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THE AUTOMATIC SEPARATOR IN ESTERIFICATIONS AND OTHER PREPARATIONS.

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When a mixture of 2 immiscible liquids of different densities is introduced into one limb of a U-tube and separation takes place, the levels of the liquids in the 2 limbs will be different, that containing the layer of lighter liquid being the higher. By introducing a side-arm at a suitable level on each limb, it is possible to effect a continuous separation of the 2 components, each flowing off from an arm.

The principle, while by no means novel, has not, so far as the authors are aware, been applied in the laboratory to organic preparations; and though its application is restricted to the separation of substances the mixed vapors of which separate on condensation into 2 liquid phases of limited mutual solubility which differ in density by not less than 2%, nevertheless its uses in the laboratory have been found to be so wide that an account of some of these has been considered advisable.

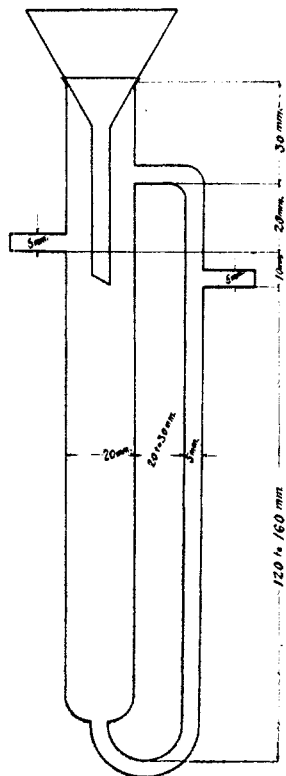


Fig. 1.

The separator itself is of extremely simple construction (Fig. 1). To the side arms are attached tubes leading to the appropriate receivers; these tubes must be so arranged that they do not incline upwards at any part of their length. It will be noted that disturbance of the equilibrium by siphoning is excluded by the junction of the limbs above the liquids. The suspension of liquids is introduced through the funnel, the stem of which reaches a short distance below the point at which the side arm is attached; by this means none of the heavy liquid is held (by surface tension) above the lighter liquid. Before starting the flow of mixed liquids the apparatus should be partly filled with the heavier liquid, thus preventing the passage of the lighter liquid into the narrow limb. The depth of the layer of lighter liquid varies inversely as the difference

in the densities of the liquids.

The separator, in all the experiments described below, is employed in conjunction with an apparatus for distillation, when it is desired to remove

one of the liquids and return the other to the distillation vessel. In Fig. 2 is shown the arrangement when the lighter liquid is to be returned. The tube by which the returned liquid enters the distillation vessel must be constricted at the lower end and, if the liquid is very volatile, project below the surface of the boiling mixture, in order to prevent the escape of vapor. When the heavier liquid is to be returned, the position of the separator is reversed, so that the narrow limb leads to the return tube.

The following preparations will illustrate the uses to which this apparatus may be put. We have as yet had no occasion to employ it in conjunction with distillation under reduced pressure, but believe that this should be feasible.

Steam Distillation of Aniline and Similar Liquids.

In the isolation of quinoline, aniline, and similar liquids, it is customary in laboratory manuals to recommend that the mixture of liquids obtained on steam

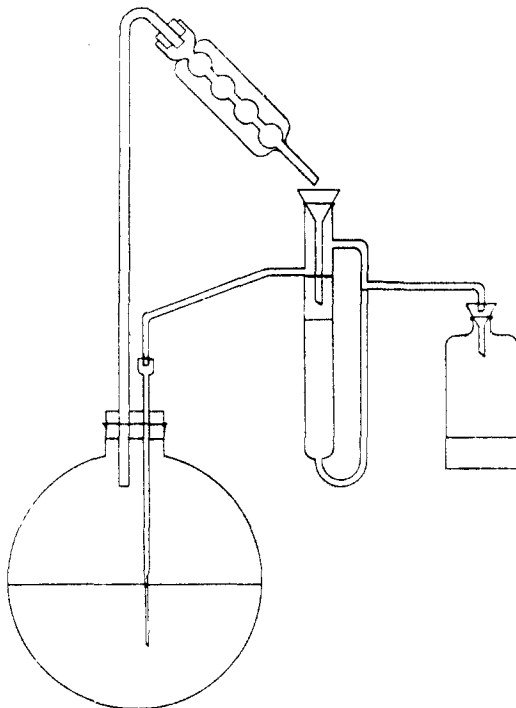


Fig. 2.

distillation be separated, and that the remaining product, which is dissolved in the aqueous portion of the distillate be recovered by saturating with salt and extracting with ether. This process is, however, far less preferable to distilling out the product from the aqueous portion, as is done in the technical preparation of aniline, but even this latter procedure is apt to be tedious when large volumes of distillate have to be treated.

The product can be obtained practically free of undissolved water in one operation, without the use of steam, by the use of the separator so adjusted that the water returns to the vessel in which the mixture is boiled. The distillation, which can be carried out entirely without attention, is stopped when no more oil passes into the receiver.

Excellent results have been obtained by this method in the purification of salicylaldehyde and quinoline.

Separation of *n*-Butyl Alcohol or *Iso*-Amyl Alcohol and Water.

An aqueous solution of butyl alcohol from which it is required to recover the alcohol is placed in the flask and the separator adjusted so as to return the heavier liquid. After half filling the separator with water the contents of the flask are distilled until no further quantity of lighter liquid collects in the receiver. The residue in the flask is now substantially free from butyl alcohol.

In order to remove the water dissolved in the alcohol, the lighter liquid is distilled with the separator reversed so as to return the upper layer. When water ceases to be delivered from the separator the alcohol contains only the amount of water retained by the upper layer in the separator, and this can be removed from the small amount of fore-run obtained on fractionally distilling the residue in the flask.

The water collected in the receiver, as well as in the fore-run, being saturated with alcohol, may be treated in the same way, either independently or in subsequent runs.

Preparation of Butyl Ether.

Six kg. of butyl alcohol and 2 kg. of conc. sulfuric acid are boiled together, with elimination of the water, until the temperature of the mixture has risen to 134°. The mixture is then distilled in a current of steam and the distillate separated from the water, washed with alkali, fractionally distilled, and the fraction boiling at 142.5–144° collected. The fore-runs, consisting principally of butyl alcohol, can be again employed for subsequent runs. The yield is about 60%; some loss is caused by the formation of non-volatile tarry products.

Preparation of Anhydrous Oxalic Acid.

The customary methods for preparing anhydrous oxalic acid are (1) the exposure of hydrated oxalic acid to air at 100–110° in an oven; (2) the distillation of the water of hydration from oxalic acid at about 60° under reduced pressure. The first method involves a considerable loss of product through sublimation; in the second it is necessary to grind the material continually in order to break up the clumps and to expose fresh surfaces. It is possible to avoid both of these disadvantages by dehydrating by means of boiling carbon tetrachloride.

Two kg. of hydrated oxalic acid, which has been sifted through a 10-mesh sieve, is suspended in 3 liters of carbon tetrachloride and heated to gentle boiling on the water-bath with mechanical stirring. The vapors are condensed in an efficient condenser, and the distillate is passed through an automatic separator, the carbon tetrachloride layer being returned through a column of calcium chloride to the mixture in the flask. The process is continued until no more water passes over, the carbon tetrachloride condensing being then no longer cloudy. The oxalic acid is now completely anhydrous, and is filtered off and freed from adhering carbon tetrachloride by warming on the water-bath in a gentle current of dry air. The yield is close to the theoretical.

Preparation of Ethyl Oxalate.

The published methods¹ for the preparation of ethyl oxalate involve

¹ For instance, Steyrer and Seng, *Monatsh*, 17, 614 (1896).

the use of absolute alcohol and anhydrous oxalic acid; and owing to the instability of the mono-acid ester, which is formed as an intermediate product, but decomposes at about 140° , the yields are even under favorable conditions most unsatisfactory. It is possible, however, by the removal of water at a temperature lower than that at which the mono-acid ester decomposes, to prepare the normal ester in yields very close to the theoretical.

Three kg. of crystallized oxalic acid, 5 kg. of ethyl alcohol, and 8 kg. of carbon tetrachloride are boiled together, and the vapors passed through an efficient column. A ternary mixture of water, alcohol, and carbon tetrachloride, which distils over at about 60° , is condensed and allowed to run into an automatic separator, when it divides into 2 layers, the lower consisting principally of carbon tetrachloride and alcohol, with only a small quantity of water. This is run over a column of potassium carbonate, which removes practically all the water, and then returned to the reaction flask. The upper layer is collected separately; a rough estimation showed it to consist of approximately 65% alcohol, 25% water and 10% carbon tetrachloride. When one or two liters of this have collected, it is distilled separately through a column, and the low boiling portions, consisting principally of alcohol, together with carbon tetrachloride, are dried with potassium carbonate, and returned to the reaction mixture. When the lighter layer no longer collects, the separator is removed, and the distillation continued until the temperature of the vapor at the head of the column reaches 85° . The residue in the flask is then distilled under reduced pressure, when 3305 g. of ethyl oxalate boiling at 105° to 107° at 25 mm. is obtained. This yield corresponds to 95% of that theoretically obtainable from the oxalic acid; the losses of alcohol and carbon tetrachloride, with careful manipulation, are very slight.

Ethyl tartrate can be prepared in satisfactory yield by a similar process. It is, however, necessary in this case to pass a very slow current of hydrogen chloride into the boiling mixture to act as a catalyst.

Preparation of *n*-Butyl Oxalate.

It is possible to prepare *n*-butyl oxalate in excellent yields merely by distilling together hydrated oxalic acid and butyl alcohol, returning to the mixture the volatilized alcohol and removing the water as fast as it is formed.

Hydrated oxalic acid is mixed with twice its weight of butyl alcohol, distilled, and the distillate collected in an automatic separator so arranged that the lighter layer of alcohol returns to the apparatus. The process is continued until no more water separates, when the contents of the vessel are submitted to vacuum distillation. Butyl alcohol together with a small amount of butyl formate first passes over, when the temperature rapidly rises and a higher fraction boiling constantly at 150° at 20 mm. is collected. The yield amounts to over 80%.

Preparation of Trimethylene Chlorohydrin.¹

To a mixture of 1000 g. of trimethylene glycol and 600 g. of conc. hydrochloric acid (33%) boiling under a reflux condenser is added 1200 g. of the same acid at such a rate that no loss of hydrogen chloride occurs (about 2 hours). The mixture is then distilled with a separator adjusted for the return of the lighter (aqueous) liquid, the heavy oil being collected separately. After about 16 hours' boiling about 700 g. of oil

¹ Cf. Norris and Mulliken, *THIS JOURNAL*, **42**, 2095 (1920).

has collected, and though it does not cease to collect, it separates very slowly. One liter of the aqueous liquid is at this point collected separately instead of allowing it to return to the reaction flask, and the boiling continued as before. After boiling for another 8 hours, very little oil separates and the reaction is discontinued. The residue in the flask is distilled as far as possible, and the combined watery distillates distilled until no more oil separates in the condensed liquid. A total of 950 g. of wet oil is obtained; less than 200 g. of residue remains in the reaction vessel after the bulk of the watery acid has been distilled out.

The product is then fractionally distilled, the water being separated from the fore-runs, and the oily portions returned for distillation, until no more water is present. On repeated fractionation of the material thus dried 421 g. of pure trimethylene chlorohydrin boiling at 160° to 162° is obtained; the fore-runs yield 115 g. of trimethylene chloride boiling at 120° to 122°. The intermediate fractions amount to 75 g.; if fractionation were continued they could be resolved into further quantities of the chloride and chlorohydrin. A high boiling fraction of 129 g. was also obtained. This was not examined closely, but probably contains ethereal condensation products.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY, HARVARD MEDICAL SCHOOL.]

INDIRECT REDUCTION OF 3-AMINO-4-HYDROXYPHENYL-ARSONIC ACID TO ARSPHENAMINE.

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In a recent paper from this laboratory² a method was described for the preparation of arspenamine by reduction of 3-amino-4-hydroxy-phenyl-arsonic acid with hypophosphorous acid followed by precipitation with hydrochloric acid. Although the product formed a gel with water at room temperature and could be dissolved easily only by warming to 55°, it was of low toxicity. It seems desirable that arspenamine should dissolve readily in water without warming in order to simplify the technic required in administering the material in medical practise. When a similar reduction was carried out starting with the hydrochloride of 3-amino-4-hydroxy-phenyl-arsenious oxide instead of the arsonic acid, the product, still of low toxicity, was readily soluble in water at room temperature. Owing to the solubility of the oxide base in water³ this substance is difficult to isolate in the pure state. However, it was found that a solution of the oxide obtained by reduction of the corresponding arsonic acid met our requirements just as well as the purified oxide. After reduction of

¹ This is the second of a series of studies on the properties contributing to the toxicity of arspenamine being made under a grant from the United States Interdepartmental Social Hygiene Board to the Harvard Medical School; the work is under the general direction of Dr. Reid Hunt, who is also responsible for the biological tests reported in this paper. Additional aid has been received from the Committee of the Permanent Charity Fund, Incorp.

² Christiansen, *THIS JOURNAL*, **42**, 2402 (1920).

³ Ehrlich and Bertheim, *Ber.*, **45**, 756 (1912).