Reactive Extraction of Acetic acid using Natural Diluents

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Abstract— Acetic acid is one of the most widely used carboxylic acids. With the growing importance of green routes for chemical synthesis the production of carboxylic acids, including acetic acid, by the fermentation route is very important. The recovery of acetic acid from the fermentation broth by conventional methods poses difficulties due to the low concentration. Reactive extraction offers an attractive alternative to the conventional routes. The reactive extraction with specific extractant and in appropriate combination with a diluent provides higher capacity and selectivity for acetic acid. In this work recovery of acetic acid by reactive extraction was studied using a natural diluent, ricebran oil. The initial concentration of acetic acid in the aqueous solution was varied in the range of 0.1 to 1 gmol/l. The extractant used was Tri-n-butyl phosphate. The distribution coefficient was found to be in the range 0.11 to 0.64.

Key words: Acetic acid, Reactive extraction, TBP, Natural Diluents

I. Introduction

A. *Reactive Extraction:*

Reactive Extraction is a process which comes under reactive separations and is a better alternative to other conventional processes, especially when extraction has to be carried out from dilute solutions. The basic motive of any Process Intensification is to select the tasks in a manner such that their combination leads to overall improved performance. Reactive extraction combines separation with reversible complexation with the component to be extracted. The reaction and separation, when combined, give effective results, as the reaction improves the separation through enhanced mass transfer rates and the separation drives the reaction to higher conversions [1-4].

Reactive Extraction of a component from its aqueous solution uses an organic extractant which reacts with the substrate and in turn forms a compound which is extracted into the organic phase. The extractants are generally viscous and therefore require diluents to accelerate the mass transfer process.

There has been lot of work done on reactive extraction for the recovery of carboxylic acids, amino acids, pesticides, pharmaceuticals, etc. Reactive extraction is a clean process as the solvent system can be regenerated completely and reused with quite simple and less expensive operations [1,5].

The choice of extractant in the reactive extraction process is crucial. It should not be toxic to the microorganisms used for the fermentation operation. Also it should selectively react with the acid present in the fermentation broth along with many other components. Tributyl phosphate (TBP) has been found to be one such extractant which has both the characteristics [1]. In addition the process can be made more eco-friendly by the use of natural oils as a diluent. The reactive extraction of citric acid and succinic acid using ricebran oil, sunflower oil, soyabean oil and sesame oil has been studied. [4,6-9]

In this work acetic acid was extracted using tributyl phosphate as an extractant, dissolved in natural diluents. The percentage extraction was studied under varying acetic acid and varying TBP concentrations. The concentration of acetic acid was varied from 0.1 to 1.0 M when extractant concentration was kept constant (0.5 M). The extractant concentration was varied from 0.1 to 1 M when acid concentration was kept constant (0.5M).

B. *Materials and methods*

In this experiment natural diluent ricebran oil was used in the extraction process. Extractant used was Tri-n-butyl Phospahate (TBP) which is a type of organophosphorous compound which provides higher distribution coefficient when used as an extractant. Acetic acid of analytical grade was used. Analysis was carried out using titration with sodium hydroxide solution with phenolphthalein as indicator. All chemicals were used as received without further purification.

II. Experimental procedure

A. *Preparation of solutions:*

The aqueous solutions of acetic acid were prepared in distilled water. Solutions of the extractant Tri-N-Butyl phosphate were made in ricebran oil. NaOH solution of required strength was prepared in distilled water.

B. *Extraction:*

Equal volumes of the organic and aqueous solutions were shaken for 60 mins in a shaker with water bath, for mass transfer to occur. The phases were then separated. The aqueous phase was collected and a sample analyzed. The amount of acid remaining in the aqueous phase was then calculated and the acid transferred to the organic phase was found by material balance.

Extraction process is analyzed by means of the degree of extraction and distribution coefficient. The distribution coefficient, K_D, is calculated using Eq (1).

$$K_D = \frac{\overline{C_{HN_C}}}{C_{HN_C}} = \frac{\overline{HAS_{n(org)}}}{[HA_{aq}]-[A_{aq}]} \qquad (1)$$

The degree of extraction is defined as the ratio of acid concentration in the extracted phase to the initial acid concentration in aqueous solution by assuming no change in volume at equilibrium as given by Eq. (2).

$$\%E = \frac{K_D}{1+K_D} \times 100 = \text{Extraction Efficiency} \qquad (2)$$

Loading Factor (Z): It is the ratio of moles of solute in organic phase to the concentration of extractant in organic phase.

III. RESULTS AND DISCUSSION

The effect of varying concentration on the extraction process was studied and it yielded the following results.

A. Constant Extractant Concentration and Varying Initial Acid Concentration:

When the initial concentration of Tri-n-butyl Phosphate was taken as 0.5M and the initial concentration of Acetic Acid was varied from 0.1 to 1 N, maximum value of the distribution coefficient obtained was 0.624. The results are tabulated in Table 1 and depicted in figure 1.

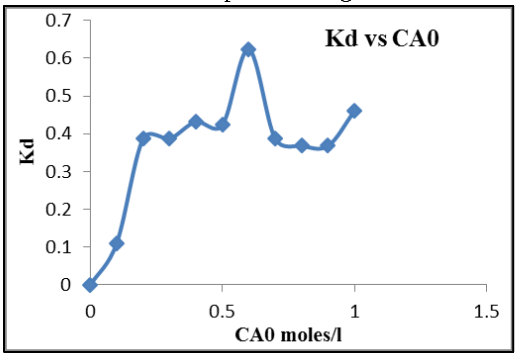

Fig. 1: Kd Vs Initial Concentration of Acetic Acid in Aqueous phase

C_A^0	%E	K_d	Z
0.1	9.91	0.11	0.022
0.2	27.93	0.387	0.124
0.3	27.93	0.387	0.186
0.4	30.18	0.432	0.268
0.5	29.73	0.423	0.33
0.6	38.44	0.624	0.512
0.7	27.93	0.387	0.496
0.8	26.93	0.368	0.538
0.9	26.93	0.368	0.7
1.0	31.531	0.460	0.834

Table 1: Chemical Equilibrium data for extraction of Acetic acid for constant Tri-n-butyl phosphate concentration (0.5 M) in ricebran oil and varying initial concentration of acid.

The distribution coefficient was found to increase initially with increase in the acetic acid concentration and then remain nearly constant.

B. Constant Initial Acid Concentration and Varying Extractant Concentration:

When initial concentration of Acetic Acid was kept constant at 0.5 N and the initial extractant concentration was varied from 0.1 to 1.0 M, the maximum distribution coefficient obtained was 0.468. The results are depicted in table 2 and figure 2.

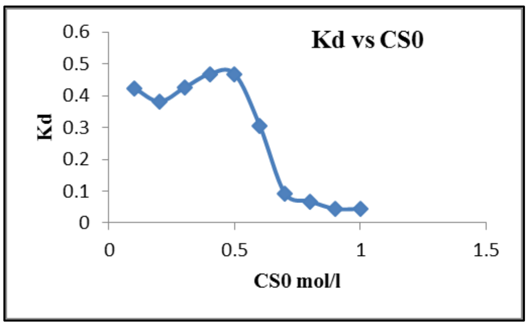

Fig. 2: Kd Vs initial Concentration of TBP in Natural Diluent

The distribution coefficient initially increased with increase in the concentration of TBP but at higher concentrations the value decreased.

C_S^0	%E	K_d	Z
0.1	29.77	0.424	1.4
0.2	27.64	0.382	0.65
0.3	29.77	0.425	0.46
0.4	31.88	0.468	0.325
0.5	31.88	0.468	0.2
0.6	23.37	0.305	0.183
0.7	8.5	0.0930	0.057
0.8	6.36	0.068	0.037
0.9	4.25	0.0444	0.02
1	4.25	0.0444	0.02

Table 2: Chemical Equilibrium data for extraction of Acetic acid for constant initial concentration of acetic acid (0.5 N) and varying concentration of Tri-n-butyl phosphate concentration (0.1 to 1 M) in ricebran

For both sets of data the loading factor z was calculated. The loading *z* is defined as

$$z = C_{A,org} \big/ B_0$$

Where $C_{A,org}$ = concentration of acid in the organic phase and B_0 = concentration of the extractant in the organic phase. The values of z are found to vary from 0.02 to 1.4 suggesting the formation of 1:1 complexes and also higher complexes like 1;2 and 1:3 between the acid and extractant [4,10].

z/(1-z) versus $C_{A,aq}$ at equilibrium and z/(2-z) versus $C_{A,aq}^2$, were plotted and it was found that for lower concentration of acetic acid the z/(1-z) versus $C_{A,aq}$ plot gave a linear fit and the z/(2-z) versus $C_{A,aq}^2$, gave a good fit over the entire range of concentrations of acid used. z/(3-z) vs $C_{A,aq}^3$ did not yield a straight line.

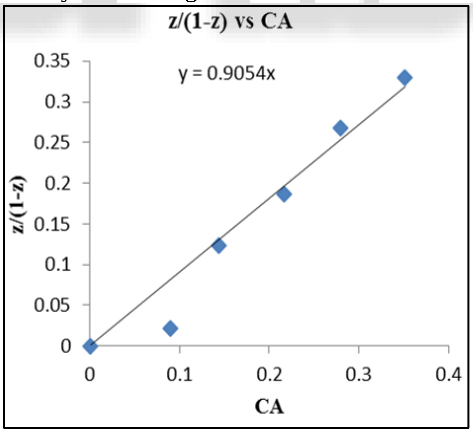

Fig. 3: z/(1-z) Vs C_A Concentration of Acetic Acid in Aqueous phase at equilibrium (for lower concentrations of acid)

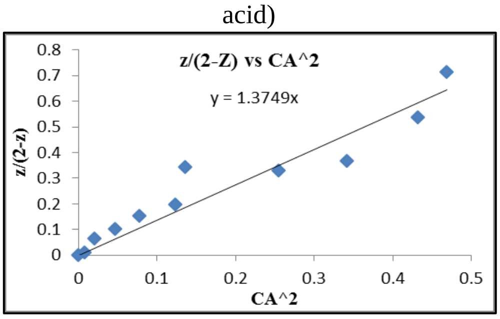

Fig. 4: z/(2-z) Vs C_A^2 Concentration of Acetic Acid in Aqueous phase at equilibrium

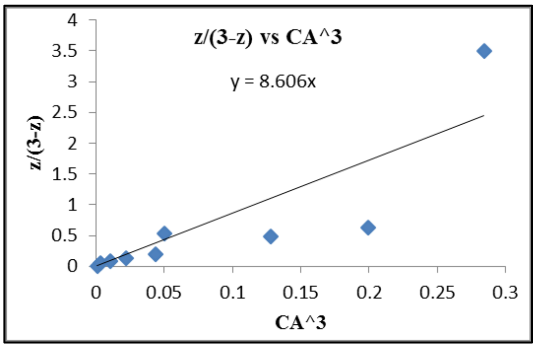

Fig. 5: z/(3-z) Vs C_A^3 Concentration of Acetic Acid in Aqueous phase at equilibrium

IV. CONCLUSION

The extractant Tri-n-butyl phosphate used in the present study was found to be an efficient extractant for the extraction of Acetic acid from aqueous solution. The study on the effect of diluent and nature of diluent has confirmed that naturally available diluents are comparable in their extraction efficiency with synthetic organic diluents. The distribution coefficients (K_D) and the degree of extraction (E %) is found to increase with an increase in Tri-n-butyl phosphate concentration upto a certain limit after which the value decreases. They also with an increase in the initial acid concentrations initially and then the increase in acetic acid concentration does not have a pronounced effect.

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