

PURIFICATION OF ESTERIFIED FUSEL OIL BY EXTRACTION OF ACETIC ACID

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Extraction of acetic acid produced from esterification of fusel oil with acetic anhydride was experimentally investigated. The selective solvent used to extract the formed acetic acid was water. Solubility data and equilibrium curves for ternary system (water-acetic acid-acetates) were experimentally determined. The results have provided useful data in designing and operating the counter-current multistage extraction unit.

Key words : Extraction, Acetic acid, Fusel oil.

Introduction

The present article is considered as an extension of the previous work [1]. It is concerned with purification of acetates resulting from esterification of fusel oil with acetic acid anhydride. The approach was followed encompass: the liquid-liquid extraction as an applied process in the recovery of formed acetic acid from acetates. The principle aspect of this approach is the determination of equilibrium data of ternary system (water-acetic acid-acetates), where acetic acid is the solute, water is the solvent and acetates are the inert part.

The equilibrium diagram was conducted by the turbidity method [2] at normal temperature. The ultimate goal of the present work is to determine the optimum conditions of acetic acid extraction and to calculate the number of equilibrium stages as well with the aim of enhancing basic design and separation of the extraction system.

Experimental

Experimental solubility data was obtained by the turbidity method [2]. For this method one component is added dropwise into a known quantity of the other while shaking until a slight turbidity is observed. In this case the constant temperature procedure is considered.

Tie lines data determined experimentally was used to provide a means of graphical interpolation of tie lines for this system using Sherwood and Coolidge's methods [3,4]. Other methods of interpolation are also available [5].

The number of stages required to accomplish a certain separation can be calculated using the same graphical methods of handling simultaneous material balance and equilibrium relation [6]. The counter current extraction battery is shown in Fig. 1.

A total material balance around the battery is:

$$L_o + V_{n+1} = L_n + V_1 = M \quad (1)$$

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Knowing feed composition (x_o), solvent composition (y_{n+1}) and solvent/feed ratio, the summation point (M) is located on line ($y_{n+1} x_o$) through the balance:

$$L_o \cdot x_o + V_{n+1} \cdot y_{n+1} = L_n \cdot x_n + V_1 \cdot y_1 = M x_M \quad (2)$$

$$x_M = \frac{(L_o \cdot x_o + V_{n+1} \cdot y_{n+1})}{M} \quad (3)$$

The operating polar is located by applying the following equation:

$$V_{n+1} - V_1 = L_n - L_o = R \quad (4)$$

The intersection between the two extended lines ($y_1 x_o$) and ($y_{n+1} x_n$) is the polar (R).

Trials were made in order to obtain the maxim. extract composition ($y_{1 \max}$) at infinite number of stages. Taking the final extract composition (y_1) smaller than ($y_{1 \max}$) then extending ($y_1 M$) to obtain the final raffinate composition (x_n) on raffinate layer. The number of stages may be obtained by the stepwise construction between the equilibrium curve (x_j vs y_j) and the projected operating curve (x_i vs y_{i+1}).

Realizing the considerable experiments involved in the extraction of acetic acid, the following procedure was adopted.

A certain amount of water (solvent) was added to the acetic acid-acetates mixture (feed), in order to find out the composition of the extract phase and the necessary amount of solvent, to achieve a given purity of the feed. In each experiment a specified amount of water was mixed with a certain amount of acetic acid - acetates mixture. These amounts are 50/25, 25/25, 25/50, 10/40 and 5/50. The mixture was stirred

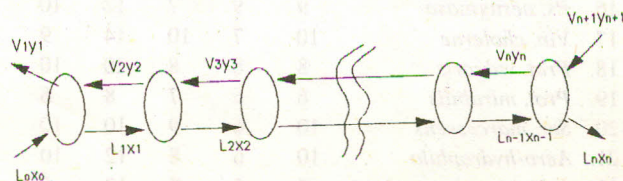


Fig. 1. Counter current multistage extraction.

for half an hour to ensure steady state conditions. The temperature of the extraction was maintained constant at room temperature while mixing the two phases thoroughly for a period of half an hour. The container was closed in order to avoid any evaporation of the components. The two layers formed were separated using separating funnel after settling. Each layer was then determined volumetrically and analysed. The acetates layer was submitted to a gas chromatographic analysis. Water-acetic acid layer was titrated with sodium hydroxide. Also solubility data of the ternary system, acetic acid-water-acetates, was determined using turbidity at 25°C. The previously prepared acetic acid - acetates solution obtained from a highly converted esterification reaction was used with distillate water.

Results and Discussion

Solubility data. Points enclosing the solubility curve for ternary system (water-acetic acid- acetates) at 25°C shown in Tables 1 and 2 depict the volumes of two layers obtained by extraction. The tie lines for this ternary system plotted on Hand's coordinates fall on a curve and the conjugate lines meet the solubility curve at the plait point.

Calculation of the number of extraction stages. Various trials were made at different amounts of solvent/feed ratios to obtain the optimum conditions as shown in Table 3.

TABLE 1. SOLUBILITY DATA (WT%) OF WATER-ACETIC ACID-ACETATES AT 25°C.

Acetic acid	Water	Acetates
0	25	75
5	19	76
20	8	72
35	2	63
48	4	48
60	26	14
50	45	5
40	57	3
25	72	3
13	80	7

TABLE 2. VOLUMES OF THE TWO LAYERS OBTAINED BY EXTRACTION.

V_{n+1}/L_0	Acetates layer (vol c.c)	Water - acetic acid layer (vol c.c)
50/25	37	38
25/25	14	36
25/50	12	63
10/40	5	45
5/50	1.3	50.7

The maximum extract composition ($y_{1 \max}$) was found to be 0.52 which lies on the tie line going through the feed composition x_0 . Taking the operating extraction composition $y_1 = 0.48$ smaller than $y_{1 \max}$, the graphical treatment is shown in Fig. 2.

The relation between the theoretical number of stages and different operating values of (solvent/feed) ratio is shown in Fig. 3. From Table 2, the smallest acetates composition is: $x_n = 0.02$ at solvent/feed ratio of 0.5 with theoretical number of stages 4.7. Increasing raffinate composition to 0.05 at (solvent/feed) ratio 0.673 gives the number of stages 3.4. This means higher acetates content in acetic acid-water layer, which means unefficient separation (Fig. 4). This means that in order to obtain a required raffinate composition from a given feed composition by using known solvent composition, the number of stages and the final extract composition (y_1) increases as (solvent/feed) ratio decreases. If the efficiency of the extraction units is taken between 40-30% the number of

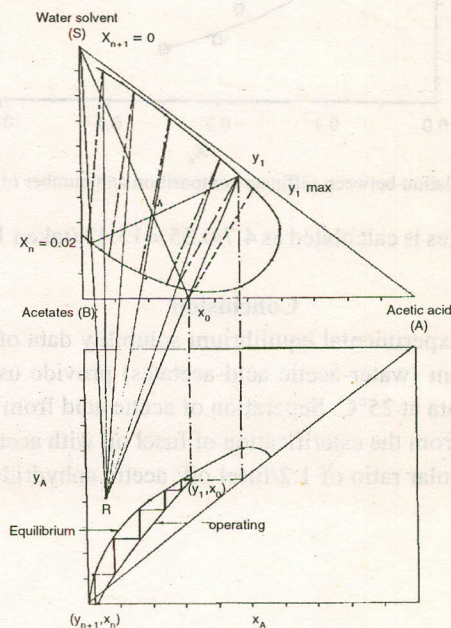


Fig. 2. Counter current contact.

TABLE 3. RELATION BETWEEN (SOLVENT/FEED), RAFFINATE COMPOSITION AND NUMBER OF STAGES.

Solvent feed	Final raffinate composition (x_n)	Number of stages (n)
0.6538	0.02	4.733
0.673	0.05	3.4
0.72	0.1	2.5
0.75	0.18	1.9
0.8	0.2	1.22
0.885	0.25	1.05

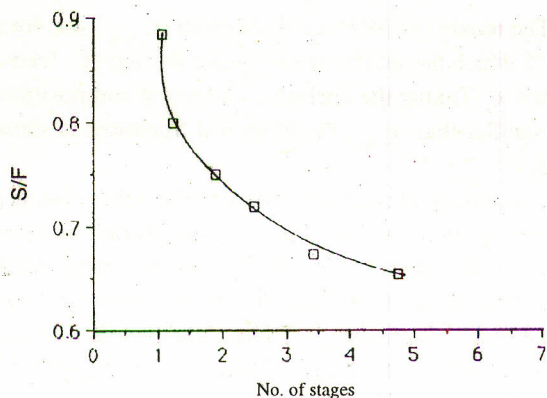


Fig. 3. Relation between number of stages and (solvent/feed) ratio.

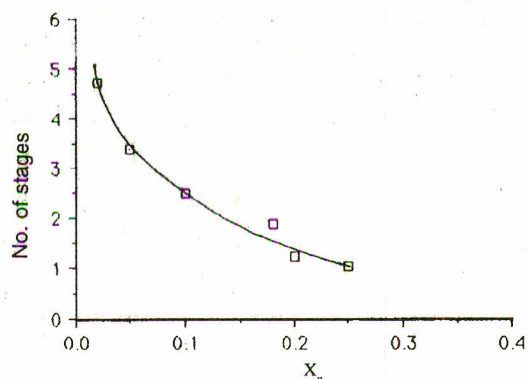


Fig. 4. Relation between raffinate composition and number of stages.

actual stages is calculated as $4.7/0.35 = 13.43$ (taken 14 actual stage).

Conclusion

The experimental equilibrium solubility data of the ternary system (water-acetic acid-acetates) provide useful extraction data at 25°C. Separation of acetic acid from acetates resulting from the esterification of fusel oil with acetic anhydride at molar ratio of 1:2/fusel oil: acetic anhydride can be

made by extraction. The number of stages was calculated by using the most convenient operating conditions which are helpful for the basic design and operation of liquid-liquid extraction system.

NOMENCLATURE

SYMBOLS

L	=	Raffinate, mass/time
L ₀	=	Feed, mass/time
x	=	Mass fraction of raffinate
y	=	Mass fraction of extract
V	=	Extract, mass/time
V _{n+1}	=	Solvent, Mass/time

SUBSCRIPTS

0	=	Feed
1	=	Stage 1, where feed enters
n	=	Stage n, where solvent enters
M	=	Mixture
x _i , y _j	=	x In equilibrium y
x _i , y _{i+1}	=	x Operating with y

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