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Recovery of Volatile Acids from Aqueous Solution by Tri-n- Butyl Phosphate dissolved in laboratory Made Nontoxic Diluent

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Abstract : The present work was carried out to study the extraction of volatile acids like acetic and propionic with tri-n-butyl phosphate (as extractant) dissolved in laboratory-modified nontoxic diluent. A graphical method was used to calculate the values of Dimerization coefficient (D) and partition coefficient (P) from distribution coefficient (K_D) data of both volatile acids. The extraction equilibrium constants($K_{E(1:1)}$) and loading factors (Z) for both volatile acids were also determined. Based on the values of Z it can be concluded that there is a formation of 1:1 complexes between Tri Butyl Phosphate and Volatile acids.

Keywords : Tri Butyl Phosphate(TBP),Volatile acids, Laboratory modified diluent, Toxicity.

Introduction

Carboxylic acids contain carboxy (COOH) functional group in which central carbon atom forms double bond with the oxygen atom and singly bond with other oxygen atom. They are sp^2 hybridized and are polar in nature because of electro negativity of oxygen atoms present in the C-O and O-H bonds. Carboxylic acids having carbon atoms less than five dissolve in water very easily due to hydrogen bonding but higher acids show a decrease in solubility due to the large size of nonpolar alkyl portion. The extraction of these hydrophilic acids from dilute aqueous solution is burning area of research today and is important for sustainable development of society(recovery of dilute products fermentation broth & wastewater stream). The production of these acids via fermentation is a need of the hour to utilize enormous organic matter generated by humans. The discharge of these acids by industries in rivers consumes considerable amount of oxygen and also harms aquatic life. The recovered acids when used in synthetic chemistry field will generate revenue that will reduce the water treatment cost.

The production of acetic acid by fermentation is a century old technology. Now a days propionic acid production by fermentation has reached design stage and is on the verge of commercialization. Both the volatile carboxylic acids are widely used in the food and beverages industry so their production via fermentation is gaining more importance as health conscious human beings are looking for organic products even at a higher rate. Moreover, the gap in the cost of production via fermentation with respect to petroleum feed (rising prices

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due to fast depletion) is narrowing down. The demand of these volatile acids is increasing day by day. A part of this demand can be met through production through fermentation or by recovery from wastewater [1]-[2].

The biggest challenge in making fermentation a viable option lies in decreasing the cost of recovery of these acids from very dilute concentrations (less than 10%). The distillation which is most widely used method for recovery of pure substances from solutions(based on the difference in boiling point) is rarely used because the boiling points of these acids are marginally higher than water. Traditionally, carboxylic acids are separated by precipitation method which results in the formation of a large amount of calcium sludge. The disposal of this sludge is another problem as sustainability and eco-friendliness is the need of the hour.

Reactive extraction (described as an advanced form of liquid-liquid extraction) uses extractants which are insoluble in the aqueous phase or has very small solubility. These extractants should have the capability to form complexes with acids. One of the biggest problems with these extractants is their toxicity because of which they cannot be used for in-situ extraction of acids from the fermentation broth. There is a need and scope to lower the toxicity of these extractants by blending them with nontoxic diluents for in-situ extraction of acids. .

Recently the researchers [3]-[12] used vegetable oils as diluent in order to decrease toxicity so that they can be integrated with fermentation broth for in-situ recovery without harming microorganisms. The present study, it is intended to test laboratory made eco-friendly non-toxic diluent to recover volatile carboxylic acids such as acetic and propionic acids using cheap but effective TBP as the extractant.

Experimental Section:

Materials Procured

All the chemicals in the experiments were used without any kind of treatment. The solutions were prepared using de-ionized water. Propionic acid and Acetic acid was supplied by Thomas baker whereas Tri-n-butyl phosphate (TBP) was supplied by SRL Pvt. Limited through a local vendor. The nontoxic natural diluent was prepared in the lab from vegetable oil by applying a chemical process. A solution of phenolphthalein was prepared in the laboratory and was used as an indicator. Each time a freshly prepared NaOH was used to determine aqueous phase acid concentration. The concentration of NaOH was standardized with0.1 N Oxalic acid (laboratory prepared solution).

Experimental setup used and Procedure

Initially, a stock solution of concentration 0.5 kmols/$m^3$of both volatile acids were prepared using de-ionized water. The desired diluted concentrations were prepared from the stock solution with de-ionized water for use in the experiment. The extractant (TBP) was dissolved in natural non-toxic diluent and solutions of 10%-40% by volume of extractant (TBP) were prepared. Equal volume (10 ml) of aqueous and organic solutions was poured in 250 ml conical flasks. These flasks were shaken in the Orbital shaking incubator at 150 rpm at 25^OC and at 25^OC for 16 hours. The mixed phases were separated by using Centrifuge (Make: REMI) and was operated at 10,000 rpm for 10 minutes. The amount of acid in the organic phase which is extracted by TBP was determined by applying mass balance. Only a few runs were duplicated to check the reproducibility of the data and were observed to be ±2% of accuracy.

Theory:

Physical extraction [extraction without extractant (TBP)]:

The physical extraction of both acids (Acetic & Propionic Acid) was carried out to calculate the distribution coefficient (K_D) for evaluation of Dimerization Coefficient (D) &partition coefficient (P) graphically. The theory involved in physical extraction is given below [13]:

1. Weak acids Ionize in the aqueous phase as:

$$[HA]_{aq} \leftrightarrow [H^+] + [A^-] \quad (1)$$

$$K_{HA} = [H^+]\,[A^-] / [HA] \quad (2)$$

2. Some amount of the undissociated molecular acid undergoes partition as given below between the two phases, aqueous (aq) and organic (org):

$[HA]_{aq} \leftrightarrow [HA]_{org}$ (3)

$P = [HA]_{org} / [HA]_{aq}$ (4)

3. The acid undergoes dimerization in the organic phase as:

$2[HA]_{org} \leftrightarrow [HA]^2_{org}$ (5)

$D = [HA]_{2,org} / [\ HA]^2_{org}$ (6)

Overall distribution coefficient ($K_D^{diluent)}$)can be written in terms of P and D as:

$$K_{\mathrm{D}}^{\mathrm{diluent}} = \frac{[\mathrm{HA}]_{\mathrm{org\,Total}}}{[\mathrm{HA}]_{\mathrm{aq\,Total}}} = \frac{[\mathrm{HA}]_{\mathrm{org}} + 2[\mathrm{HA}]_2}{[\mathrm{HA}]_{\mathrm{aq}} + [\mathrm{A}^-]} = \frac{P + 2P^2 D[\mathrm{HA}]_{\mathrm{aq}}}{1 + K_{\mathrm{HA}} / [\mathrm{H}^+]_{\mathrm{aq}}} \quad (7)$$

The last termof above equation which is present in the denominator can be dropped due to dilute the concentration of acid used in the study. The above expression becomes

$$K_{\mathrm{D}}^{\mathrm{diluent}} = P + 2P^2 D[\mathrm{HA}]_{\mathrm{aq}} \quad (8)$$

Final Equation of Physical Extraction:

The experiments were been conducted with adapting the standard method of extraction to study the physical extraction of acids with different solvents and after extraction, it is found that; the distribution coefficient can be given as follows:

$$K_{\mathrm{D}}^{\mathrm{diluent}} = P + 2P^2 D[\mathrm{HA}]_{\mathrm{aq}}$$

Where P = Partition coefficient, D = Dimerization coefficient and $K_D^{diluent}$ = Distribution coefficient

Or

It can also be rearranged into another form as:

$[HA]_{org} = P\ [HA]_{aq} + D\ [HA]_{aq}^2$ (9)

The degree of extraction (E %) of carboxylic acid in the diluent is expressed as:

$E\ \% = K_D^{diluent} \times 100 / (1 + K_D^{diluent})$ (10)

Reactive extraction:

It is well known that weak carboxylic acid dissociates in aqueous solution to some extent but when the pH is maintained at a value smaller than pKa of the acid, the effect of the acid dissociation can be neglected. The equation given below can be used to describe the extraction of the carboxylic acid by TBP in the natural non-toxic diluent.

$[HA]_{aq} + p[E]_{org} < \xrightarrow{K_S} > [HA.\ (E)_p]_{org}$ (11)

By applying the law of mass action, the general equation of interaction between the extractant and the extracted species to Extraction equilibrium constant (K_S) can be written as:

$K_s = [(HA).(E)_p]_{org} / [HA]_{aq}\ [E]^p_{org}$ (12)

Where $[HA]_{aq}$represents concentration in the aqueous phase and $[E_{org}]$, $[HA.\ (E)_p]_{org}$ represents extractants and complex concentrations in the organic phase and K_s depends upon properties of acids and the solvation(dissolving capacity) of the diluent used.

At pH below pKa, acids exist in undissociated form so the extraction process can be analyzed by means of the distribution coefficient (K_D) .The Overall degree of extraction (E%) in terms of distribution coefficient can be calculated as given below:

$$\% E = K_D^{total} \times 100 / (1+K_D^{total}) \qquad (13)$$

Model for Prediction of nature of Complexes between extractant and acid

Loading ratio (Z) is defined as the extent of loading of the organic phase (extractant + diluent) with carboxylic acid andis given below as:

$$Z = \frac{[HA]_{org}}{[E]} \qquad (14)$$

The chem.model predicts the nature of complexes on the basis of values of the loading ratio. The various types of complexes (1:1, 2:1 and 3:1) between acid and extractant can be formed. For low values of Z< 0.5, a complex of (1:1) is formed as given by

$$Z/(1-Z)=K_{E(1:1)}[HA]_{aq} \qquad (15)$$

A straight line through the origin in the plot of Z/(1-Z) versus $[HA]_{aq.}$ will make the model valid for (1,1) complex and slope of the line gives the value of extraction complexation constant ($K_{E(1:1)}$).For higher values of Z> 0.5,(1:2 and 1:3) complexes are formed.

Results and Discussions:

Physical Extraction:

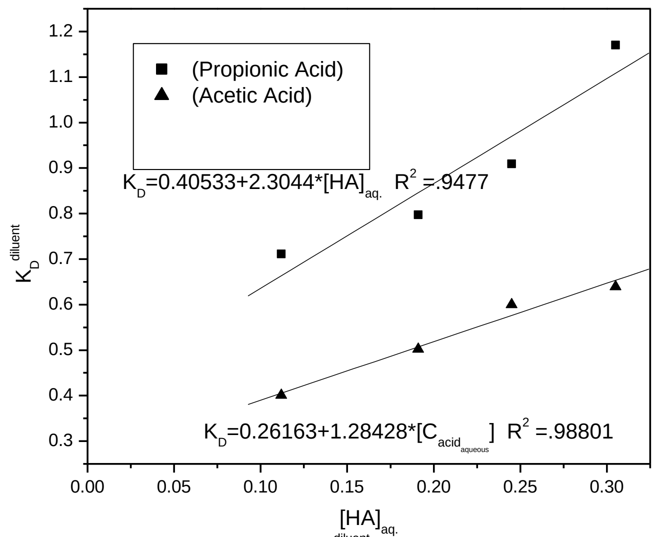

FIgure 1: $K_D^{diluent}$ vs [HA](aq.)

The extraction of acetic acid and propionic acid by nontoxic natural solvent (physical extraction) was studied to find out the Partition coefficient (P) and Dimerization coefficient (D) and Distribution coefficient ($K_D^{diluent}$). The graphical method used for determining the values of P and D is shown in Figure 1 and results are tabulated in Table1.The extractability of carboxylic acids during physical extraction is mainly affected by two factors.

(a) The ease at which it can lose hydrogen (the acid hydration extent orpKa values)
(b) Thestrength of the bond with the water molecule(hydrophobicity)

The carboxylic acids with lower molecular weight have the higher affinity towards water than nontoxic diluents so extraction of acidsby these diluentsis usually small. The results show that the extraction efficiency of propionic acid is higher than acetic acid and this may be because of lower extent of hydration due to inductive effect by an additional methyl group {as pKa valueof aceticacid (4.76) is smaller than propionic acid (4.88)}. Both acids are highly miscible with water but acetic acid has a higher affinity for water than propionic acid because solubility of acids decreases with the increase in carbon chain length (acetic acid has lower partition coefficient than propionic acid).

Table 1: The values of the partition coefficient (P), Dimerization coefficient (D)& % Extraction efficiency (%E) for physical extraction of acids.

Acid	**P**	**D(m^3/kmol)**	**The range of E%**
Acetic Acid	0.26163	9.37	28.8—38.0
Propionic Acid	0.40533	7.01	41.55—53.9

Effect of Extractant concentration:

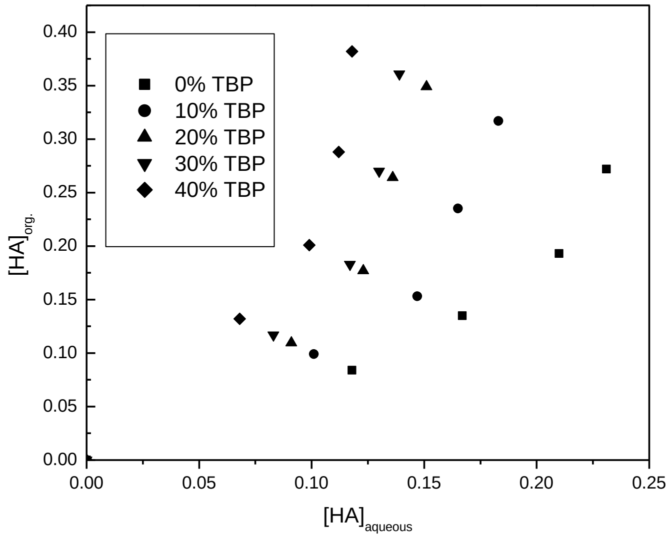

Figure 2: Chemical Equilibria for Extraction of Propionic acid

Figure 2 showsthe equilibrium isotherms for propionic acid obtained from four TBP concentrations and four initial aqueous solutions (0.1-0.4 kmols/m^3) and Figure 3 shows the equilibrium isotherms of acetic acid.

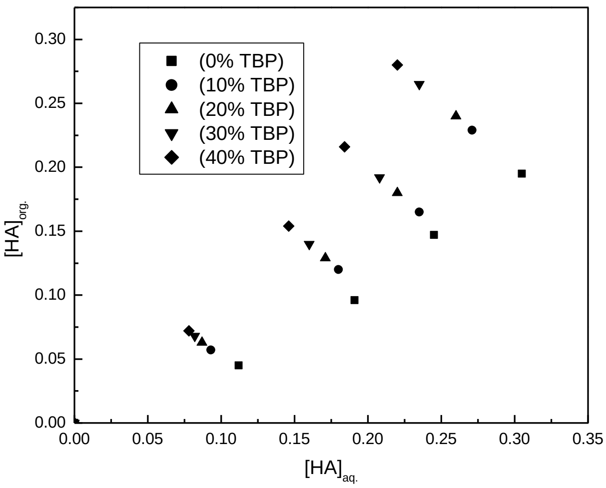

Figure 3: Chemical Equilibria for extraction of Acetic acid

From the figures, it is evident that the extraction efficiency of both volatile acids increases with the increase in %TBP indicating the strong influence of TBP on the extraction of acetic acid and propionic acids. The average % extraction of propionic acid at 40% TBP is 70.34% whereas for acetic acid is around 52.25%.The results also show that the lab made nontoxic diluent is effective as it provides a proper solvation media for the reversible complex. Theisotherms shown here are steeper forpropionic acid than acetic acid indicates a higher degree of extraction for the same amount extractant used(TBP).These isotherms also show nonlinear behavior at higher acid concentrations (due to non-ideal behavior).

Loading ratios (Z):

The loading ratio gives the stoichiometric relation that exists between acid and extractant in the complex depending on the value of Z. The strength of the acid-extractant interaction and concentration of acid in aqueous phase determines thevalue of Z. The low values of Z obtained in the experimentsi.e. $(Z < 0.5)$means scarcely loading of the organic phase due to the formation of 1:1 complex between acid and extractant. This may bedue to the low concentration range of Propionic acid (0.1-0.4 kmol/m^3) and Acetic acid (0.015 - 0.5 kmol/m^3) used.

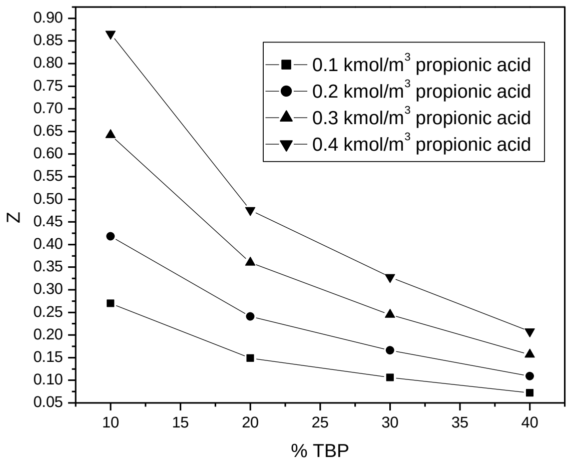

Figure 4: Loading ratios for extraction of propionic acid using natural nontoxic diluent

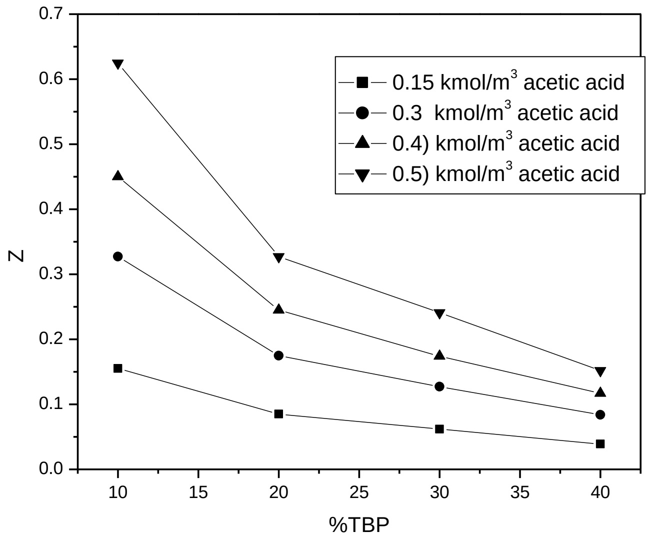

Figure 5:Loading ratios for the extracion of Acetic acid using natural nontoxic diluent

For all concentrations of both the acids (propionic and acetic acid), the overall loading ratio (Z) is found to decrease with an increase in the percentage of TBP concentration. The loading of Z>0.5 is observed at the low concentration of TBP and at higher propionic and acetic acid concentrations. The loading ratios below 0.5 are obtained for most cases of both the acid. Only a few values of Z were higher than 0.5 as shown in Figure 4 & 5 so we can conclude that there is a formation of only 1:1 complex of TBP with acetic and propionic acid with no overloading. Similar results are obtained in literature for propionic acids using other diluents with TBP [5].

Estimation of $K_{E(1:1)}$ based on Z:

The values of $K_{E(1:1)}$for the extraction of propionic and acetic acids were estimated by fitting a straight line through origin on a plot between Z/(1-Z) vs $[HA]_{aq.}$ The corresponding values of slope and R^2 for both acids are shown in Figure 6 and 7. Equilibrium extraction constant ($K_{E(:,1)}$) for 1:1 complex of propionic and acetic acid and extractant (TBP)are 3.209 and 1.07479 respectively.

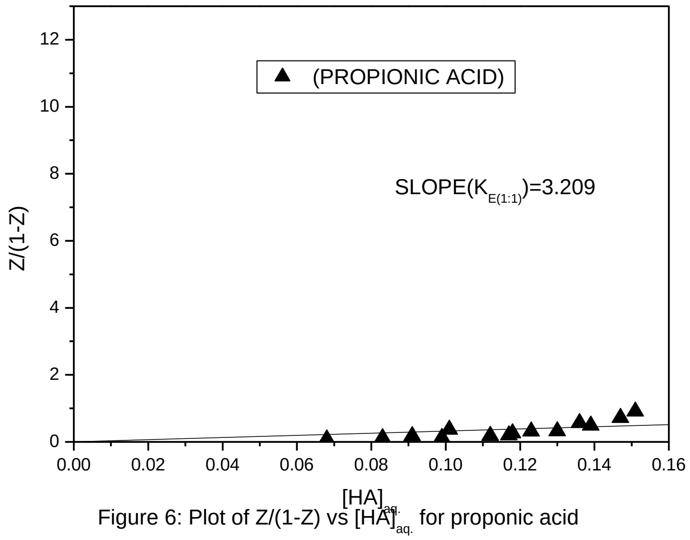

Figure 6: Plot of Z/(1-Z) vs $[HA]_{aq.}$ for proponic acid

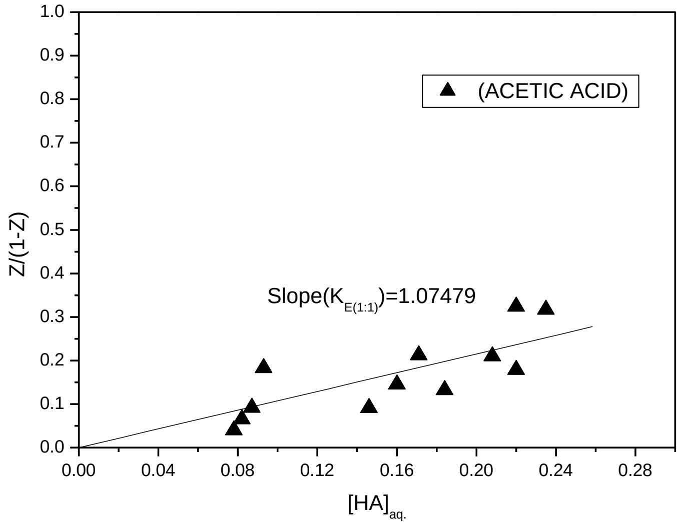

Figure 7:Plot of Z/(1-Z) vs $[HA]_{aq.}$ for Acetic acid

Conclusions:

Most of the solvents that are studied in the recovery of acids are derived from depleting petroleum resources and are toxic in nature. The toxicity is preventing the process intensification of extraction and reaction step i.e. in-situ extraction of acids produced by fermentation so there are need and reason to explore the various non-toxic solvents for reactive extraction. In this study, laboratory-modified non-toxic natural diluent is used for recovery of propionic and acetic acid from aqueous solution as a trial. The physical extraction by the solvent used as diluent showed higher affinity of propionic acid as compared to acetic acid.The addition of extractant increases the recovery of both the acids (propionic and acetic) and extraction is significant until a composition of 40% TBP. The loading ratios(Z) for propionic acid at 10% TBP is greater than acetic acid indicating high affinity of acetic acid for water as compared with propionic acid. The Equilibrium extraction constant ($K_{E(1:1)}$) for 1:1 complex of propionic and acetic acid and extractant (TBP) are graphically found out to be 3.209 (m^3/kmol) and 1.07479(m^3/kmol) respectively. The higher value of extraction constant for propionic acid over acetic acid indicates the ease with which it can be extracted over acetic acid by the extractant due to its higher hydrphobicity.

Symbols Used:

$[A^-]$ = concentration of dissociated acid inthe diluteaqueous phase (kmol/m^3)
[E] = concentration of extractant in diluent rich organic phase (kmol/m^3)
$[H^+]$ = H^+ ion concentration in the dilute aqueous phase (kmol/m^3)
[HA]= acid concentration in the dilute aqueous phase, (kmol/m^3)
(K_S)=Extraction equilibrium constant assuming a reaction between acid and extractant
D = Dimerization constant of acid in organic phase(m^3/kmol)
E% =degree of extraction of acid from aqueous phase
K_D = distribution coefficient of acid between aqueous and organic phase
$K_{E(1:1)}$ = extraction equilibrium constant for (1:1) acid-extractant complex, (m^3/kmol)
K_{HA} = Ionization constant
P = Partition coefficient
Z= loading ratio

Subscripts

aq = aqueous phase
org = organic phase

Superscript

diluent = for diluent only
chemical= chemical extraction

References

1. Zacharof, M.P., Lovitt, R.W., 2012. Use of complex effluent streams as a potential source of volatile fatty acids (VFA) a review article. Waste Eng. Conference Series (Ed.), the 4th International Conference on Engineering for Waste and Biomass Valorisation (WasteEng12), Porto.
2. Baumann, I., Westermann, P. Microbial Production of Short Chain Fatty Acids from Lignocellulosic Biomass: Current Processes and Market". BioMed Research International, 2016.
3. Harington T and HossainMd M,(2008)." Extraction of lactic acid into sunflower oil and its recovery into an aqueous solution" , Desalination Vol ,218 pp287-296
4. Uslu H, Gemici A, Gok A and Kirbaslar I,(2014)," Reactive extraction of (E)-butenedioic acid (fumaric acid) by nontoxic diluents".,JChemEng Data 59:3767-3772 .
5. Keshav, A., Wasewar, K. L., Chand, S., (2009), "Reactive Extraction of Propionic Acid using Tri-n-Octylamine, Tri-n-butyl Phosphate and Aliquat 336 in Sunflower Oil as Diluent", Journal of Chemical Technology and Biotechnology, Vol. 84 (4), pp. 484-489.
6. Keshav, A., Norge, P., Wasewar, K. L., (2012), "Reactive Extraction of Citric Acid Using Tri-n-octylamine in Nontoxic Natural Diluents: Part 1—Equilibrium Studies from Aqueous Solutions", Applied Biochemistry and Biotechnology, Vol. 167 (2), pp. 197–213.
7. Waghmare, M. D., Wasewar, K. L., Sonawane, S. S., Shende, D. Z., (2011), "Natural Nontoxic Solvents for Recovery of Picolinic Acid by Reactive Extraction", Industrial and Engineering Chemistry Research, Vol. 50 (23), pp. 13526–13537.
8. Waghmare, M. D., Wasewar, K. L., Sonawane, S. S., Shende, D. Z., (2013), "Reactive Extraction of Picolinic and Nicotinic Acid by Natural Non-toxic Solvent", Separation and Purification Technology, Vol. 120, pp. 296-303.
9. Wasewar, K. L., Shende, D., Keshav, A., (2011), "Reactive Extraction of Itaconic Acid Using Tri-n-butyl Phosphate and Aliquat 336 in Sunflower Oil as A Non-toxic diluent", Journal of Chemical Technology and Biotechnology, Vol. 86 (2), pp. 319-323.
10. Mustafa E. Marti., (2017)," Recovery of formic acid by reactive extraction using an environmentally friendly solvent" SUJEST, c.5, s.1, 2017
11. Wisniewski M. and Pierzchalska M, (2005)"Recovery of carboxylic acids C1–C3 with organophosphine oxide solvating extractants", J. Chem. Technol. Biotechnol. 80: 1425–1430.
12. AparajitaKar, AshwiniBagde, Kanti Kumar Athankar, Kailas L. Wasewar, Diwakar Z. Shende, (2017), "Reactive Extraction of Acrylic Acid with Tri-n-Butyl Phosphate in Natural Oils", Journal of Chemical Technology and Biotechnology, Vol. 92 (11), pp. 2825-2834.
13. Kertes, A. S., and King, C. J. (1986). "Extraction chemistry of fermentation product carboxylicacids", Biotechnol. Bioeng. 28, 269–282.

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