

## Effective Parameters in Extraction of Sulfuric Acid by Trioctylamine (TOA) as Organic Extractant

Aidin HEIDARI<sup>1</sup>, Shahryar SHAHINI<sup>1</sup>, Davoud H. FATMEHSARI<sup>1</sup>, and Eskandar K. ALAMDARI<sup>1,\*</sup>,

<sup>1</sup> *Department of Mining and Metallurgical Engineering, Amirkabir University of Technology, P.O. Box. 15875-4413, Tehran, Iran*

Trioctylamine (TOA) is used as organic extractant in this research. In this study, the effects of several parameters such as concentration of trioctylamine (TOA) as the extractant, concentration of octanol as the modifier, temperature and ratio of organic phase ( $V_{org}$ ) to aqueous phase ( $V_{aq}$ ) were investigated. At the end, the stoichiometric coefficients of reaction were estimated by applying slope method analysis. Also, two equations are proposed (developed) for the extraction of sulfuric acid with TOA by statistical modeling.

### 1. Introduction

Acids, among other chemicals, are used in many industries for several purposes. So recovery of acids has been investigated in chemical industries [1]. Till date, several acids such as acetic acid, sulfuric acid, lactic acid, adipic acid, myristic acid, succinic acid, chloroacetic acid and glycolic acid were recovered from their dilute solutions. Also recovery of acids can be done by several methods. Membrane processes, electro-dialysis (ED), pervaporation, reverse osmosis (RO), biological processes, ion exchange/adsorption, reactive separation, reactive distillation, reactive chromatography (RC) and solvent extraction are important methods for recovery of acids [1-8]. Acid structure, economical efficiency and other conditions are the effective parameters to choose one of those methods.

Solvent Extraction is one of the most effective methods for separation/ recovery of metallic ions from the aqueous media. In recent years, this technique has been used for the recovery of different acids including sulfuric acid. Sulfuric acid has been widely used in metallurgical industries. As a result, large amounts of waste sulfuric acid solution have been generated, causing environmental problems. The waste sulfuric acid solution may contain valuable metals such as Fe, Ni, and Co. It is thus appropriate to develop an alternative method to recover sulfuric acid and the metals, simultaneously. Recovery of sulfuric acid by solvent extraction has been investigated yet by TEHA, Alamine 336, Alamine 308 and Cyanex 923 as organic extractants [2,9-11]. Researches shows amines are more effective for extraction of sulfuric acid [12]. Extraction of sulfuric acid by solvent extraction has not been investigated yet by trioctylamine (TOA) as organic extractant. Trioctylamine (TOA) is used as organic extractant and the effects of several parameters were investigated in this research.

### 2. Experimental

## 2.1 Reagents

Commercial extractant trioctylamine (TOA) was supplied by Merck Co., kerosene was supplied by Tehran refinery Co. as the diluent, and octanol were supplied by Merck Co. as the modifier. Sulfuric acid (95-98vol%) was purchased from Scharlau (by titration, it was found that it is 98vol%) which is used with distilled water to prepare aqueous solutions. Potassium hydroxide (KOH) titrisol was supplied by Carlo Erba which is used with distilled water to prepare titrant solution for titration. Also phenolphthalein was purchased from Daejung as indicator.

## 2.2 Preparation of solution and experiments

Experiments were carried out in flasks containing 25 mL of aqueous and organic solutions. Initial concentrations of sulfuric acid in the aqueous phase varied from 20 to 380 g/L. Trioctylamine volume percentages in organic phase were set at 10, 25 and 40%. Moreover, the octanol volume percentages were 5, 10 and 15%. The volume was adjusted with kerosene as diluent. The mixtures were agitated at different temperatures of 5, 20 and 35°C and different phase ratios. Samples were then retained in the flask for 30 min to allow complete separation of the phases. Potassium hydroxide titration was employed to determine sulfuric acid concentration in the aqueous and organic solutions, using phenolphthalein as an indicator.

## 3. Results and Discussion

### 3.1 Initial analysis of extraction behavior

For initial analysis of extraction behavior of sulfuric acid by TOA, experiments were done in a wide range of initial acid concentration from 20 to 380 g/l and three organic phases of 5, 10 and 15 volume percentage of TOA respectively and constant 10 volume percent for octanol. Figure 1 shows that by increasing the concentration of TOA, extraction of sulfuric acid increases. But for initial sulfuric acid concentration of more than 200 g/l, increasing in extraction of sulfuric acid is not considerable and TOA was closed to its loading capacity. Therefore, Subsequent experiments were done with acid concentrations of lower than 200 g/l as shown in Table 1.

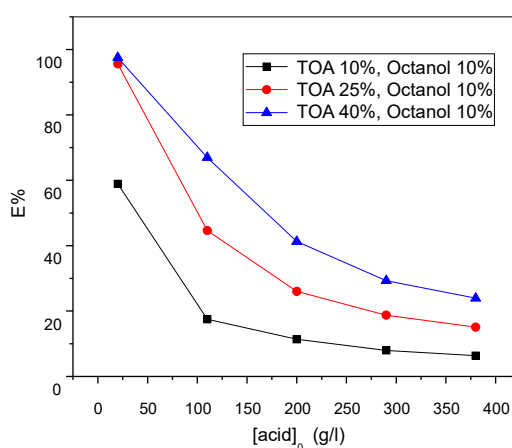


Figure 1. Extraction percentage of sulfuric acid against initial concentration of sulfuric acid;  
 $T=20\text{ }^{\circ}\text{C}$ ; octanol=10vol%.

Table 1. Experiments and investigated parameters.

no	Acid concentration (g/l)			TOA concentration (volume percent)			Octanol concentration (volume percent)			Temperature (°C)			$V_{org}/V_{aq}$		
1	20	85	150	10	25	40		10			20			1	
2	20	85	150		25		5	10	15		20			1	
3	20	85	150		25			10		5	20	35		1	
4	20	85	150		25			10			20		0.5	1	2

### 3.2 Effect of TOA concentration on sulfuric acid extraction

Figure 2 shows that the sulfuric acid extraction increases with increasing in TOA concentration. But for sulfuric acid with 20 g/l concentration, extraction was completed by TOA with 25vol% concentration and extraction percent is about 100%. It should also be noted that viscosity of organic phase increases with increasing extractant concentration, which makes the separation process difficult. So TOA with 25vol% concentration was used in next experiments for investigation of other parameters.

### 3.3 Effect of modifier concentration (octanol) on sulfuric acid extraction

For this solvent extraction system, the presence of octanol is necessary to modify the organic phase. Figure 3 shows that increasing octanol concentration has no effect on sulfuric acid extraction and just accelerated separation of organic and aqueous phases and so two curves were superposed. But systems with octanol of 5vol% or less, resulted in a third phase formation. Thus octanol with concentration higher than 5vol% is necessary for this system. In subsequent experiments octanol with 10vol% was used for investigation of other parameters.

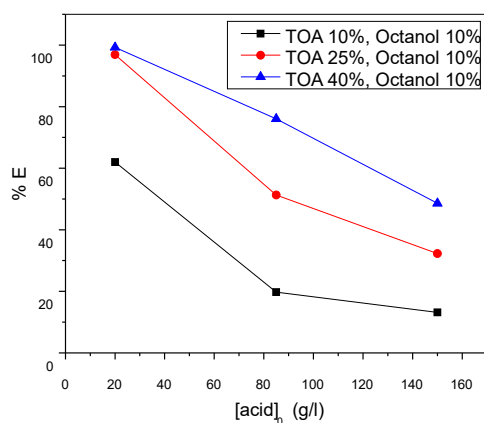


Figure 2. Effect of TOA concentration on extraction percentage of sulfuric acid against initial concentration of sulfuric acid;  $T=20^{\circ}\text{C}$ ; octanol=20vol%.

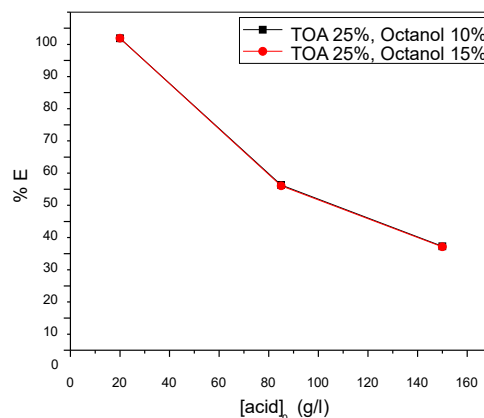


Figure 3. Effect of octanol concentration on extraction percentage of sulfuric acid against initial concentration of sulfuric acid;  $T=20^{\circ}\text{C}$ ; TOA=25vol%.

### 3.4 Effect of temperature on sulfuric acid extraction

Figure 4 shows the effect of temperature on sulfuric acid extraction. Although experiments show the extraction reaction is exothermic, effect of temperature was not considerable and the curves of these three temperatures were approximately superposed. So, later experiments for investigation of other parameters were done in 20°C.

### 3.5 Effect of $V_{org}/V_{aq}$ on sulfuric acid extraction

Figure 5 shows that the sulfuric acid extraction increases with increasing in  $V_{org}/V_{aq}$  ratio. But for sulfuric acid with 20 g/l concentration, extraction percent of sulfuric acid with  $V_{org}/V_{aq}=1$  was about to 100% thus for this sulfuric acid concentration and less,  $V_{org}/V_{aq}>1$  is not required. Also separation of organic and aqueous phases is more difficult by increasing ratio of  $V_{org}/V_{aq}$ .

### 3.6 Extraction mechanism

Extraction mechanism of sulfuric acid by TOA is performed according to reaction 1:



Equilibrium constant of reaction 1 is written as follows:

$$K = \frac{[\text{TOA} \cdot n\text{H}_2\text{SO}_4]}{[\text{TOA}] [\text{H}_2\text{SO}_4]^n} \times \frac{\gamma_{\text{TOA} \cdot n\text{H}_2\text{SO}_4}}{\gamma_{\text{TOA}} \gamma_{\text{H}_2\text{SO}_4}^n} = \frac{[\text{TOA} \cdot n\text{H}_2\text{SO}_4]}{[\text{TOA}] [\text{H}_2\text{SO}_4]^n} \times Q \quad (2)$$

Where  $Q$  is the ratio of activity coefficients and  $n$  is the number of sulfuric acid molecules extracted by one molecule of TOA. Equation 2 can be written like below:

$$\log \frac{K}{Q} = \log[\text{TOA} \cdot n\text{H}_2\text{SO}_4] - \log[\text{TOA}] - n \log[\text{H}_2\text{SO}_4] \quad (3)$$

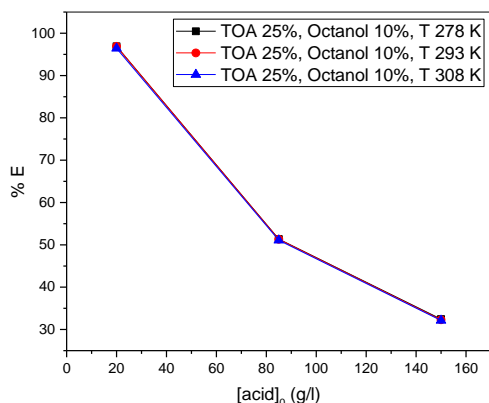


Figure 4. Effect of temperature on extraction percent of sulfuric acid against initial concentration of sulfuric acid; TOA=25vol%; octanol=10vol%.

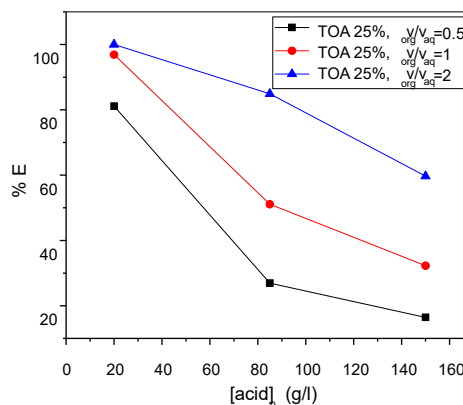


Figure 5. Effect of  $V_{org}/V_{aq}$  on extraction percentage of sulfuric acid against initial concentration of sulfuric acid; TOA=25vol%; octanol=10vol%.

According to stoichiometric coefficients of reaction:

$$\begin{aligned} [\text{Acid}]_{org} &= n \times [\text{TOA} \cdot n\text{H}_2\text{SO}_4] \\ [\text{Acid}]_{aq} &= [\text{H}_2\text{SO}_4] \\ [\text{TOA}] &= [\text{TOA}]_0 - [\text{TOA} \cdot n\text{H}_2\text{SO}_4] \end{aligned} \quad (4)$$

In which  $[\text{Acid}]_{aq}$  and  $[\text{Acid}]_{org}$  are sulfuric acid concentration in aqueous and organic phases

respectively. By substituting equation 4 in equation 3, equation 5 is obtained:

$$\log \frac{K}{Q} = \log \frac{[\text{Acid}]_{\text{org}}}{n} - \log([\text{TOA}]_0 - \log \frac{[\text{TOA}]_{\text{org}}}{n}) - n \log[\text{Acid}]_{\text{aq}} \quad (5)$$

By rewriting equation 5, equation 6 is obtained:

$$f(\text{Acid}) = \log \frac{[\text{Acid}]_{\text{org}}}{n} - n \log([\text{TOA}]_0 - \frac{[\text{Acid}]_{\text{org}}}{n}) = n \log[\text{Acid}]_{\text{aq}} + \log \frac{K}{Q} \quad (6)$$

according to equation 6,  $n$  can be obtained by slope analysis method. By guessing a number for  $n$  and plotting  $f(\text{acid})$  against  $\log[\text{Acid}]_{\text{aq}}$  a linear graph should be obtained, the slope of this graph should be  $n$ . So when the guessed number for  $n$  is equal to the slope of the related linear graph, it is the number of extracted sulfuric acid molecules extracted by one molecule of TOA. Using the above method by guessing  $n=0.83$  this guessed number is equal to the slope of the related graph. The resulting graph is shown in Figure 6.

#### 4. Conclusions

Initial studies indicated that at concentrations of more than 1.5 moles per liter (approximately 150 grams per liter) concentration of acid in the organic phase remains nearly fixed. This result is then used in the design of experiments. Extraction percentage and acid concentration in the organic phase increases with increasing in concentration of TOA. At acid concentrations of 20 g/l with TOA concentration of 25% extraction was almost complete and extraction percentage was close to 100.

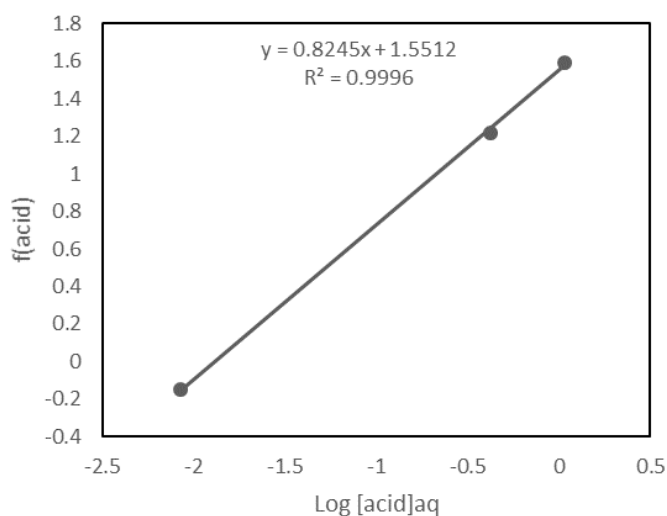


Figure 6. Application of slope analysis method for  $n=0.83$

Therefore, to extract the acid concentrations of less than this amount TOA concentration of 25% seems to be suitable. Presence of octanol as modifier has no effect on the acid extraction and only facilitates the separation of the two phases. In extraction systems with octanol concentrations of 5% and less forms a three-phase mixture. Therefore, octanol concentrations of more than 5% should be used to prevent forming this three-phase mixture. Changes in temperature do not affect the absorption of sulfuric acid

by TOA. With increase in  $V_{org}/V_{aq}$  extraction percentage increases. At acid concentration of 20 g/l with TOA concentration of 25% and  $V_{org}/V_{aq} = 1$  extraction was almost complete and extraction percentage was close to 100. Thus, for concentrations of 20 g / l and less, increase in this ratio will have no effect on the extraction. Since the temperature and volume fraction of octanol have no effect on extraction percent, for sulfuric acid extraction percent modeling through solvent extraction process with TOA, only initial sulfuric acid concentration and TOA volume percentage considered as effective parameters. Using the experimental results and formulation of them, the extraction percentage can be calculated as follows:

$$acid\ EXT\% = 49.9 - 25.2[acid]_0 + 19.82(\%TOA) + 11.35[acid]_0^2 - 5.14(\%TOA)^2 \quad (7)$$

In this equation, the initial acid concentration should be between -1 (lowest initial acid concentration, or 20 grams per liter) to 1 (maximum concentration of acid or 150 grams per liter) and TOA volume percent should be between -1 (lowest percentage of TOA or 10%) to 1 (maximum TOA percentage or 40%). The obtained model for acid concentration in organic phase is as follows:

$$[acid]_{org} \left( \frac{g}{L} \right) = 42.28 + 15.73[acid]_0 + 16.85(\%TOA) - 6.96[acid]_0^2 - 3.91(\%TOA)^2 + 12.43[acid]_0 \times (\%TOA) \quad (8)$$

Extraction number is equal to 1, calculated using slope analysis method and so the reaction seems to be:



### References

- 1) V. D. Talnikar, Y. S. Mahajan, *Korean J. Chem. Eng.*, **31**, 1720-1731 (2014).
- 2) D. F. Haghshenas, D. Darvishi, H. Rafieipour, E. K. Alamdari, A.A. Salardini, *Hydrometallurgy*, **97**, 173-179 (2009).
- 3) A. Amornchai, K. Kittipong, A. Suttichai, *J. Ind. Eng. Chem.*, **14**, 796-803 (2008).
- 4) T. Xu, W. T. Yang, *J. Membr. Sci.*, **183**, 193-200 (2001).
- 5) N. Senad, K. Teeraporn, D. K. Klaus, *J. Membr. Sci.*, **166**, 99-104 (2000).
- 6) W. Zhixin, L. Yunbai, Y. Ping, *J. Membr. Sci.*, **280**, 134-137 (2006).
- 7) D. J. Benedict, S. J. Parulekar, P. T. Shih, *J. Membr. Sci.*, **281**, 435-445 (2006).
- 8) Y. Lixin, G. Qingfeng, H. Jihua, J. Weijun, *Desalination*, **129**, 283-288 (2000).
- 9) F.J. Alguacil, F.A. Lopez, *Hydrometallurgy*, **42**, 245-255 (1996).
- 10) K. Viljoen, K. C. Sole, L. J. Bryson, *Fif. SAIMM. Bas. Met. Conf.*, Btwn. (2009).
- 11) F. W. Ntengwe, *Int. J. Chemtech. Res*, **2**, 2131-2139 (2010).
- 12) L.Sadoun; F.Hassaine-sadi, *Desalination*, **167**, 159-163 (2004).