Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.911707

55 (2015) 193–198
June

Taylor & Francis
Taylor & Francis Group

Reactive extraction of acrylic acid using trioctylamine (TOA) in versatile diluents

Amaç Fatih Tuyun*, Hasan Uslu

Engineering & Architecture Faculty, Chemical Engineering Department, Beykent University, Ayazağa, 34396, Istanbul, Turkey, Tel. +90 212 4441997; Fax: +90 212 8675066; email: aftuyun@gmail.com

Received 20 November 2013; Accepted 1 April 2014

ABSTRACT

Herein, since the extraction of organic acids is very important for recovery, acrylic acid was investigated from aqueous solutions by different diluents of trioctylamine (TOA). The extraction of acrylic acid with TOA dissolved in various individual solvents has been worked. Solvents have selected as dimethyl phthalate (DMP), cyclohexyleacetate (CHA), methyl isobutyl ketone, 2-octanone, 1-octanol, and 1-decanol. The experimental results of experiments are reported as distribution coefficients, *D*, loading factors, *Z*, and extraction efficiency, *E*. It is essential to improve extraction by adding extractant. The maximum removal of acrylic acid is 97.32% with DMP 1.15 mol/kg initial concentration of TOA. Here in, the LSER model has been applied to TOA + alcohol systems on extraction of acrylic acid to make predictions of distribution coefficient.

Keywords: Extraction; Acrylic acid; Trioctylamine; Reactive extraction

1. Introduction

The acrylic acid is a sharp smell colorless liquid which is easily polymerized and miscible with water. It is inflammable, mildly toxic, and of high industrial importance. Acrylic acid or namely prop-2-enoic acid (CH_2=CH–COOH) is most basic acid containing unsaturated vinyl group at the first carbon. Most of the polymers are made from acrylic acid and its derivatives. Most of the polymers are extremely finding ample uses ranging from fibers, detergent, textiles, adhesives, paper technologies, polishes, leather, surface coatings to super-absorbent materials [1–3].

Manufacture of acrylic acid using bioroute has still proven to be an attractive alternative. One of the most important problems of fermentation is low concentration value since the product distribution is highly sensitive to reaction medium acidity. In the chemical industry, there are a lot of versatile methods for separation of acrylic acid. Reactive extraction is most important especially for separation of acids from the bioreactor. Basically, reactive extraction is mainly combined from extractant and diluents. Additionally, reactive extraction also provides some important advantages such as high selectivity and fractional recovery [4–7].

Extraction (physically) with highly pure organic diluents has not been confirmed good enough for the separation of most organic acids without amine and phosphorus compounds. Amine compounds are very important compounds since their high efficiency and selectivity are so high. It is essential to note that the basicity increased in the following order: tertiary > secondary > primary [8–10]. Amine or phosphorus

---

*Corresponding author.

compounds and a diluent are also mostly added in order to improve the physical properties for better solvatation and extraction power. Versatile active polar diluents containing electron-donating groups (halogenated aliphatic/aromatic hydrocarbons, ketones, nitrobenzenes, higher alcohols) increase the extraction efficiency. While active polar diluents increase the extraction, inert diluents (paraffin, benzene etc.) decrease the capacity of solvent [11–14].

The behavior and different extractant types having different basicity in the extraction in diluents have been worked [15–17]. Tamada et al. has also explained the effect of different diluents on extraction (physically) [13]. As a result, reactive extraction differs from general solvatation and specific solvatation caused by hydrogen bonding [18].

Herein, we have explored the separation of acrylic acid from aqueous solutions using trioctylamine (TOA) as an extractant dissolved in various diluents in different amine solution concentrations ranging from 0.23 to 1.15 mol/kg. All extractions were conducted with TOA dissolved in ketones (methyl isobutyl ketone (MIBK), 2-octanone), dimethyl phthalate (DMP), cyclohexyleacetate (CHA), and alcohols (1-octanol, 1-decanol). Distribution coefficients, extraction efficiencies, and loading factors of each sequential were calculated from the results of the experiments.

2. Theoretical

The extraction of acrylic acid (HA) with trioctylamine (R_3N) can be described by the following reaction.

$$\mathrm{HA}(1) + {}^{*}\mathrm{R_3N}(2) \leftrightarrow {}^{*}(\mathrm{HA}).(\mathrm{R_3N})(3) \tag{1}$$

where HA represents the nondissociated part of the acid present in the aqueous phase and organic phase species is marked with an asterisk (*). Reaction 1 can be characterized by the overall thermodynamic extraction constant K.

The loading of the extractant, Z, is defined as the total concentration of acid in the organic phase divided by the total concentration of amine in the organic phase [14]. The expression for Z can be written in the form

$$Z = C_a/C_{e,\mathrm{org}} \tag{2}$$

In Eq. (2), C_a is the total concentration of acid in the organic phase, mol kg^{-1} and $C_{e,\mathrm{org}}$ is the total concentration of amine in the organic phase. The partitioning coefficients, D, for acid extracted from the water into the organic phase were determined by:

$$D = C_{a,\mathrm{org}}/C_a \tag{3}$$

The efficiency of extraction, E, is expressed as:

$$E = (1 - (C_a/C_{ao})) \times 100 \tag{4}$$

where C_a is the concentration of acid in the aqueous phase after extraction and C_{ao} is the initial concentration of acid in the aqueous phase [19–25].

3. Materials and methods

TOA ($M = 353.67$ g.mole^{-1}) (purity > 99% in mass), acrylic acid, and the solvents (DMP, CHA, MIBK, 2-octanone, 1-octanol, 1-decanol) were purchased from Merck Co., (Darmstadt, Germany). All chemicals were of reagent grade and used without further purification. In most cases, the relative uncertainty of aqueous phase determination did not exceed 3%. The pH value of the aqueous phase was determined with a pH meter (Mettler Toledo pH meter) with the uncertainty of 1%. The solubilities of amine salts and diluents in the aqueous phase were negligible in the range of variables investigated. Acrylic acid was dissolved in distilled water to prepare the different solutions with initial concentrations of acid of 1.56 mol kg^{-1}. The organic phase has been obtained by mixing TOA with organic solvents to prepare six different concentrations between 0.23 and 1.15 mol kg^{-1}. Liquid–liquid equilibrium experiments were conducted on an Erlenmeyer flask. The extraction was done in a closed 50 mL Erlenmeyer flask in which both aqueous solutions of a acrylic acid and organic phase (pure solvent or solvent enriched with TOA) were introduced. The concentration of TOA in diluents as an organic solvent was varied between 0 (pure solvent) and 1.15 mol kg^{-1}. After the introduction of both phases, the Erlenmeyer flasks were agitated in a GFL shaker (an orbital shaking incubator at 100 rpm) for 2.5 h at 25 ± 0.1℃ to ensure equilibrium. After agitation, the Erlenmeyer flasks were transferred into trays, and a settling time of at least 6 h was allowed and shown to be sufficient. After settling, samples of the aqueous phase were taken. The concentration of acrylic acid in the aqueous phase was determined by titration with aqueous 0.1 mol kg^{-1} sodium hydroxide (relative uncertainty 1%) in the presence of phenolphthalein as the indicator with each measurement being performed in duplicate [14,17].

4. Results and discussion

Most of the extracts used for reactive extraction are toxic for bacteria in the reactor so that low concentration of acrylic acid (around 10%) is used in the present studies.

The results of the reactive extraction of acrylic acid using TOA in different diluents are listed in Table 1. It is noteworthy that increasing extractant concentration increases the distribution coefficient. The concentrations of TOA in diluents were between 0.23 and 1.15 mol/kg. The acrylic acid concentration in the initial aqueous phase was 1.56 mol/kg.

The equilibrium data on the distribution of acrylic acid between water and organic phase dissolved in DMP, CHA, MIBK, 2-octanone, 1-octanol, and 1-decanol are listed in Table 1. Table 1 demonstrates that 95–97% of acrylic acid are recovered by 1.15 mol/kg TOA from starting aqueous solutions. Hence the recovery of acrylic acid completely related with both the amount of amine and type of dilutes. The maximum removal of acrylic acid was 97.32% with DMP and 1.15 mol/kg initial concentration of TOA. Distribution coefficient increases from 3.07 to 36.34 with increasing the amount of TOA from 0.23 to 1.15 mol/kg for DMP.

As it can be seen from Fig. 1, distribution of organic diluent between two phases (water and organic phase) depends on extractant concentration. The extraction efficiency of mixture (TOA and diluent) changes at higher initial concentration of extractant (TOA) in the organic phase.

Fig. 2 demonstrates the extraction efficiency of TOA—diluents mixture changes when increasing the initial concentration of TOA. The highest extraction efficiency of acrylic acid was found as 97.32% using DMP at 1.15 mol kg^{-1} initial concentration of TOA.

Table 1
Experimental results of the extraction of acrylic acid with TOA/individual diluents at 25°C

Diluent	Concentration of amine in the organic phase (mol/kg)	Concentration of acid in the aqueous phase (mol/kg)	Concentration of acid in the organic phase (mol/kg)	pH	D	D_{model}	Z	E (%)
DMP	0.23	0.38	1.18	2.36	3.07	–	5.12	75.42
	0.46	0.24	1.32	2.48	5.59	–	2.88	84.84
	0.69	0.08	1.48	2.95	17.41	–	2.14	94.57
	0.92	0.05	1.51	3.15	27.69	–	1.64	96.51
	1.15	0.04	1.52	3.32	36.34	–	1.32	97.32
MIBK	0.23	0.29	1.27	2.35	4.31	–	5.51	81.17
	0.46	0.10	1.46	2.46	14.54	–	3.17	93.56
	0.69	0.09	1.47	2.75	17.20	–	2.14	94.51
	0.92	0.06	1.50	2.98	24.17	–	1.63	96.03
	1.15	0.05	1.51	3.14	30.22	–	1.31	96.80
2–Octanone	0.23	0.33	1.23	2.36	3.66	–	5.33	78.55
	0.46	0.27	1.29	2.44	4.84	–	2.81	82.89
	0.69	0.10	1.46	2.71	14.67	–	2.12	93.62
	0.92	0.07	1.49	2.95	22.69	–	1.62	95.78
	1.15	0.06	1.50	3.08	24.40	–	1.30	96.06
1-Octanol	0.23	0.35	1.21	2.47	3.44	3.62	5.25	77.47
	0.46	0.22	1.34	2.59	5.96	5.79	2.90	85.63
	0.69	0.14	1.42	2.68	10.29	10.41	2.06	91.14
	0.92	0.08	1.48	2.90	18.29	18.22	1.61	94.82
	1.15	0.05	1.51	3.10	28.35	28.72	1.31	96.59
CHA	0.23	0.35	1.21	2.31	3.41	–	5.24	77.31
	0.46	0.20	1.36	2.51	6.68	–	2.95	86.98
	0.69	0.10	1.46	2.78	14.06	–	2.11	93.36
	0.92	0.08	1.48	2.91	18.51	–	1.61	94.87
	1.15	0.07	1.49	3.07	21.83	–	1.30	95.62
1-Decanol	0.23	0.32	1.24	2.34	3.84	3.65	5.38	79.34
	0.46	0.26	1.30	2.47	4.91	4.85	2.82	83.09
	0.69	0.14	1.42	2.77	9.99	9.82	2.06	90.90
	0.92	0.08	1.48	2.99	18.03	18.21	1.61	94.75
	1.15	0.06	1.50	3.08	24.10	24.27	1.30	96.02

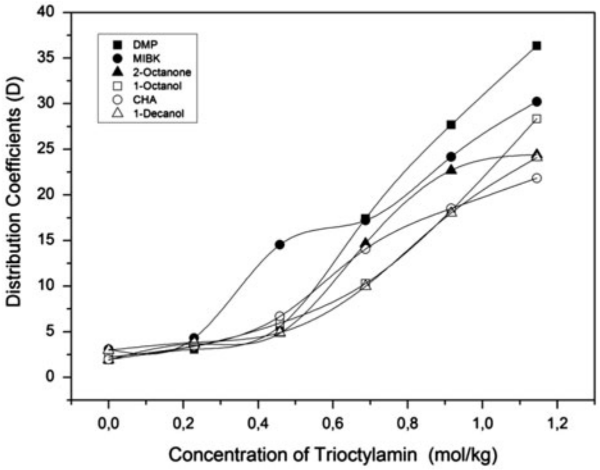

Fig. 1. Variation of distribution coefficients with concentration of TOA in different individual diluents at 25˚C (Δ, DMP; ■, MIBK; ▲, 2-octanone; 1-octanol; ●, CHA; □, 1-decanol).

Obviously, it can be seen from Table 1, the increase of amine concentration brings about the gradual increase of extraction efficiency. The equilibrium data about distribution of acrylic acid between water and TOA dissolved in different diluents are presented in Table 1. It is noteworthy that the TOA extraction power is more effective in the presence of DMP (Fig. 3).

The equilibrium data about distribution of acrylic acid between water and TOA dissolved in different diluents (DMP, CHA, MIBK, 2-octanone, 1-octanol, and 1-decanol) are listed in Table 2 and shown in Fig. 4.

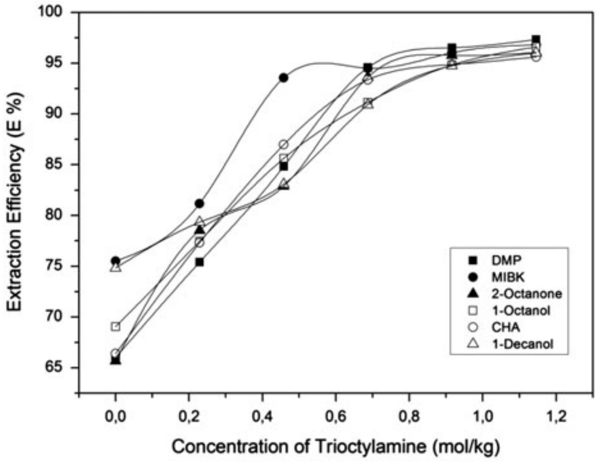

Fig. 2. Variation of *E*% with concentration of TOA in different diluting diluents at 25˚C (Δ, DMP; ■, MIBK; ▲, 2-octanone; 1-octanol; ●, CHA; □, 1-decanol).

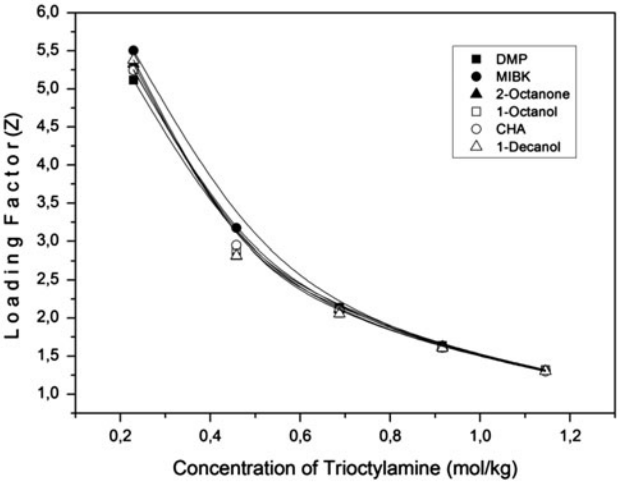

Fig. 3. Variation of loading factors with concentration of TOA in different diluents at 25˚C (Δ, DMP; ■, MIBK; ▲, 2-octanone; 1-octanol; ●, CHA; □, 1-decanol).

Table 2
Distribution of acrylic acid between diluents and water at 25˚C

Diluent	Concentration of acid in the aqueous phase (mol/kg)	$(C_a)^E$ (mol/kg)	*D*	*E* (%)
DMP	0.530	1.03	1.94	66.03
MIBK	0.382	1.18	3.08	75.51
2-Octanone	0.535	1.03	1.91	65.69
1-Octanol	0.483	1.08	2.23	69.06
CHA	0.524	1.04	1.98	66.41
1-Decanol	0.530	1.17	2.97	74.83

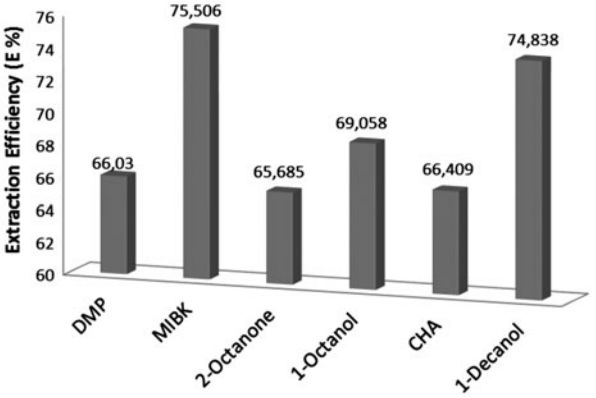

Fig. 4. Distribution coefficients of acrylic acid between water and diluents used in this study.

4.1. Model equation

A new approach namely linear solvation energy relationship (LSER) approach was introduced by Kamlet and Taft [26] and subsequently improved by Abraham [27]. Some solvatation effects by means of nonspecific and hydrogen bonding interactions have been characterized. Bizek et al. [28] have improved a modified version of LSER in order to predict the extraction equilibrium of an amine-diluent-acid triple system.

Herein, the LSER model has been applied to TOA + alcohol systems on extraction of acrylic acid to make predictions of distribution coefficient. Uslu has described some calculation on distribution coefficients of alcohols in his previous study [8]. To calculate the effect of diluents on values of distribution coefficient values, the following equation could be used:

$$\ln D = \ln D^0 + s\,(\pi^* + d\,\delta) + b\,\beta + a\,\alpha \tag{5}$$

where π^* and δ are the solvatochromic parameters in Eq. (5), that each one measures solute–solvent, dipole–dipole, and dipole–induced dipole interactions. The ability donation of a proton from the solvent to solute hydrogen bond is described by solvatochromic parameter α scale of solvent hydrogen-bond donor (HBD) acidity. The ability acception of a proton from the solvent to solute hydrogen bond is provided by β scale of hydrogen-bond acceptor (HBA) basicity. The all coefficients s, d, a, and b including the solution properties coming from regression [26].

An examination of regressed distribution coefficients with solvatochromic parameters of the solvents can be seen from Table 3 [26,29] according to Eq. (6). After obtaining all distribution coefficients for each alcohols, alcohols have been regressed by applying program SPSS v14.0. The results for 1-octanol and 1-decanol with regard to D^{model} have been shown in Table 1. The LSER model values are in agreement with the experimental data. Table 4 shows the estimated value of parameters of the model. Distribution coefficients of acrylic acid between two phases (water and the amine + solvent system) have been presented using this model. As a consequence, a new revised regression equation (Eq. (6)) has been revised in order to estimate the distribution coefficients:

$$\ln D = (1.142) + (-16284)\cdot(v\,\pi^* - 0.v\,\delta) + 26.276\cdot(v\,\beta) + (-2.356)\,(v\cdot\alpha) \tag{6}$$

Table 3
Solvatohromic parameters HBD acidities: π^* and δ; hydrogen-bond acceptor basicities: α and β for alcohols used in this study

Solvents	π^*	δ	β	α
1-Octanol	0.40	0	0.81	0.77
1-Decanol	0.40	0	0.81	0.72

Table 4
mLSER model parameters of acrylic acid extraction by TOA

LSER	$\ln D^0$	s	d	a	b	R^2
	1.142	−16.284	0	26.276	−2.356	0.98

5. Conclusion

Extraction characteristics of acrylic acid using TOA were examined in the presence of DMP, CHA, MIBK, 2-octanone, 1-octanol, and 1-decanol as diluents. TOA is slightly viscous and can be thus used in different diluents. The present study was to examine the effectiveness of the respective diluents in the extraction of acrylic acid using TOA. The distribution coefficients, loading factors, and extraction efficiencies were calculated for these extraction systems. More convenient diluents are mostly polar diluents, as shown by their higher distribution coefficients. On the other hand, the most suitable diluents for extraction are polar diluents containing proton-donating groups such as alcohols since they give the highest distribution coefficients with TOA for the extraction. The best distribution ratio of acrylic acid is obtained with DMP 97.32%. For other solvents, E% values are: CHA 95.63%, 1-octanol 96.59%, 2-octanone 96.06%, 1-decanol 96.02%.

The max. extraction efficiencies for diluents used at the max. TOA (1.15 mol/kg) concentration were determined as DMP > MIBK > 1-octanol > 2-octanone > 1-decanol > CHA. Additionally, the LSER model values are in agreement with the experimental data.

Acknowledgments

Authors would like to thank the board of trustees of Beykent University for supplying the equipments and materials.

Symbols and abbreviations

C_a — molar concentration of acid in the aqueous phase, mol/kg
C_{ao} — initial molar concentration of acid in the aqueous phase, mol/kg

$C_{a,\ org}$ — molar concentration of acid in the organic phase, mol/kg
$C_{e,\ org}$ — molar concentration of amine in the organic phase, mol/kg
CHA — cyclohexyl acetate
D — distribution coefficient
DMP — dimethyl phthalate
E — the efficiency of extraction
HA — acrylic acid
LSER — linear solvation energy relationship
MIBK — methyl isobutyl ketone
R_3N — tertiary amine
TOA — trioctylamine
Z — loading factor
$(\ )^E$ — organic phase
$(\ )^R$ — aqueous phase

References

[1] Kirk-Othmer, Encyclopedia of Chemical Technology, Wiley Interscience, Ann Arbor, MI, 1981, ISBN 0-471-02066-4.

[2] A. Keshav, K.L. Wasewar, S. Chand, Extraction of acrylic, propionic, and butyric acid using aliquat 336 in oleyl alcohol: Equilibria and effect of temperature, Ind. Eng. Chem. Res. 48(2) (2009) 888–893.

[3] Y.S. Aşçı, I. Inci, Reactive extraction equilibria of acrylic acid from aqueous solutions with amberlite LA-2 in different diluents, J. Chem. Eng. Data 55(7) (2010) 2385–2389.

[4] Y.S. Aşçı, I. Inci, Extraction equilibria of succinic acid from aqueous solutions by amberlite LA-2 in diluent solvents, J. Chem. Eng. Data 55 (2010) 847–851.

[5] Y.S. Aşçı, I.M. Hasdemir, Removal of some carboxylic acids from aqueous solutions by hydrogels, J. Chem. Eng. Data 53 (2008) 2351–2355.

[6] A. Keshav, S. Chand, L.L. Wasewar, Reactive extraction of acrylic acid using tri-n-butyl phosphate in different diluents, J. Chem. Eng. Data 54 (2009) 1782–1788.

[7] A. Keshav, K.L. Wasewar, S. Chand, Extraction of propionic acid with tri-n-octyl amine in different diluents, Sep. Purif. Technol. 63 (2008) 179–183.

[8] K. Uslu, Reactive extraction of levulinic acid using TPA in toluene solution: LSER modeling, kinetic and equilibrium studies, Sep. Sci. Technol. 43 (2008) 1535–1548.

[9] D. Yankov, J. Molinier, J. Albet, G. Malmary, G. Kyuchoukov, Lactic acid extraction from aqueous solutions with tri-n-octylamine dissolved in decanol and dodecane, Biochem. Eng. J. 21 (2004) 63–71.

[10] A. Keshav, K.L. Wasewar, S. Chand, H. Uslu, Effect of binary extractants and modifier-diluents systems on equilbria of propionic acid extraction, Fluid Phase Equilib. 275(1) (2009) 21–26.

[11] A. Keshav, K.L. Wasewar, S. Chand, Recovery of propionic acid from an aqueous stream by reactive extraction: Effect of diluents, Desalination 244(1) (2009) 12–23.

[12] S. Kumar, K.L. Wasewar, B.V. Babu, Intensification of nicotinic acid separation using organophosphorous solvating extractants: Reactive extraction, Chem. Eng. Technol. 31(11) (2008) 1584–1590.

[13] J.A. Tamada, A.S. Kertes, C.J. King, Extraction of carboxylic acids with amine extractants 1: Equilibria and law of mass action modelling, Ind. Eng. Chem. Res. 29 (1990) 1319–1326.

[14] A.F. Tuyun, H. Uslu, Extraction of D-(-)-quinic acid using an amine extractant in different diluents, J. Chem. Eng. Data 57 (2012) 190–194.

[15] K.L. Wasewar, Separation of lactic acid: Recent advances, Chem. Biochem. Eng. Q. 19 (2005) 159–172.

[16] I. Inci, Y.S. Aşçı, A.F. Tuyun, Reactive extraction of L-(+)-tartaric acid by amberlite LA-2 in different solvents, E-J. Chem. 8 (2011) S509–S515.

[17] A.F. Tuyun, H. Uslu, Reactive extraction of cyclic polyhydroxy carboxylic acid using trioctylamine (TOA) in different diluents, J. Chem. Eng. Data 57 (2012) 2143–2146.

[18] I. Inci, Y.S. Aşçı, H. Uslu, LSER modeling of extraction of succinic acid by tridodecylamine dissolved in 2-octanone and 1-octanol, J. Ind. Eng. Chem. 18(1) (2012) 152–159.

[19] P. Zhang, S.-H. Cai, Q.-H. Zhang, Z.-C. Luo, Solvent extraction of hydroxyacetic acid, J. East China Univ. Sci. Technol. 20 (1994) 148–153.

[20] I. Inci, S.S. Bayazit, Y.S. Aşçı, Separation of succinic acid from aqueous solution by alumina adsorption, J. Chem. Eng. Data 56(12) (2011) 4449–4453.

[21] Y.S. Aşçı, I. Inci, Extraction equilibria of propionic acid from aqueous solutions by amberlite LA-2 in diluent solvents, Chem. Eng. J. 155(3) (2009) 784–788.

[22] A.F. Tuyun, H. Uslu, Extraction equilibria of picolinic acid from aqueous solution by tridodecylamine (TDA), Desalination 268 (2011) 134–140.

[23] A.F. Tuyun, H. Uslu, S. Gokmen, Y. Yorulmaz, Recovery of picolinic acid from aqueous streams using a tertiary amine extractant, J. Chem. Eng. Data 56 (2011) 2310–2315.

[24] Y.S. Aşçı, I. Inci, A novel approach for itaconic acid extraction: Mixture of trioctylamine and tridodecylamine in different diluents, J. Ind. Eng. Chem. 18(5) (2012) 1705–1709.

[25] A.F. Tuyun, H. Uslu, Investigation of picolinic acid extraction by trioctylamine, IJCRE 9 (2011) A29.

[26] M.J. Kamlet, M. Abboud, M.H. Abraham, R.W. Taft, Linear solvation energy relationships, 23. A comprehensive collection of the solvatochromic parameters, pi*, alpha, beta, and some methods for simplifying the generalized solvatochromic equation, J. Org. Chem. 48 (1983) 2877–2887.

[27] M.H. Abraham, Scales of solute hydrogen-bonding – Their construction and application to physicochemical and biochemical processes, Chem. Soc. Rev. 22 (1993) 73–83.

[28] V. Bizek, J. Horacek, R. Rericha, M. Kousova, Amine extraction of hydrocarboxylic acids, Ind. Eng. Chem. Res. 31 (1992) 1554–1562.

[29] D.N. Legget, Modeling solvent extraction using the solvatochromic parameters alpha, beta, and pi*, Anal. Chem. 65 (1993) 2907–2909.