Reactive Extraction: A Review of Some Major Parameters

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Abstract: Reactive extraction has been emerged as economic technique for the separation of the valuable chemicals from fermentation broth, waste water etc. The beauty of the process lies in the fact that it may be used for the dilute solutions. Various researchers have reflected the competence of the technique for the separation of the carboxylic acids especially from the fermentation broth. This paper aims to study and review some major parameters like distribution coefficient, extraction efficiency and loading ratio emphasized by the researchers. This review of their experimental studies will be beneficial for the beginners to understand the process more clearly. The back extraction process has also been reviewed to understand the complete design of the extraction column.

Keywords: Reactive extraction, distribution coefficient, extraction efficiency, loading ratio and back extraction.

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I. INTRODUCTION

Reactive extraction is an efficient and cleaner technique; with an intensifying approach; for the separation of valuable chemicals especially from the dilute solutions. Unlike the liquid liquid extraction; in the reactive extraction the chemical reaction takes place between solute and reactant in the organic phase and this is the prime step in the process of reactive extraction. In this reaction the chemical reactants used should be such that they can reversibly complex with the solute and the complex with low bond energy is formed (less than 50KJ/mol). If the bond energy is high then the complex will be difficult to reverse and get the component of interest back Here first phase is the aqueous phase containing solute and it is contacted with the second phase; organic phase; containing reactant. These reactants which react reversibly are dissolved in diluents. The diluents play a major role and provide appropriate physical properties to the system [1].

Usually three types of reactants are used- (i) Carbon- bonded Oxygen-donor reactants i.e. inert hydrocarbons and substituted hydrocarbons, (ii) Phosphorus –bonded oxygen donor reactants such as tri-n-butylphosphate (TBP) (iii) Aliphatic amine reactants such as Alamine336, Aliquat 336,Amberlite LA-2. The diluents are grouped as (i) inactive (inert) diluents such as Kerosene, Cyclohexane (ii) active or polar diluents (modifiers) such as Decane 1-ol, 4- methylpentan-2-one. Some natural non toxic diluents like soybean oil, sunflower oil, sesame oil etc are also used by various researchers. The mixture of one inert and one active diluents has been employed. The modifiers have certain advantages like they provide the better salvation medium and enhance the extraction power of extractant as compared to the inert diluents whereas inert diluents control the viscosity and density of the organic phase. [2, 3]

Various process parameters have been studied by different researchers like distribution coefficient, extraction efficiency, loading ratio, effect of temperature, effect of pH, effect of mixed diluents, effect of salts, water co-extraction, toxicity etc. Here in this paper the work on three major parameters i.e distribution coefficient, extraction efficiency and loading ratio has been studied.

II. DISTRIBUTION COEFFICIENT

Wasewar et.al, 2011 have studied the equilibrium for the reactive extraction of Caproic acid using tri-butyl phosphate (TBP) in methyl isobutyl ketone( MIBK) and Xylene. The reasons for the selection of TBP are stated as – TBP being an organophosphorous compound contains a strong lewis base which leads to high distribution coefficient.

Distribution coefficient = \[
\frac{\text{total acid concentration in organic phase}}{\text{total acid in aqueous phase}}
\]
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It was stated that the distribution coefficient increases with the increase in TBP concentration but the concentration more than 40% was not used because it increases the viscosity of the system also. It was found that the distribution coefficient of caproic acid in xylene only was low but it was high for the MIBK only[4].

Wasewar et.al, 2002 have assumed that in the reactive extraction of lactic acid using alamine 336 in MIBK if 1:1 acid-alamine complex is formed then

\[ \log K_D = \log K_e + \log[B] \]

Where \( K_D \) is distribution coefficient, \( K_e \) is equilibrium complexation constant and [B] is concentration of alamine 336 in organic phase[5].

If the assumption is valid then plot of \( \log K_D \) v/s \( \log[B] \), should be a straight line with the slope of unity but they found the slope much less than one which indicates the presence of extra acid than would be expected. At very low concentration of lactic acid 1:1 complex was formed and at some higher values 1:2 complex was formed. In this study they have limited the concentration of the solute such that it may not form 3:1 complex.

Keshav et.al, 2009 have stated that; in the extraction of propionic acid using TOA as an extractant and MIBK as diluents; the \( K_D \) value decrease gradually with the increasing pH and the \( K_D \) was found to first increase and then decrease with the increase in \( K_a(HPO_4) \) concentration it decreased greatly with the increase in NaCl. They studied three model systems and observed the variations in \( K_D \) value for the three systems but overall there is only slight effect of temperature on extraction of the solute [6].

Keshav et.al, 2008 studied the extraction of Acrylic, Propionic and Butyric acid using Aliquat 336 in Oleyl Alcohol and they found that \( K_D \) value follow the trend butyric acid > propionic acid > acrylic acid also they computed the equilibrium complexation constant and it was found highest for the butyric acid [7].

Datta et.al, 2011 studied the reactive extraction of benzoic acid(BA) and pyridine -3-carboxylic acid (NA) using tri butyl phosphate (TBP) and N-dioctyloctan-1-amine (TOA) extractant dissolved in binary diluents mixtures. They found that \( K_D \) values for both acids are found to be increased 3 to 4 times with TBP and 5 to 24 times with TOA dissolved in diluents over when these diluents are used alone. It was experimentally found by them that \( K_D \) values depend on the acid strength and the dipole moment of both acids[3].

III. EXTRACTION EFFICIENCY

Degree of extraction is defined in terms of \( K_D \) as

\[ E\% = \frac{(K_D*100)}{(1+ K_D)} \]

Various researchers have studied the effect of temperature, pH, salts etc on the extraction i.e. extraction efficiency. Keshav et.al, 2009 have experimentally studied the extraction of propionic acid using TOA as an extractant and MIBK as diluent. They stated that 40% TOA in MIBK was the optimum to achieve the highest % of extraction, below and above this there was reduction in extraction efficiency. They showed that as the pH is increased from natural pH (2.8-3.5) there is a decrease in extraction. They suggested that different salts have different effects on the extraction of solute like presence of NaCl reduces the extraction whereas (NH_4)_2SO_4 and K_a(HPO_4) have little effect on the extraction of the solute. They concluded that reactive extraction of solute had negligibly affected by the temperature variation of 305 to 333 K [6].

The extraction of Acrylic, Propionic and Butyric acid using Aliquat 336 in Oleyl Alcohol was studied by Keshav et.al, 2008 and it was stated that the value of E% depends on three factors (1) The association ability between acid and extractant (2) the hydrophobicity of the solute and the extractant and (3) the steric effect between the solute and the extractant. It was found by them that higher molecular weight and lower density acid led to a higher value of complexation constant. The optimum concentration of Aliquat 336 for the higher E% was 30% because using the concentration of Aliquat 336 above 30% led to the formation of three phase mixture because of the high viscosity of Aliquat 336 [7].

Datta et.al, 2011 explained in their work of reactive extraction of benzoic acid(BA) and pyridine -3-carboxylic acid (NA) using tri butyl phosphate (TBP) and N-dioctyloctan-1-amine (TOA) extractant dissolved in binary diluents mixtures that benzene ring of BA makes it more hydrophobic and thus more easily extractable by polar and protic diluents and thus this hydrophobicity contributes to higher values of E%. The values of E for BA are found to be increased with an initial BA concentration and the hydrophobic nature of NA makes its molecules more likely to attach with water before coming to contact with the extractant/diluent molecules [3].

IV. LOADING RATIO

Loading ratio (z) is defined as extent to which the organic phase can be loaded with acid. It is defined as a ratio of total (undissociated, dimer and complex form) concentration of acid in the organic phase and the initial concentration of acid in the organic phase. The value of loading ratio depends on the extractability of the acid and its aqueous concentration and is independent of the amine content in an inert diluent [2].

At the very low loading ratios i.e. low concentration of the organic phase the 1:1 complex is formed and the plot of z/(1-z) v/s acid concentration in aqueous phase is a straight line whose slope gives the
value of complexation constant and if the loading ratio is high then 1:2 complex is formed and plot of \( z/(2-z) \) vs. acid concentration in aqueous phase is a straight line whose slope gives the value of complexation constant for 2:1 complex.[5]

Keshav et.al, 2009 have shown in their work of extraction propionic acid using TOA as an extractant and MIBK as diluent that the experimentally found values of loading factor was less than 0.5 and this indicates the formation of only 1:1 complex and by plotting \( z/(1-z) \) vs. acid concentration in aqueous phase was a straight line passing through origin so that the value of complexation constant could found by graph[7].

Keshav et.al, 2008 compared the extraction of Acrylic, Propionic and Butyric acid using Aliquat 336 in Oleyl Alcohol and it was shown by them experimentally that the loading ratio comes less than 0.5 for all the three acids i.e Acrylic, Propionic and Butyric acid[6].

It was stated that the diluent alone also solvates some amount of solute from aqueous solution by physical extraction and they taken m as loading of acid in the organic phase by a diluent mixture and explained m as a ratio of total (undissociated, dimer and complex form) concentration of acid in the organic phase when only diluent is used (physical extraction) and the initial concentration of acid in the organic phase. It was found that plots of \((z-vm)/[1-(z-vm)]\) vs. acid concentration in aqueous phase yield a straight line whose slope gives the value of complexation constant [3].

V. BACK EXTRACTION

The reversal of the reaction is needed for the recovery of the solute in the product stage and regeneration of the solvent for the recycle purpose. There are various methods of regeneration e.g. use of NaOH, HCl or Trimethyl Amine (TMA) or temperature or diluents swing[1, 9].

Using NaOH: In this method the loaded organic phase was contacted with NaOH to get the recovery of acid.

Using HCl: Concentrated HCl in stoichiometric excess can be used to recover acid(solute) and the solvent may be regenerated by distilling diluents in the dispersed phase.

Using TMA: In this method strong volatile amine like Trimethyl amine (TMA) is used in aqueous phase this enables the thermal decomposition of the acid-base complex and this forms the acid as product and freebase as a vapor that can be reabsorbed in water and reused. The advantage of this method is that it avoids consumption of chemicals and formation of salts.

Temperature swing regeneration: The extraction has been carried out at a relatively low temperature and during regeneration the acid loaded organic extract was contacted with a fresh aqueous stream at a higher temperature to produce an acid-laden aqueous product stream and an acid free organic phase.

Diluent swing regeneration: this is based on a shift of the equilibrium distribution of the acid from the aqueous phase to the organic phase between forward and backward extraction caused by a change in the composition of the diluent. By this diluents composition swing the acid could be back extracted into an aqueous product stream [1,9].

Keshav and Wasewar, 2010 found that NaOH in the molar ratio slightly higher than the molar ratio of acid in the organic phase was able to recover 100% acid but in this process both sulfuric acid and NaOH are consumed and waste salt is formed which requires disposal. Also they found that the Temperature swing regeneration is not successful for the regeneration of acid from loaded organic phase of TOA + alcohols, however if MIBK was used as diluents then the technique is successful [8].

VI. CONCLUSION

By this review it can be concluded that reactive extraction is much more efficient than the physical one. The hydrophobicity of the solute is key factor to be separated by using reactive extraction. If the loading ratio comes less than 0.5 it may be assumed that acid – extractant form 1:1 complex and complexation constant could be calculated with the help of this loading ratio. The extraction efficiency increases with the increasing concentration of the acid but there is the optimum value of this concentration as with the increase of the extractant concentration the viscosity of the system also increases and this increased viscosity leads to the formation of three-phase system which is undesirable. The mixed diluents system (active+ inert) may be used to overcome this problem of increased viscosity and also to get benefit of active diluents as better solvating medium. The use of natural non toxic diluents is also a wise step to reduce toxicity. The solute can be recovered and solvent can be regenerated by back extraction. There are various methods of back extraction as discussed above but it was found that using TMA was better among all.

REFERENCES


