = 0.1\text{ mol/L}$ ;  $T = 20\text{ }^\circ\text{C}$ )

### 3.4. Effect of Initial Concentration of Solute

According to the results table 4 below, we get a good extractability over the solution is concentrated in formic acid, beyond a concentration of 0.3 mol/L, distribution coefficient and yield of extraction remain constant ( $D=0,93$  ;  $R=48.14$  %). Amit K. *et al* [11] has studied the effect of initial lactic acid concentration by n-heptane, petroleum ether, decan-1-ol and octan-1-ol, the values of distribution coefficient obtained were found to be much higher with alcohols and increased with initial concentration of organic acid. Distributions coefficients and efficiency of extraction are more significant when the alcohols are mixed with Aliquat 336.

Table 3: VALUES OF DISTRIBUTION COEFFICIENT AND THE YIELD FOR THE EXTRACTION OF FORMIC ACID EXTRACTION AS A FUNCTION OF VOLUME RATIO  $V_{org}/V_{aq}$  (SOLVENT: BUTAN-1-OL; pH = 2.91; T = 20 °C)

$V_{org}/V_{aq}$	$[HA]_{aq}^T$	$[HA]_{org}^T$	D	R %
0.25	0.0705	0.1178	1.67	29.46
0.33	0.0656	0.1041	1.59	34.36
0.5	0.0592	0.0816	1.38	40.78
1	0.0538	0.0462	0.86	46.15
2	0.0362	0.0319	0.88	63.79
3	0.0306	0.0231	0.76	69.45

Table 4: VALUES OF DISTRIBUTION COEFFICIENT AND THE YIELD FOR THE EXTRACTION OF FORMIC ACID EXTRACTION AS A FUNCTION OF INITIAL CONCENTRATION (SOLVENT: BUTAN-1-OL;  $V_{aq}/V_{org} = 1:1$ ; T = 20 °C)

[Ci]	pH	$[HA]_{aq}^T$	$[HA]_{org}^T$	D	R %
0.05	2.51	0.0276	0.0224	0.81	44.82
0.1	2.29	0.0538	0.0462	0.86	46.15
0.3	2.16	0.1553	0.1447	0.93	48.22
0.5	2.00	0.2598	0.2402	0.92	48.05
1	1.85	0.5186	0.4814	0.93	48.14

### 3.5. Effect of Temperature

In investigation of the effect of temperature on distribution coefficient, we have used the **Van't Hoff** approach expressed as  $d(\log D)/dT$  (eqn.3.), which involves measuring the distribution coefficient of formic acid at different temperatures (from 283,15 to 318,15 K), the method relies on the enthalpy of partitioning being constant over the temperature range considered [12-13].

$$\frac{d(\log D)}{dT} = \frac{\Delta H}{2.3026.R.T^2} \quad (3)$$

From equation 3,  $\log D$  can be expressed as a linear function of  $1/T$ :

$$\log D = -\frac{\Delta H}{2.3026.R} \times \frac{1}{T} + Cte \quad (4)$$

The table 5 summarizes the results of distribution coefficient and yield found at different temperatures. Figure 4 shows that  $\log D$  decreases with increasing  $1/T$  in a linear correlation according to the equation:  $\log D = -0,387(1/T) + 1,269$ ; with a correlation factor:  $r^2 = 0,978$ .

Table 5: VALUES OF DISTRIBUTION COEFFICIENT AND THE YIELD FOR THE EXTRACTION OF FORMIC ACID EXTRACTION AS A FUNCTION OF TEMPERATURE (SOLVENT: BUTAN-1-OL;  $V_{aq}/V_{org} = 1:1$ )

T(K)	pH	$[HA]_{aq}^T$	$[HA]_{org}^T$	D	R
283.15	2.18	0.0449	0.0551	0.82	44.93
288.15	2.26	0.0454	0.0546	0.83	45.44
293.15	2.29	0.0462	0.0538	0.86	46.15
303.15	2.5	0.0492	0.0508	0.97	49.18
308.15	2.57	0.0504	0.0496	1.02	50.38
313.15	2.64	0.0519	0.0481	1.08	51.87
318.15	2.71	0.0532	0.0468	1.14	53.23

The slope of the line can evaluate the value of the enthalpy of partitioning:  $\Delta H=1,782 \text{ Kcal.mol}^{-1}$  deduced from eqn. 4 above. The sign of the enthalpy of solubilisation is positive; it means that D is an increasing function of temperature. The acid is more soluble in hot than in cold conditions.

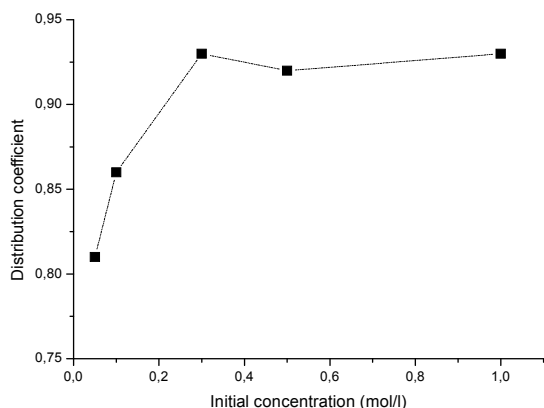


Fig. 3: Distribution coefficient as a function of initial concentration on formic acid in butan-1-ol ( $V_{org}/V_{aq} = 1:1$ ;  $T = 20 \text{ }^\circ\text{C}$ )

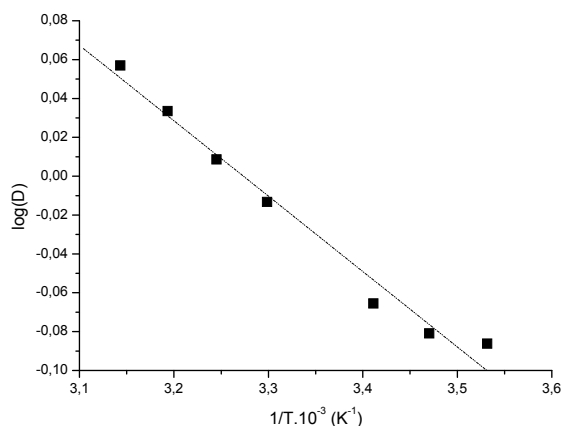


Fig. 4: Distribution coefficient  $\log D$  as a function of  $1/T$  for formic acid in butan-1-ol ( $V_{org}/V_{aq} = 1:1$ ;  $C_i = 0.1 \text{ mol/l}$ )

## 4. Conclusion

The effect of some parameters governing the liquid-liquid extraction of formic acid, from its aqueous solution, was carried out in this study. We noticed, on one hand, that a good extractability of acid is obtained in the neighbourhood of a pH: 2.29, 46.15 % of formic acid were found in the organic phase, the acid is in its undissociated form for pH less than its pKa: 3.75. On the other hand, in comparison to the other two alcohols (pentan-1-ol and cyclohex-1-ol), butan-1-ol provides a good physical equilibrium with formic acid and gives the higher values of yield and distribution coefficient. It should be noted that the results will be better when the extraction involves alcohols mixed with chemicals extractants. Moreover, we noted that, a departure solution concentrated on acid and a high volume ratio between organic and aqueous phases are in favour of the extraction (nearly 65.45 % of the acid were extracted for  $V_{org}/V_{aq}=3:1$ ). Concerning the effect of temperature, as organic acids are more soluble in water, in hot than in cold conditions, an elevation of temperature facilitates the extraction, we get an extractability of 53.23 % of formic acid at 318.15.

## 5. References

- [1] Yang, S.T., Zhu, H. Continuous propionate production from whey permeate using a novel fibrous bed reactor. *Biotech. Bioeng.* 1994, **43**: 1124-1130.
- [2] Kertes, A. S.; King, C. J. Extraction chemistry of fermentation product carboxylic acids. *Biotechnol. Bioeng.* 1986, **28**: 269-282.
- [3] Tamada, J.A.; Kertes, A.S. King, C.J. Extraction of Carboxylic Acid acids with Amine extractants. 1. Equilibrium and Law of Mass Action Modeling. *Ind. Eng. Chem.* 1990, **29**:1319-1326.
- [4] Yang, S.T.; White, S.A.; Hsu, S.T. (). Extraction of Carboxylic Acids with Tertiary and Quaternary Amines. Effect of pH. *Ind. Eng. Chem. Res.* 1991, **30**:1335-1342.
- [5] Cehreli, S. Liquid-Liquid Equilibria of the Acetic Acid-Water-Mixed Solvent (Cyclohexyl acetate- Cyclohexanol) System. *Brazilian Journal of Chemical Engineering.* 2002, **19** (1): Sao Paulo.
- [6] Kalaichelvi, P. Perumalsamy, A. Arunagiri, A. Sofia, K. Synergistic Extraction of Acetic Acid From its Aqueous Solution. *Journal of the University of Chemical Technology and Metallurgy.* 2007, 42:291-194.
- [7] Kanungnit C. and Panarat R. n-Butanol as an Extractant for Lactic Acid Recovery. *World Academy of Science, Engineering and Technology.* 2011, 80:239-242.
- [8] Kim, H.S, Ahn, J.W. Kim, J.Y. Shin, C.H. Method for Treating of Etching Acid Waste Containing Phosphoric Acid,

Acetic Acid and Nitric Acid. *Korean Journal Patent* 2005, 20,050,003.996.

- [9] Wasewar, K.L. Heesink, A.B.M et al., Intensification of Enzymatic Conversion of Glucose to Lactic Acid by Reactive Extraction. *Chem. Eng. Sci.* 2003, **58**(15):3385-3394.
- [10] Yang, S.T.; White, S.A.; Hsu, S.T. Extraction of carboxylic acids with tertiary and quaternary amines- effect of pH. *Ind. Eng. Chem. Res.* 1991, 30:1335–1342.
- [11] Amit K, Shri C, Kailas L. W. Recovery of propionic acid from aqueous phase by reactive extraction using quaternary amine (Aliquat 336) in various diluents. *Chemical Engineering Journal*. 2009,152:95-102.
- [12] Alberto A, Antonio B, Pilar S, and Isabel V. Liquid-Liquid Equilibria of Ternary System Water+Propionic Acid+Methyl Isobutyl Ketone at Various Temperatures. *J.Chem.Eng.Data*, 1993, 38:201-203.
- [13] Deardea ,J.C. and Bresnen. G.M. Thermodynamics of Water-octanol and Water-cyclohexane Partitioning of some Aromatic Compounds. *International Journal of Molecular Sciences. Int. J.Mol. Sci.* 2005,6:119-129.