Study of the Effect of Some Parameters Governing the Recovery Process of Acetic Acid from Waste Water by Alcohols

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Abstract. Optimization of experimental conditions of acetic acid recovery from its aqueous solution by a liquid-liquid extraction, with alcohols, was carried out in this study. The effect of parameters governing the process such as: pH of aqueous solution, partition coefficient and initial concentration on acid, volume ratio between phases and temperature, were studied. Variation of distribution coefficient and yield of extraction of acetic 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, a yield of 64.4 % was obtained at pH 1.40 . A departure solution concentrated on acid and a high volume ratio of organic solvent favor the extraction (79.78 % 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 69.62 % of acetic acid were extracted at 318.15 K.

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

Keywords: *Acetic acid, liquid extraction, distribution coefficient, yield.*

1. Introduction

Liquid-liquid extraction is a separation method of one or more components from a liquid 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, these entities are influenced by several parameters such as solutes concentrations, nature of solvent, *pH* of medium, temperature and hydrophobicity of extracted substances [1].

Acetic acid is one of the simplest carboxylic acids. It is the main component of vinegar and mainly used in food industry as an acidity regulator, as a condiment and as food additive E260 [2-4]. Acetic acid is also an important chemical reagent and industrial chemical, used in the production of cellulose acetate for photographic film and polyvinyl acetate for wood glue, as well as synthetic fibres and fabrics [5].

Various technologies have been reported for the separation of organic acids, especially acetic 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 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

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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 acetic acid, by butan-1-ol, was studied and carried out in this work.

2. Experimental section

2.1. Materials

Acetic acid (99-100 %), butan-1-ol (99 %) and cyclohex-1-ol (99%) were purchased from Biochem Chemopharma Co (Canada), pentan-1-ol (98%) was purchased from Alfa Aesar, 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/ºC).

2.2. General procedure

20 mL of acetic acid solution was shacked at room temperature with a similar amount of the extractive organic solvent 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 one 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 acetic 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 acetic 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:

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

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

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 acetic acid from an aqueous solution at a concentration of 0.1 M are summarized in Table-I. The highest yield of the extraction of the acid is 64.4 % at *pH* 1.40, less than *pKa* value (i.e., 4.75), 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-I: VALUES OF DISTRIBUTION COEFFICIENT AND THE YIELD FOR THE EXTRACTION OF ACETIC ACID AS A FUNCTION OF *pH* (SOLVENT: BUTAN-1-OL; $V_{aq}/V_{org} = 1:1$; T = 20 ℃)

pH	$[HA]^T_{aq}$	$[HA]^T_{org}$	D	R %
1.40	0.0356	0.0644	1.81	64.40
2.31	0.0450	0.0550	1.22	55.00
3.32	0.0467	0.0533	1.14	53.30
3.57	0.0489	0.0511	1.04	51.10
4.36	0.0674	0.0326	0.48	32.62
4.59	0.0688	0.0312	0.45	31.17
6.04	0.0971	0.0029	0.03	2.90

3.2. Effect of partition coefficient

Table II below, includes the results of experimental values of the overall distribution coefficient for acetic 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 witch have a partition coefficient with acetic acid value respectively: 1.32, 0.96 and 0.66. The results show that butan-1-ol gives the highest distribution (D=1.23 ; R=55.25 %). The distribution coefficient is even larger than partition coefficient is large.

TABLE-II: VALUES OF DISTRIBUTION COEFFICIENT AND THE YIELD FOR THE EXTRACTION OF ACETIC ACID WITH DIFFERENT SOLVENTS (Ci=0.1 mol/l; $V_{org} : V_{aq} = 1:1$; T = 20 ℃)

Solvent	$[HA]^T_{aq}$	$[HA]^T_{org}$	D	R %
butan-1-ol	0.0448	0.0552	1.23	55.25
pentan-1-ol	0.0548	0.0452	0.83	45.21
cyclohex-1-ol	0.0593	0.0407	0.69	40.73

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 III. The extraction is better when the volume ratio of solvent is higher than the volume of aqueous solution (D=1,32 and R=79.78 % 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 phase ratio.

TABLE-III: VALUES OF DISTRIBUTION COEFFICIENT AND THE YIELD FOR THE EXTRACTION OF ACETIC ACID EXTRACTION AS A FUNCTION OF VOLUME RATIO V_{org} / V_{aq} (SOLVENT: BUTAN-1-OL; *pH* = 2.91; T = 20 ℃)

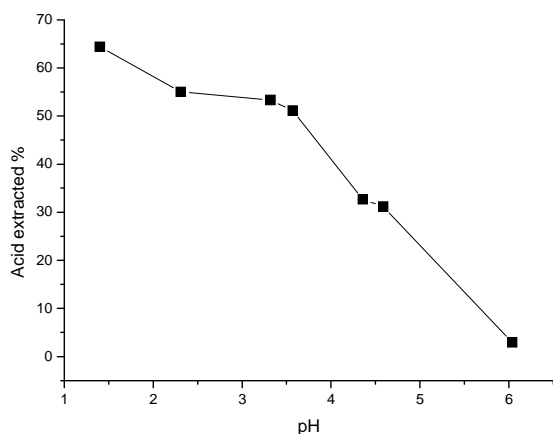| V_{org}/V_{aq}	$[HA]^T_{aq}$	$[HA]^T_{org}$	D	R %
0.25	0.0742	0.1034	1.39	25.85
0.33	0.072	0.0841	1.17	27.99
0.5	0.0613	0.0775	1.26	38.73
1	0.0448	0.0552	1.23	55.25
2	0.0517	0.0483	0.93	65.12
3	0.0432	0.0568	1.32	79.78

Fig. 1: Yield of extraction as a function of pH for acetic acid in butan-1-ol
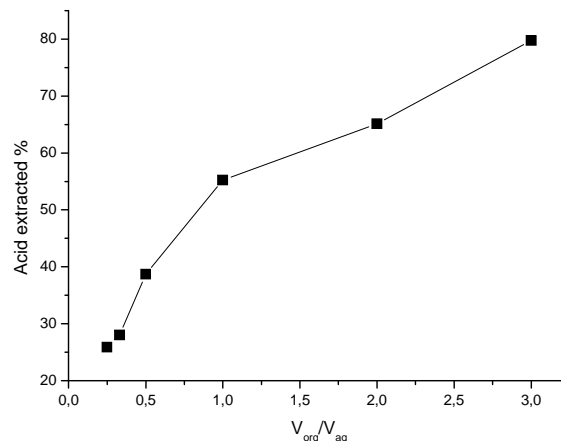(Ci = 0.1 mol/L ; V_{org}/V_{aq} = 1:1; T = 20 ℃)

Fig. 2: Yield of extraction as a function of volume ratio acetic acid in butan-1-ol
(Ci = 0.1 mol/L ; T = 20 ℃)

3.4. Effect of initial concentration of solute

According to the results table IV below, we get a good extractability over the solution is concentrated in acetic acid, beyond a concentration of 0.3 mol/L , distribution coefficient and yield of extraction remain constant (D=0,35 ; R=57.49 %). 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-IV: VALUES OF DISTRIBUTION COEFFICIENT AND THE YIELD FOR THE EXTRACTION OF ACETIC ACID AS A FUNCTION OF INITIAL CONCENTRATION ON ACID
(SOLVENT:BUTAN-1-OL; V_{aq}/V_{org} = 1:1; T = 20 ℃)

[Ci]	pH	$[HA]^T_{aq}$	$[HA]^T_{org}$	D	R %
0.05	3.05	0.0228	0.0272	1.20	54.46
0.1	2.88	0.0448	0.0552	1.23	55.25
0.3	2.70	0.1275	0.1725	1.35	57.49
0.5	2.48	0.2099	0.2901	1.38	58.02
1	2.32	0.4221	0.5779	1.37	57.79

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(logD)/dT (eqn.3.), which involves measuring the distribution coefficient of acetic 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].

$$\frac{d(logD)}{dT} = \frac{\Delta H}{2.3026.R.T^2} \qquad (3)$$

From equation 3, logD can be expressed as a linear function of 1/T:

$$logD = -\frac{\Delta H}{2.3026.R.} x \frac{1}{T} + Cte \qquad (4)$$

The table V summarizes the results of distribution coefficient and yield found at different temperatures. Figure 4 shows that logD decreases with increasing 1/T in a linear correlation according to the equation: logD = -1,441(1/T) + 4,92; with a correlation factor: r^2 = 0,93.

The slope of the line can evaluate the value of the enthalpy of partitioning: ΔH=6,64 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.

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

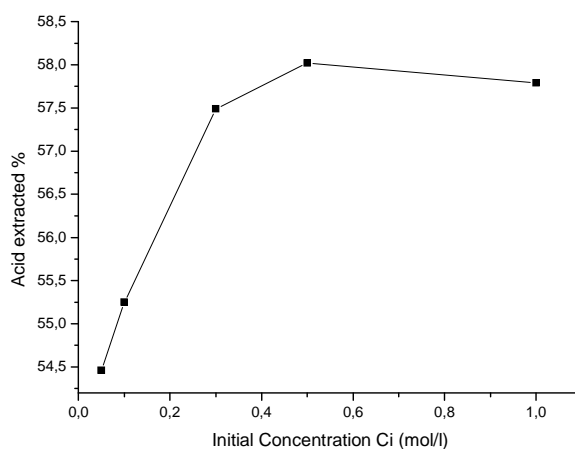| T(K)	pH	$[HA]^T_{aq}$	$[HA]^T_{org}$	D	R
283.15	2.86	0.0651	0.0349	0.54	34.92
288.15	2.87	0.0545	0.0455	0.83	45.47
293.15	2.88	0.0448	0.0552	1.23	55.25
303.15	3.00	0.0342	0.0658	1.93	65.84
308.15	3.07	0.0352	0.0648	1.84	64.76
313.15	3.13	0.0369	0.0631	1.71	63.05
318.15	3.19	0.0304	0.0696	2.29	69.62

Fig. 3: Distribution coefficient as a function of initial concentration on acetic acid in butan-1-ol
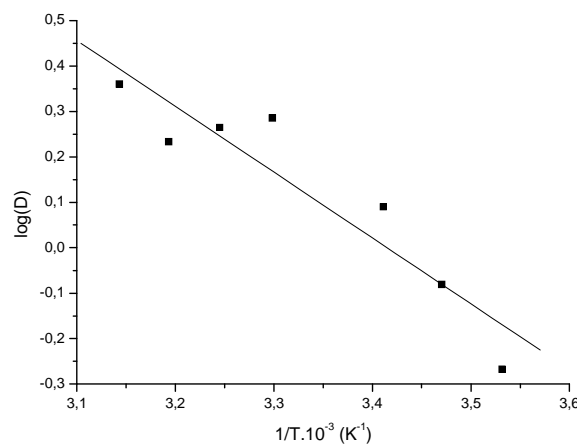(V_{org}/V_{aq} = 1:1; T = 20 ºC)

Fig. 4: Distribution coefficient logD as a function of 1/T for acetic acid in butan-1-ol
(V_{org}/V_{aq} = 1:1; Ci = 0.1 mol/l)

4. Conclusion

The effect of some parameters governing the liquid-liquid extraction of acetic 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*: 1.40, 64.4 % of acetic acid were found in the organic phase, the acid is in its undissociated form for pH less then 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 acetic 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 79.78 % of the acid were extracted for $V_{org}/V_{aq}=3:1$). Concerning the effect of temperature, 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 69.62 % of acetic acid at 318.15.

5. References

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