[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

Amplified Distillation of Binary Aliphatic Acid Mixtures

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In view of the success in resolving mixtures of nitrogen bases by means of amplified distillation,[1] this process was extended to the separation of aliphatic acids since, from theoretical considerations, it was probable that a similar efficiency would result. Accordingly, amplified distillation was applied to the separation of the component acids of two binary systems, namely, propionic–butyric and butyric–isovaleric. A comparison of the analytical data of fractions, obtained in amplified and straight distillation, clearly demonstrates the superiority of the former method in separating the individual acids from the mixtures.

tedious processes requiring cumbersome mathematical treatment. In this work the more rapid and less complex procedure of Dyer[8,9] was used in evaluating the composition of distillation fractions.

The Dyer analysis, tested in connection with this problem, revealed several faults which give rise to erratic results. Using acids of reasonable purity, it was found impossible to duplicate the original distilling constants (i. e., the percentage of acid in 100 cc. of distillate from a steam distillation at a constant volume of 150 cc.). Since a constant volume in the distilling flask is of primary importance, this was maintained by the dropwise addition of water at a rate equal to the condensate being delivered into the receiver. The steam distillations were carried out at a rate of approximately 5 cc. per minute. Slight variations did not affect the constants; however, very slow distillations gave high values and rapid distillations gave low values. To minimize the reflux and to prevent the carrying over of spray, an insulated Kjeldahl trap was placed between the flask and the condenser. With these slight modifications the constants given in Table I were determined and used quite satisfactorily in the analyses.
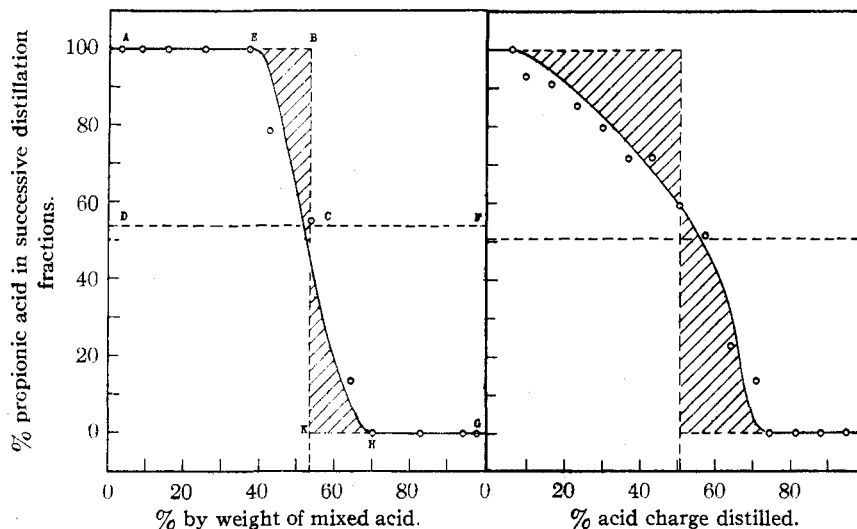
Fig. 1.—Amplified distillation of propionic-butyric acid mixture (II).

Fig. 2.—Straight fractional distillation of propionic–butyric acid mixture.

Analysis of Distillation Fractions

Following amplified distillation the separation of the acids from the hydrocarbon oil carrier can be effected quantitatively by extraction with 0.1 N potassium hydroxide solution.

The various schemes which have been proposed for the analysis of binary acid mixtures[2-6] are all based on Duclaux's[7] original method and involve

TABLE I

PER CENT. OF ACID DISTILLING OVER INTO THE FIRST 100 CC. OF DISTILLATE FROM A CONSTANT VOLUME OF 150 CC. OF AQUEOUS SOLUTION

	Propionic	Butyric	Isovaleric
Modified procedure	56.39	73.10	89.87
Dyer[8] procedure	52.67	69.88	87.51

Distillation Procedure

For each amplified distillation, a binary mixture was prepared from 7.5-cc. weighed portions of each of the two

(1) Bratton, Felsing and Bailey, Ind. Eng. Chem., 28, 424 (1936).
(2) Boekhout and de Vries, J. Chem. Soc., A112 (ii), 50 (1917); Centr. Bakt. Parasitenk., 46 (ii), 505 (1916).
(3) Gillespie and Walters, THIS JOURNAL, 39, 2027 (1917).
(4) Knetemann, Rec. trav. chim., 47, 950 (1928).
(5) Richmond, Analyst, 42, 125, 133 (1917); 44, 255 (1919).
(6) Upson, Plum and Schott, THIS JOURNAL, 39, 731 (1917).
(7) Duclaux, Ann. chim. phys., 2, 289 (1874).

(8) Dyer, J. Biol. Chem., 28, 445 (1917).
(9) Lamb, THIS JOURNAL, 39, 746 (1917).

respective acids (propionic–butyric or butyric–isovaleric). To this mixture was added 150 cc. of hydrocarbon oil having a boiling range extending from 30° below to 10° above that of the acids. In the straight distillations, approximately the same volume (150 cc.) of binary mixture, without hydrocarbon oil, was used.

A 200-cc. round-bottomed flask surmounted by a 110-cm. by 0.7-cm. spirally indented glass column comprised the distillation unit. A reflux condenser was provided and adiabatic operation was ensured by surrounding the column with a larger resistance-wire wound jacket, electrically heated. Finally, a well-lagged glass mantle enclosed the column assembly.

The still was operated under total reflux for one-half hour before beginning to take off fractions. After setting the reflux ratio at 5:1, one drop of distillate per second was removed. The 10-cc. fractions, whose temperature ranges were noted, were analyzed by the following procedure: (1) quantitative extraction of the hydrocarbon–acid mixture with standard alkali; (2) the determination of the total acidity of the fraction; (3) neutralization of the sodium salts of the acids and adjustment of the total volume of solution so that volumetric samples containing approximately 0.5 cc. of acid were available for final analysis; (4) steam distillation of the preceding sample; (5) titration of the first 100 cc. of distillate with standard alkali; (6) calculation of the distilling constant of the sample which is in turn used in arriving at the percentage composition of the sample as described by Dyer. In the case of the straight fractional distillations the volume cuts were weighed and 0.5-cc. portions were subjected to the same analytical procedure. The refractometer was used as a check on the analysis of fractions indicated to be pure by the chemical analysis.

Percentage composition of successive fractions is plotted against total amount of mixed acid charge distilled over as shown in Figs. 1–4. If Fig. 1 is considered, it can be seen that a perfect separation would follow the 100% line to the vertical median line, the latter representing the composition of the total acid mixture. If no separation is realized the composition will remain unchanged as represented by the horizontal median line. Since experimental curves must fall between these two extremes, the ratio

$$\text{Area}_{AECD}/\text{Area}_{ABCD}$$

expressed in per cent. should be a measure of the efficiency of separation, by distillation, of propionic acid from butyric acid. The same reasoning applies to the area CFGK where an expression for the separation of butyric acid from propionic is obtained. Since the experimental curves did not always pass through the intersection of the median lines, the over-all efficiency of separation, as expressed in Table

II, was obtained by subtracting the sum of the shaded areas from the sum of the theoretical areas and dividing this value by the sum of the theoretical areas. Table II summarizes the efficiency of separation realized and shows the increased quantity of pure constituents realized through amplified distillation as compared with that from ordinary fractional distillation.

TABLE II
COMPARISON OF DISTILLATION EFFICIENCY
Propionic–Butyric Acid Mixture

	% of theoretical area	% CH_3CH_2-COOH recovered pure	% $CH_3(CH_2)_2$-COOH recovered pure
Straight fract. dist.	70.0	13.5	50.4
Amplified dist.	91.5[a]	72.0[a]	73.0[a]

Butyric–Isovaleric Acid Mixture

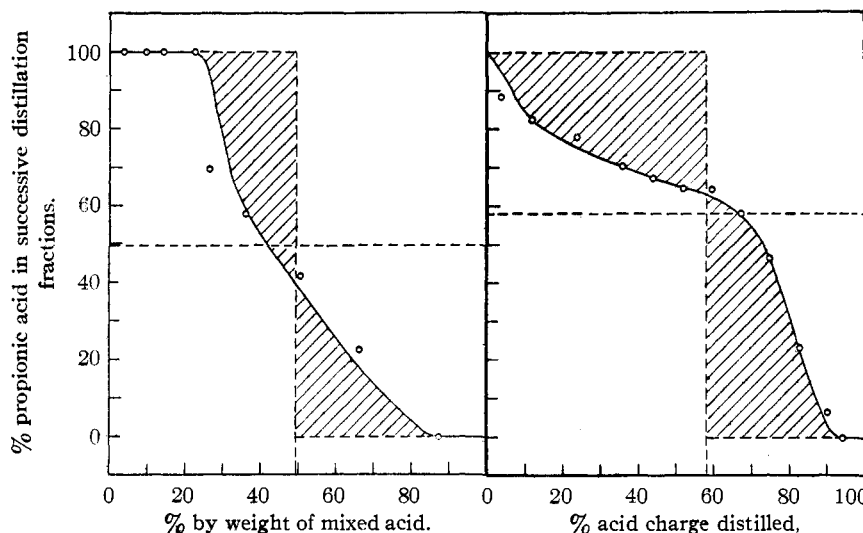|		% $CH_3(CH_2)_2$-COOH recovered pure	% $(CH_3)_2$-CHCH_2COOH recovered pure
Straight fract. dist.	44.2	0	13.2
Amplified dist.	67.4	45.5	16.5

[a] Average of two distillations.

Fig. 3.—Amplified distillation of butyric-isovaleric acid mixture.

Fig. 4.—Straight fractional distillation of butyric–isovaleric acid mixtures.

Obviously a better separation in both types of distillation could have been realized through the use of a more efficient column, but a mere comparison of the two methods was the object of this work. Resolution of fatty acid mixtures is at best, however, a difficult procedure.

Summary

1. Dilution of acid mixtures with ten volumes of hydrocarbon oil prior to distillation greatly increases the efficiency of separation of the acids.

2. A modified Dyer analytical method for the acid distillation fractions is proposed.