

SOLVENT EXTRACTION OF ACETIC ACID FROM AQUEOUS MEDIA USING TRIOCTYL PHOSPHINE OXIDE (TOPO) – BASED SOLVENT SYSTEMS

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ABSTRACT

Acetic acid is a very important commodity chemical with several applications in the chemical and food industry. Although acetic acid can be produced readily via fermentation processes, various factors such as low yield, the presence of secondary fermentation products and the rather complex separation requirements make the production high quality acetic acid via the fermentation route rather expensive. This study examined the reactive extraction of acetic acid from aqueous media using trioctyl phosphine oxide (TOPO) with *n* – hexane, toluene, methyl isobutyl ketone (MIBK) and methyl ethyl ketone (MEK) as diluents. Effect of various parameters such as phase ratios, and concentration of TOPO in the diluents on the degree of extraction of acetic acid were studied and the results obtained showed that while MEK on its own gave a higher extraction yield than MIBK, a reversal in trends was observed on adding TOPO to these solvents with the MIBK – TOPO system having a greater degree extraction, compared to the MEK – TOPO system. The extractions performed using *n*-hexane and toluene as diluents gave higher extraction yields with toluene. The degree of effectiveness of the diluents in the extraction of acetic acid from aqueous media is MIBK > MEK > Toluene > *n* – hexane.

Keywords: Acetic acid, MIBK, MEK, Reactive Extraction, TOPO.

1. INTRODUCTION

Frequently, chemical engineers and organic chemists must separate organic compounds of interest from a mixture of compounds, often derived from natural sources or product of synthetic reactions. One method commonly used to separate such mixture of compounds is known as solvent extraction or liquid-liquid extraction (Cox and Rydberg, 2004; Wasewar, 2012; Ingle *et al.*, 2017; Sas *et al.*, 2018; Alves De Oliveira *et al.*, 2020). In separation and purification technology, liquid-liquid extraction plays an important role and has been successfully applied in the isolation of organic compounds such as lactic acid (Udachan and Sahoo, 2014; Komesu *et al.*, 2017; Li *et al.*, 2021), citric acid (Araújo *et al.*, 2017), itaconic acid (Kreyenschulte *et al.*, 2018), and other valuable organic acids from fermentation broths. Another very important organic acid which can be recovered from fermentation media using this method is acetic acid.

Acetic acid is a commodity chemical with several applications in the food and chemical industry. Acetic acid is used in several industrial sectors such as

chemical, pharmaceutical, textile, polymer and paints, food and beverages, with a substantial proportion of the global production being used in the production of cellulose acetate (Candido *et al.*, 2017) and vinyl acetate monomer (VAM) which is used in the production of a wide range of polymers and resins for paints, adhesives, films, and a myriad of other industrial and consumer applications (Das *et al.*, 2009; Li *et al.*, 2022). Acetic acid also finds uses in the food industry as food additive (code E260) as an acidulant and as a condiment (Derossi *et al.*, 2011; Awuchi *et al.*, 2020).

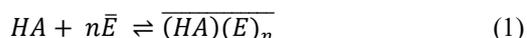
Acetic acid is produced industrially synthetically via the carbonylation of methanol (Haynes, 2006; Kalck *et al.*, 2020), oxidation of acetaldehyde (Han *et al.*, 2019) or by fermentative oxidation of ethanol (Gullo *et al.*, 2014). Unfortunately, the disadvantage of fermentation is that it produces rather dilute solutions of acetic acid due to the inhibitory nature of the acid to the fermentation microorganisms (Lin and Tanaka, 2006). In addition, the fermentation broth always contains many impurities including cell biomass, other organic acids, and unconsumed nutrients (Zi *et al.*, 2013; Zentou *et al.*,

2021). Recovery and purification of acetic acid from dilute media requires many steps and unit operations, which consequently contribute to high cost of production.

Reactive extraction has been one of the attractive methods for the recovery of carboxylic acids and has been studied by several researchers. Some extractants that have been investigated include tri-n-octylamine (Uslu, 2009; Inyang and Lokhat, 2020), tributyl phosphate (Djas and Henczka, 2018) and trioctyl phosphine oxide (Djas and Henczka, 2018) as well as neutral extractants with oxygen-containing polar groups (Djas and Henczka, 2018; Pandey and Kumar, 2018; Mungma *et al.*, 2019). This work studied the extraction of acetic acid with methyl isobutyl ketone (MIBK), methyl ethyl ketone (MEK), trioctyl phosphine oxide (TOPO) and their blends. The objective is to examine the influence of different variables such as phase ratio, initial feed concentration and nature of organic extractant on the extraction of acetic acid.

1.1 Reactive Solvent extraction of carboxylic acids

The reactive extraction of a carboxylic acid (HA) with an extractant (E) gives a reaction complex, which remains in the organic phase (Mukherjee and Munshi, 2020):



Where HA represents the unassociated part of the acid present in the aqueous phase and the overbar represents the species in the organic phase. From equation (1), the equilibrium extraction constant k_{ex} can be written:

$$k_{ex} = \frac{\overline{(HA)(E)_n}}{[HA][\bar{E}]^n} \quad (2)$$

Where the square brackets are the concentrations of the respective species. The distribution coefficient of acetic acid in the aqueous and organic phases (K_D) is defined by:

$$K_D = \frac{\overline{[HA]}}{[HA]} \quad (3)$$

where [HA] and $\overline{[HA]}$ are the concentrations of the acid in the aqueous and organic phases, respectively. It is noteworthy that here, $\overline{(HA)(E)_n}$ and $\overline{[HA]}$ represent the same quantity. Thus, equation (2) becomes:

$$k_{ex} = \frac{K_D}{[\bar{E}]^n} \quad (4)$$

The value of the extraction constant can be determined from a plot of $\log(K_D)$ against $\log[\bar{E}]$ where (4) is written in a linear form:

$$\log k_D = \log k_{ex} + n \log[\bar{E}] \quad (5)$$

2. MATERIALS AND METHODS (OR METHODOLOGY)

Methyl isobutyl ketone (MIBK), methyl ethyl ketone (MEK), n – hexane and toluene were obtained from BDH chemicals while tri-n-octyl phosphine oxide (TOPO) was obtained from Sigma-Aldrich. All solvents used as organic phase or extractant were of analytical grade and were used without further purification. Glacial acetic acid (Merck) was used to prepare the various concentrations used in the study. All experiments were performed at 300 ± 2 K. For the purpose of the experiment, isothermal condition was assumed.

Aqueous acetic acid solution was prepared by dissolving glacial acetic acid in distilled water until the desired concentration was achieved, with the highest concentration used in this study being 16.9 g/L (or, 0.28 mol/L). The initial concentration of acetic acid in the aqueous phase was determined by titration against 0.1 M NaOH using phenolphthalein as indicator. The extraction and stripping experiments were carried with 20cm³ of the aqueous phase shaken with specified volumes of the organic solvents in stoppered 250 ml glass flasks on a tabletop mechanical shaker at 300 rpm for 20 min, after which the mixtures were poured into 250 ml separating funnels and allowed to settle for 3 h for complete phase separation. The quantity of acetic acid left in the aqueous phase was determined by titration with 0.1 M NaOH solution, while the acid content of the organic phase was obtained by material balance. The process was repeated for 2, 3, 4 and 5 successive extractions using equal volume of aqueous and organic phases in each case for batch extraction in stages and varying volume of solvent for single batch extraction. This procedure was repeated for the various solvent blends used.

The level of extraction for each solvent system was expressed in terms of the percentage extraction which is defined as (Inyang and Lokhat, 2020):

$$\text{Percentage Extraction (\%E)} = \left(\frac{V_o C_o - V_{eq} C_{eq}}{V_o C_o} \right) \times 100 \quad (6)$$

Where V_o and V_{eq} are the initial and equilibrium volumes of the aqueous phase, respectively. In addition, C_o and C_{eq} are the initial and equilibrium concentrations of acetic acid in the aqueous phase, respectively.

3. RESULTS AND DISCUSSION

3.1 Acetic acid extraction with MIBK and MEK

A comparison of the solvent extraction of acetic acid was made for both MIBK and MEK for single batch and crosscurrent extractions and the result obtained (Tables 1 and 2) shows MEK to be a better extractant than MIBK. The general trend in the degree of extraction can be

improved on using stage-wise crosscurrent extraction systems, compared to single extraction batches with the volume of the organic phase (V_o) increased as shown in Table 2. The equilibrium curves for the extraction of acetic acid using MIBK, MEK or their 1:1 blend (Figure 1) also showed MEK to be the better extractant.

Table 1: Single Batch Extraction of Acetic Acid into MEK and MIBK ($C_o = 0.28$ Mol/L)

Phase Ratio ($V_o:V_A$)	%E		
	MIBK	MEK	1:1 blend of MIBK and MEK
1:1	31.80	41.61	36.16
2:1	48.41	64.02	57.18
3:1	59.07	77.70	67.67
4:1	65.43	85.46	76.44
5:1	71.14	89.14	79.86

V_o = volume of organic phase. V_A = volume of aqueous phase.

Table 2: Batch-wise Extraction of Acetic Acid into MEK and MIBK ($V_o:V_A = 1:1$) ($C_o = 0.28$ Mol/L)

No. of batches	%E		
	MIBK	MEK	1:1 blend of MIBK and MEK
1	31.80	41.61	36.16
2	55.42	71.55	70.32
3	70.26	88.63	81.63
4	80.74	95.64	88.63
5	87.34	98.23	93.88

V_o = volume of organic phase. V_A = volume of aqueous phase.

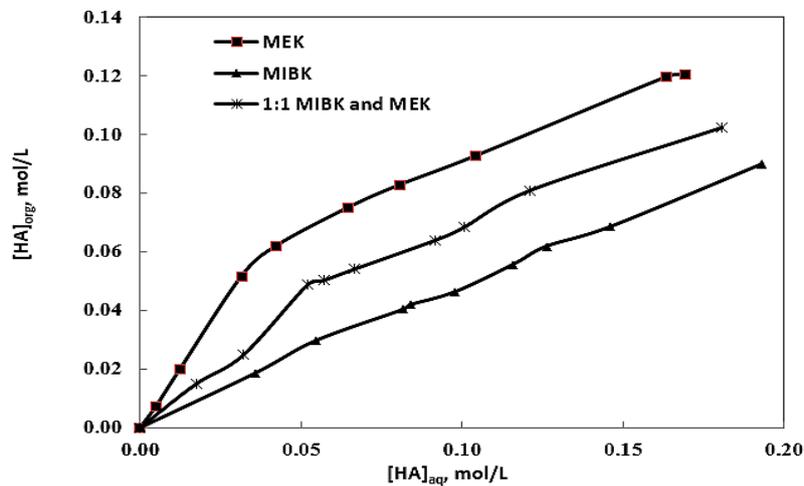


Figure 1: Distribution of acetic acid between phases for MIBK and MEK

3.2 Effect of adding a second extractant

The addition of small amounts of a second extractant (TOPO) to the organic phases gave an even greater separation for acetic acid as shown by the equilibrium plots in Figure 2. The highest percentage extraction for an extractant containing 1 % v/v TOPO in MIBK was found to be 74.15 % for a phase ratio of 5:1, compared

to pure MIBK which gave a 71.14% recovery for the same phase ratio (Table 1). Also, a 1% (v/v) TOPO–MIBK solvent blend gave 88.57% recovery of acetic acid, compared to pure MIBK which gave 87.34 % for the same number of extraction batches as shown in Tables 3 and 4. Thus, the interaction between TOPO and MIBK is synergistic with respect to the extraction of

acetic acid from aqueous media. The addition of TOPO to MEK however had an antagonistic effect on the extraction of acetic acid as shown in Figure 3. The highest percentage extraction for a solvent system

containing 1% TOPO in MEK was found to be 84.60 % for a phase ratio of 5:1 and 96.81 % for five extraction batches as shown in Tables 3 and 4.

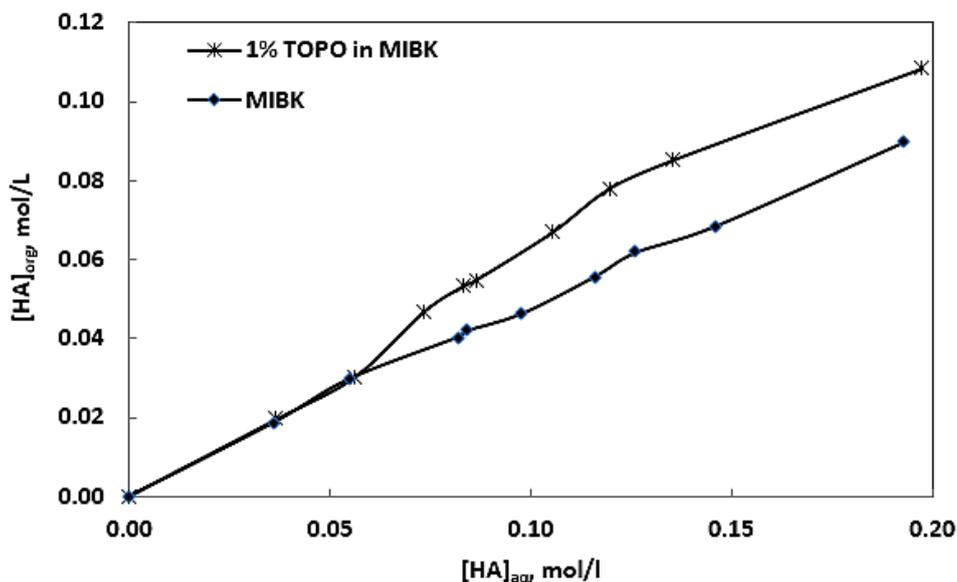


Figure 2: Distribution of acetic acid between phases using 1 % TOPO in MIBK as extractant

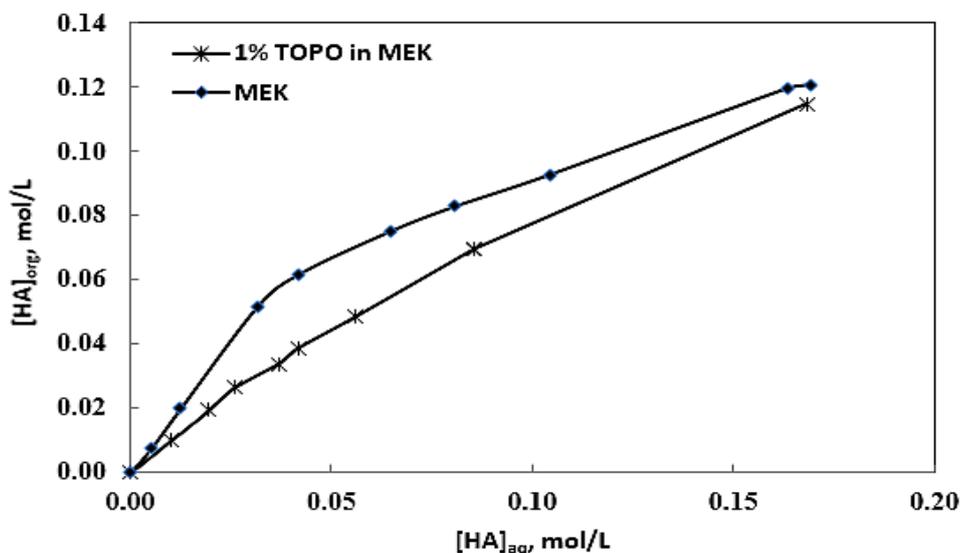


Figure 3: Distribution of acetic acid between phases using 1 % TOPO in MEK as extractant

Table 3: Single Batch Extractions of Acetic Acid with 1% TOPO in MEK and MIBK

Phase Ratio ($V_o:V_A$)	%E	
	1% TOPO in MIBK	1% TOPO in MEK
1:1	35.46	40.52
2:1	52.12	61.11
3:1	62.78	72.22
4:1	69.43	78.68
5:1	74.15	84.60

Table 4: Batch-wise Extraction of Acetic Acid 1% TOPO in MEK and MIBK ($V_o:V_A = 1:1$)

No. of batches	%E	
	1% TOPO in MIBK	1% TOPO in MEK
1	35.46	40.52
2	60.95	70.01
3	72.88	86.44
4	82.46	93.63
5	88.57	96.84

To further examine the extraction of acetic acid using TOPO, two additional solvents were introduced, which are n-hexane (an aliphatic hydrocarbon) and toluene (an aromatic solvent). Figure 4 illustrates the behavior of a 1 percent (w/v) solution of TOPO in n-hexane and toluene. From Figure 4, there use of toluene gave an

increased extraction yield for acetic acid, when compared to n- hexane. These results are similar to those reported by Wasewar *et al.* (2011) and Inyang and Lokhat (2020).

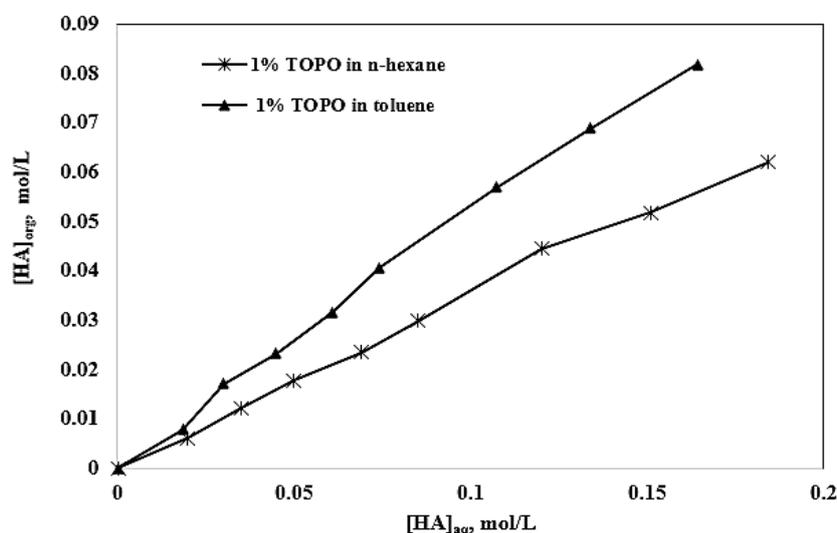


Figure 4: Distribution of acetic acid between phases using 1 % TOPO using toluene and n-hexane as extractants ($V_o:V_A = 1:1$)

Figure 5 shows the effect of increasing the concentration of TOPO on the acetic acid extraction yield. The concentration of TOPO in the solvents were varied from 0.02 and 0.30 mol/L while the initial aqueous phase concentration of the acetic acid was kept constant at 0.28 mol/L. From Figure 5, it can be inferred that the use of active diluents such as MIBK and MEK gave higher extraction yields with TOPO, compared with what was extracted using inert such as n – hexane and toluene. This is in agreement with the results obtained by Pal and Keshav (2014), and Sprakel and Schuur (2019). The use of an aromatic diluent such as toluene gave higher extraction yields than those obtained using an aliphatic diluent such as n – hexane.

The plot of the distribution coefficient against the concentration of TOPO (Figure 5) was fitted to equation (4) to obtain the equilibrium extraction constant k_{ex} and the results obtained are presented in Table 5. The number of TOPO molecules per molecule of acetic acid extracted was found to decrease in the order MIBK < MEK < toluene < n – hexane and the extraction constant also follows that trend. This trend is similar to the one reported by Wasewar and Shende (2011) in the extraction of caproic acid using Aliquat 336, and Udachan and Sahoo (2014) for the extraction of lactic acid using trioctyl amine.

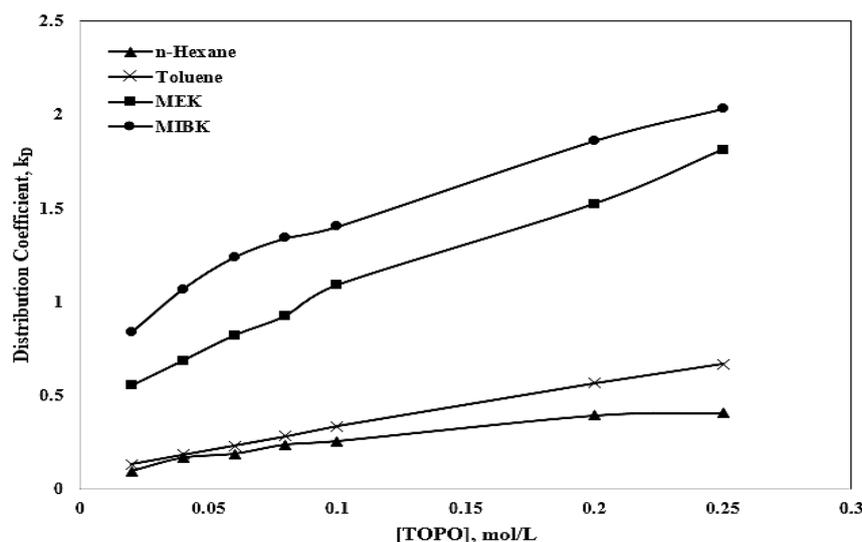


Figure 5: Effect of TOPO concentration on the extraction of acetic acid from aqueous media

Table 5: Extraction equilibrium parameters for each of the solvent systems

Diluent	Extraction constant (K_{ex})	n	R^2
n- Hexane	0.954	0.57	0.9851
Toluene	1.579	0.66	0.9896
MEK	3.237	0.48	0.9829
MIBK	3.268	0.34	0.9964

4. CONCLUSION

The extraction of acetic acid using trioctyl phosphine oxide in inert diluents (n – hexane and toluene) and active diluents (MEK and MIBK) were studied at room temperature and the following conclusions were made. MIBK and MEK on their own are good extractants for acetic acid with recovery for a phase ratio of 1:1 being 31.80% for MIBK and 41.61% for MEK, indicating that MEK is a better extractant for acetic acid from aqueous media, compared to MIBK. While synergistic extraction was observed on addition of small amounts of TOPO to MIBK, the addition of similar quantities of TOPO to MEK had an antagonistic effect, with the extraction yield dropping to 40.52 %. Although the recovery of acetic acid using TOPO in the inert diluents increased with increasing concentration of TOPO, higher solvent loading was observed when MEK and MIBK were used, with MIBK being better diluent than MEK. The degree of effectiveness of the diluents in the extraction of acetic acid from aqueous media is MIBK > MEK > Toluene > n – hexane.

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