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SEPARATION AND RECOVERY OF AROMATIC HYDROCARBONS FROM PARAFFINS AND NAPHTHENES BY ADSORPTION [1]

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ABSTRACT

A method is described for separating, by the process of adsorption, the aromatic hydrocarbons from their mixture with paraffin and naphthene (cycloparaffin) hydrocarbons, as in the gasoline or kerosine fractions of petroleum. The mixture is introduced into the top of a column containing an appropriate excess of solid adsorbent. A low-boiling paraffin hydrocarbon, such as pentane, butane, or propane, is then added in sufficient quantity to remove from the column the paraffin and naphthene hydrocarbons but not the aromatic hydrocarbons. The latter are then removed by adding an appropriate desorbing liquid, such as methanol. The paraffins, naphthenes, and pentane are thus obtained as a mixture from which the pentane is easily removed by distillation. The aromatic hydrocarbons are obtained as a mixture with pentane and methanol. The methanol is easily removed by extraction with water and the pentane by distillation.

This method of separation was tested on a known mixture of 17 pure hydrocarbons, the normal boiling points of which covered a range from 60° to 174° C and included all of the 5 normal paraffins from *n*-hexane through *n*-decane, the isoparaffin 2-methylpentane, the 4 normal alkyl cyclohexanes from cyclohexane through *n*-propylcyclohexane, and all of the 7 possible aromatic hydrocarbons from benzene through isopropylbenzene. The separation of the aromatic hydrocarbons from the paraffins and naphthenes was quantitative within the limits of measurement, and their recovery was complete within the normal operating loss of material in processing.

Experimental determinations were made of the quantity of aromatic hydrocarbon adsorbed per unit quantity of adsorbent, for a number of different binary solutions of aromatic hydrocarbons with paraffins or naphthenes, at several concentrations of the aromatic hydrocarbon, and with silica gel, carbon, magnesia, alumina, Filtrol, and Florisil as adsorbents. The results are displayed in the form of adsorption isotherms.

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[1] This investigation is part of the work of Research Project 6 of the American Petroleum Institute, from whose research fund financial assistance has been received. The experimental work described herein was performed in the period from September 1941 to March 1942. The manuscript was first completed in June 1942 and revised in March 1943.

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I. INTRODUCTION

In this paper a method is described for separating, by the process of adsorption, the aromatic hydrocarbons from their mixture with paraffin and naphthene (cycloparaffin) hydrocarbons, as in the gasoline and kerosine fractions of petroleum. The method of adsorption used for this purpose is essentially that devised by the Russian botanist M. Tswett [1] [3] and commonly known as the Tswett method or the chromatographic method. Previous applications of this method to the separation of aromatic hydrocarbons involved principally hydrocarbons of high molecular weight and of biological importance.[4] While there are a number of reports on the use of the Tswett method in the field of petroleum chemistry [6, 7, 8, 9, 10, 11], the method does not appear to have been used for the separation and recovery of aromatic hydrocarbons from naphthene and paraffin hydrocarbons.

II. GENERAL DESCRIPTION OF THE METHOD

The petroleum fraction, a mixture of aromatic, naphthene, and paraffin hydrocarbons, is filtered through a column containing more than enough solid adsorbent to adsorb all of the aromatic hydrocarbons. The filtrate (if any) is (*a*) an aromatic-free mixture of paraffins and naphthenes. In addition to the aromatic hydrocarbons (*b*) which are retained within the column principally by adsorption, there are retained some paraffins and naphthenes (*c*) in the macroscopic interstices of the adsorbent and some which are weakly adsorbed.

The paraffins and naphthenes (*c*) are displaced by adding an appropriate low-boiling hydrocarbon in the liquid state (e. g. *n*-propane, *n*-butane, or *n*-pentane). The filtrate from this operation is (*d*) a mixture of the displaced paraffins and naphthenes together with the hydrocarbon used in displacing them. The filtrates (*a*) and (*d*) now contain the paraffins and naphthenes of the original charge. The original naphthenes and paraffins are separated by distillation from the low-boiling hydrocarbon in these fractions.

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[3] Figures in brackets indicate the literature references at the end of this paper.

[4] See, for example, Chromatographic Adsorption Analysis [2] and the compilation recorded there from the work of Kuhn and Winterstein [3], Winterstein and Schön [4], and Winterstein, Schön, and Vetter [5].

The aromatic hydrocarbons on the adsorbent, together with the low-boiling hydrocarbon in the column, are displaced by the addition of a substance which is more strongly adsorbed than the aromatic hydrocarbons. The added substance may be methanol, in which case the aromatic hydrocarbons are obtained as a mixture with the low-boiling hydrocarbon and methanol. The methanol may be removed by extraction with water and the low-boiling paraffin removed by distillation, or, if pentane is used, both the methanol and the pentane may be removed by distillation, provided the amount of the pentane is more than sufficient to remove the methanol as an azeotropic mixture.

The adsorbent may then be reactivated for the next cycle.

III. STATEMENT OF PRINCIPLES INVOLVED IN THE METHOD

Certain of the principles involved in the process of adsorption are now reasonably well understood [12, 13, 14]. When a solution of an aromatic hydrocarbon with a paraffin or a naphthene is filtered through a column of solid adsorbent, the first portion of solution comes into contact with successive layers of fresh adsorbent and its aromatic content is progressively reduced to zero. The first, or top, layer of adsorbent comes into contact with successive portions of solution having the initial concentration of aromatic hydrocarbons. This layer of adsorbent soon reaches a state of equilibrium between the aromatic hydrocarbons in the solution of the original concentration and the amount of aromatic hydrocarbon adsorbed per unit quantity of adsorbent. As the solution moves down the tube, successive layers of adsorbent come into contact and into equilibrium with solution of the initial concentration. Thus, extending downward from the top layer of adsorbent, a zone is formed in which the adsorbed aromatic hydrocarbon is in equilibrium with solution of the initial concentration, which solution fills the macroscopic interstices of the adsorbent. With continued introduction of solution at the top of the column, this equilibrium zone extends farther and farther down the tube, forcing the aromatic-free material ahead of it, with (if the filtration is not too rapid) a comparatively narrow region between the equilibrium zone and the aromatic-free portion. Finally, the equilibrium zone will reach the bottom or last layer of adsorbent, and, at this point, solution containing the initial concentration of aromatic hydrocarbon will just begin to emerge as filtrate from the bottom of the column of adsorbent.

It is apparent that the treatment of a solution of an aromatic hydrocarbon in a paraffin or naphthene in the manner just described may yield a portion of the charge as aromatic-free material, but that a quantitative separation of paraffin or naphthene hydrocarbons from aromatic hydrocarbons is not possible by this process alone. The complete separation of a paraffin or naphthene hydrocarbon from an aromatic is possible if the ratio of the quantity of charge to adsorbent is selected (as described in section V) so that, when the entire charge has been introduced into the column of adsorbent, the equilibrium zone extends only part way down the adsorbent column. There is then introduced into the top of the column the displacing hydrocarbon (e. g., *n*-pentane). When the first portion of this solvent enters the first, or top, layer of adsorbent, it dissolves some of the aromatic hydrocarbons. As successive portions pass through the top layer its aromatic content is progressively reduced to zero. In the meantime the original solution is displaced down the column and comes into contact with fresh adsorbent, and consequently the lower edge of the equilibrium zone moves downward. The net effect of this process is a downward movement of the equilibrium zone, together with a substitution of the displacing hydrocarbon for the paraffin or naphthene originally in the equilibrium zone. If sufficient adsorbent and displacing liquid have been used, the original paraffin or naphthene will be completely displaced from the column before the equilibrium zone reaches the bottom and before aromatic material appears in the filtrate.

IV. ADSORPTIVE CAPACITY OF VARIOUS ADSORBENTS

1. SOLUTIONS INVESTIGATED AND METHODS EMPLOYED

To find the best adsorbent to use in this method of separation, experimental determinations were made of the quantity of aromatic hydrocarbon adsorbed per unit quantity of adsorbent, for a number of different binary solutions of aromatic hydrocarbons with paraffins and naphthenes, at several concentrations of the aromatic hydrocarbon, and with silica gel, carbon, magnesia, alumina, Filtrol, and Florisil as adsorbents.

With silica gel [5] as the adsorbent, data were obtaind for one or more concentrations of the following solutions: A, toluene+2,2,4-trimethylpentane; A′, toluene+2,2,4-trimethylpentane; A^2, toluene+2,2,4-trimethylpentane; A^3, toluene+2,2,4-trimethylpentane; B, toluene+*n*-heptane; B′, toluene+*n*-heptane; B°, toluene+*n*-heptane; C, toluene+*n*-hexane; D, toluene+methylcyclohexane; E, benzene+*n*-hexane; F, benzene+2,2,4-trimethylpentane; G, *p*-xylene+methylcyclohexane; H, "diethylbenzene"+2,2,4-trimethylpentane; I, isopropylbenzene+*n*-nonane.

All the observations for the solutions listed, except for solution B°, were made at the prevailing room temperature, which was recorded in each case and found to be within the range 23° to 28° C. Except in those cases where the letter representing the solution is characterized with a superscript, one lot of the regular silica gel, sample I–a, (see section IV–5) was used. The data, which are displayed in the form of adsorption isotherms in figures 1 and 2, were obtained from filtration experiments on solutions of known concentration, using 75 g of silica gel, and with a ratio of length to diameter of the column of adsorbent about 40 to 1. The volume of aromatic-free filtrate, corrected for the small intermediate portion, was determined as described previously [11]. The quantity of aromatic adsorbed was computed on the assumption that no paraffin or naphthene was adsorbed.[6] On this basis the quantity of aromatic adsorbed

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[5] In this paper the term "silica gel," in any given particle size, when used without qualification, refers to material stabilized at the "normal" temperature and designated as No. 659528–2000 (28 to 200 mesh) or No. 659528–420 (28 to 42 mesh), Davison Chemical Corp., Baltimore, Md. In several instances, silica gel stabilized at higher than the "normal" temperature and designated as No. 859528–2000 (28 to 200 mesh) was used and is so indicated.

[6] Actually a small amount of paraffin or napthene is adsorbed and consequently the correct values for the amount of aromatic adsorbed will be slightly greater than the values shown in figures 1 and 2.

is that quantity which in the original solution was associated with the portion rendered aromatic-free. The equilibrium concentration is in this case the concentration of the original solution.

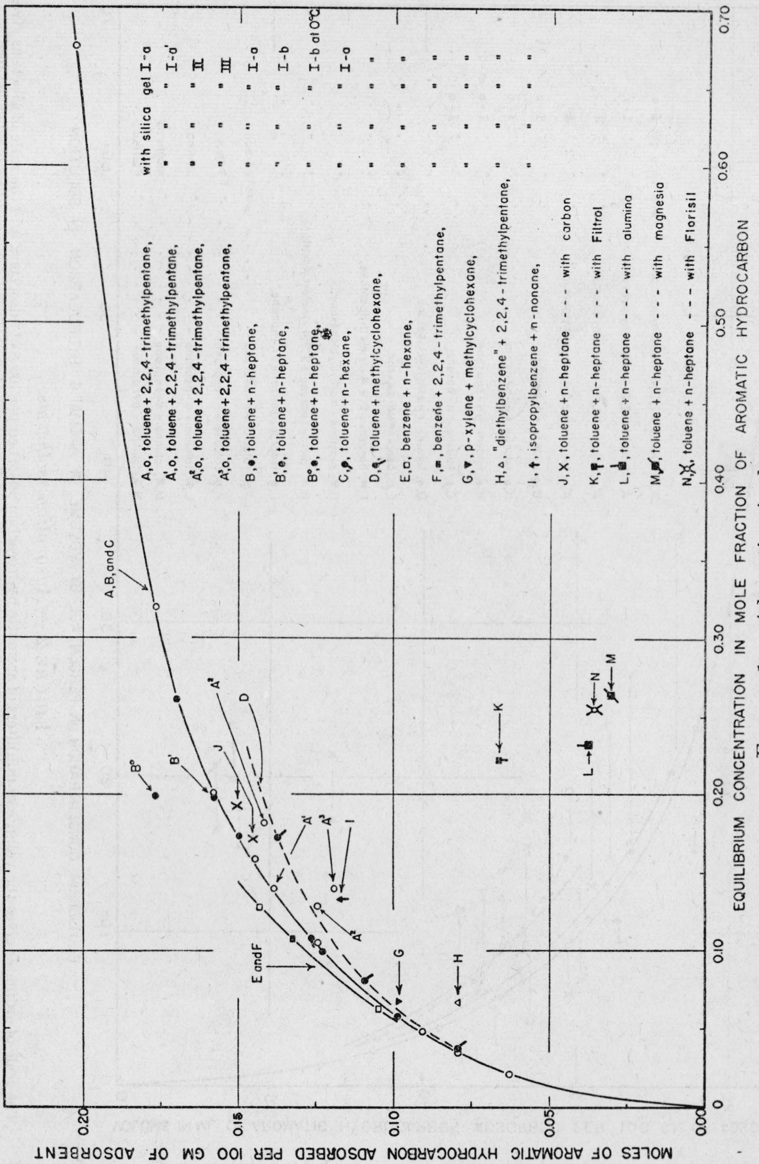

FIGURE 1.—*Adsorption isotherms.*

The scale of ordinates gives the moles of aromatic hydrocarbon adsorbed per 100 g of adsorbent, and the scale of abscissas gives the mole fraction of aromatic hydrocarbon in the solution. See text for explanation of the different samples of silica gel used.

The results of observations with carbon, alumina, magnesia, Filtrol, and Florisil, as the adsorbents, and represented, respectively, by the letters J, L, M, K, and N for solutions of toluene and *n*-heptane, are also shown in figures 1 and 2. These results were obtained from experiments performed at 25° C, in which a known weight of adsorbent was shaken with the solution until equilibrium was attained and the amount adsorbed was computed from the amount of solution and its change in concentration.[7]

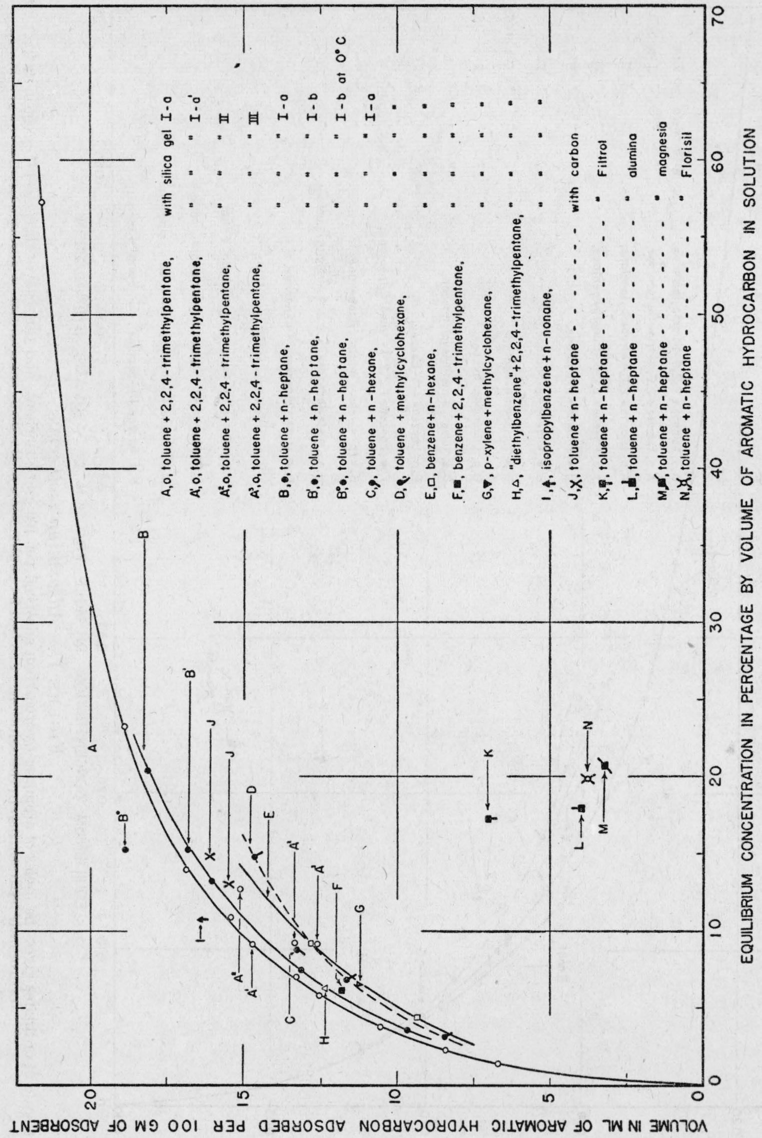

FIGURE 2.—*Adsorption isotherms.*

The scale of ordinates gives the volume in milliliters of aromatic hydrocarbon adsorbed per 100 g of adsorbent, and the scale of abscissas gives the percentage by volume of aromatic hydrocarbon in the solution. See text for explanation of the different samples of silica gel used.

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[7] Experiments performed in this manner with silica gel as the adsorbent gave results which, though somewhat less precise, were in substantial agreement with those from the filtration experiments. To avoid unduly complicating figures 1 and 2 these results are not included.

2. EFFECT OF TEMPERATURE ON THE AMOUNT OF AROMATIC HYDROCARBON ADSORBED

The effect of temperature on the amount of aromatic hydrocarbon adsorbed may be noted by comparing the points B° and B′ in figures 1 and 2, which refer to experiments performed on the same solution at 0° C and at 28° C, respectively. The amounts of aromatic hydrocarbon adsorbed per 100 g of silica gel at 0° C and at 28° C are 16.26 and 14.51 g, respectively, for this solution, which contains 15.23 percent by volume of toluene. This is a change of about 0.4 percent per degree for this concentration.

3. VARIATION IN THE COMPOSITION OF THE PARAFFIN AND NAPHTHENE HYDROCARBONS IN THE SOLUTION

When, as in figure 1, the moles of aromatic hydrocarbon adsorbed are plotted with respect to the concentration of aromatic hydrocarbon in mole fraction, a single curve may be used to represent the data for any of the paraffin hydrocarbons with a given aromatic hydrocarbon. Thus, the observations for solutions A, B, and C, which represent toluene with 2,2,4-trimethylpentane, *n*-heptane, and *n*-hexane, respectively, fall substantially on a single curve. Also, the observations for solutions E and F, representing benzene with 2,2,4-trimethylpentane and *n*-hexane, respectively, fall on a single curve. The observations for solutions of toluene with methylcyclohexane fall on a separate curve, D, which is somewhat below that for toluene with the paraffin hydrocarbons.

Since, in the separation process, it is convenient to work with volumes, the results are plotted in figure 2 in terms of the volume of aromatic adsorbed with respect to its concentration in percentage by volume.

4. VARIATION IN THE COMPOSITION OF THE AROMATIC HYDROCARBONS IN THE SOLUTIONS

The observations on solutions E, F, G, H, and I involve aromatic hydrocarbons other than toluene. When expressed as in figure 1, in terms of the moles of aromatic hydrocarbons adsorbed with respect to the concentration in mole fraction, the results show that the number of moles of aromatic hydrocarbon adsorbed decreases as the molecular weight of the aromatic hydrocarbon is increased. When expressed as in figure 2, in terms of the volume of aromatic adsorbed with respect to the concentration in percentage by volume, the results show that the variation in the volume adsorbed, for different aromatics, is comparatively small, and depends to some extent on the structure of the individual aromatic hydrocarbons.

5. COMPARISON OF VARIOUS ADSORBENTS

Several lots of silica gel [8] were used for these observations. Lots I–a and I–a′ were stabilized at the normal temperature and were of 28- to 200- and 28- to 42-mesh size, respectively. Lot I–b, although delivered to the laboratory at a later date than was I–a, was from the

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[8] See footnote 5.

same manufactured batch. Lot II was prepared in the same way as lots I–a and I–b but was from another manufactured batch. Lot III was of 28- to 200-mesh size but was stabilized at higher than the normal temperature.

The observation on solution B′ was made with lot I–b, and is in accord with the rest of the observations for the B series, which were made with lot I–a. The observation for solution A′, which was made with lot I–a′, is in accord with the rest of the observations for the A series, which were made with lot I–a, and shows that these two lots of different particle size have substantially the same adsorptive capacity. The observations represented by the points A^2 were made with lot II, and the points fall substantially below the curve for the rest of the A series, which indicates a lower adsorptive capacity. The observation on solution A^3 was made with lot III. The point A^3 falls well below the curve for the A series, and indicates that the adsorptive capacity of the silica gel stabilized at the higher temperature is less than that of the material stabilized at the normal temperature. It may be noted, however, that because the apparent density of the silica gel stabilized at the normal temperature is less than that of the other, the adsorptive capacities, per unit volume, do not differ greatly.

The points J, L, M, K, and N represent the results of observations with solutions of toluene in *n*-heptane when carbon, alumina, magnesia, Filtrol, and Florisil, respectively, were used as adsorbents.[9]

By a comparison of the points J, K, L, M, and N with curve B, it is evident that of these adsorbents, and for the systems under investigation, only carbon has an adsorptive capacity which approaches that of silica gel. However, the apparent density of activated carbon is less than that of silica gel, and, on a volume basis, its adsorptive capacity is substantially less than that of silica gel.

V. ESTIMATION OF THE AMOUNT OF SILICA GEL REQUIRED FOR A GIVEN LARGE-SCALE SEPARATION

Before an estimate can be made of the quantity of silica gel required to separate a given solution, it is necessary to know the concentration of aromatic hydrocarbon and the amount of aromatic hydrocarbon absorbed per unit mass of adsorbent from a solution of the given concentration. The aromatic content of the solution may be determined from a preliminary small-scale experiment, in which a portion is filtered through a standard quantity of silica gel [11]. From the volume of aromatic-free filtrate produced in this experiment and the concentration of aromatic hydrocarbon in the original solution, the amount of aromatic hydrocarbon adsorbed per gram of adsorbent can also be determined.

It is also necessary to determine experimentally the amount of displacing liquid required to wash the adsorbent completely free from the original paraffin-naphthene mixture and carry it into the filtrate (see section VIII–1).

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[9] The identifying characteristics of these adsorbents are: Columbia Activated Carbon, Grade F, size 20 to 48 mesh, Carbide & Carbon Chemicals Corp., New York, N. Y.; Activated Alumina, Grade A, size 80 to 300 mesh, Aluminum Ore Co., East St. Louis, Ill.; Adsorptive Powdered Magnesia No. 2641, impalpable powder, California Chemical Co., Newark, Calif.; Filtrol (prepared commercial fuller's earth) X–215, M–162, size 60 to 100 mesh, special lot supplied by G. Calingaert, of the Ethyl Gasoline Corp., for this experiment; Florisil (prepared commercial fuller's earth), analytical adsorbent, 60 to 100 mesh, Floridin Co., Warren, Pa.

The estimation of the amount of silica gel required for the separation of a simple binary mixture of an aromatic and a paraffin hydrocarbon, using as a displacing liquid another paraffin hydrocarbon, is made in the following manner: As stated in section III, the displacing liquid, in addition to substituting itself for the paraffin originally present, causes a downward movement of the equilibrium zone. In the ideal case involving no mixing of the displacing liquid and the paraffin hydrocarbon of the original solution, the column would be divided into three zones: a zone at the top containing only the displacing liquid; a second zone in which the adsorbed aromatics are in equilibrium with those in the displacing liquid; and a third zone containing only the original paraffin. The minimum quantity of adsorbent required would be that quantity which would just allow the original paraffin to pass completely from the column but would not allow any of the liquid from the second zone to pass out of the column. If the displacing liquid simply forces the solution ahead of it, without any mixing between it and the original solution, and if the break between the equilibrium zone and the aromatic-free portion ahead of it is infinitely sharp, the theoretical minimum quantity of adsorbent is given by the equation

$$y=\frac{n_a}{Q_a}=\frac{n_s x_a}{Q_a}. \tag{1}$$

Here n_a is the number of moles of aromatic hydrocarbon in the solution, Q_a is the adsorptive capacity of the adsorbent in moles of aromatic hydrocarbon per gram of adsorbent for the given concentration of aromatic hydrocarbon, y is the number of grams of adsorbent, n_s is the number of moles of original solution, and x_a is the mole fraction of aromatic hydrocarbon.

The ideal case just described does not represent the actual situation accurately, because in practice there is some mixing between the displacing liquid and the original solution. Furthermore, the amount of the original paraffin or naphthene that is actually adsorbed must be desorbed.[10] For these reasons it is necessary to pass an additional amount of the displacing liquid through the column to wash out the original paraffin completely and to carry it into the filtrate.

To estimate the total quantity of adsorbent required, the process may be regarded as taking place in a series of steps. In the first step, the quantity of adsorbent required to adsorb the aromatic hydrocarbons from the original solution may be computed. Similarly, in each succeeding step there may be computed the quantity of adsorbent which is necessary to adsorb the aromatic hydrocarbons from the displacing liquid required in the preceding step. The quantity of adsorbent required in the first step is that given by the following equation, which is equation 1 converted to a volume basis:

$$y=\frac{V_s c_a}{Q_{va}} \tag{2}$$

Here V_s is the volume of the solution, c_a is the volume fraction of aromatic hydrocarbon in the solution, and Q_{va} is the adsorptive capacity in volume of aromatic hydrocarbon per gram of adsorbent.

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[10] See footnote 6.

If b is the volume of displacing liquid required per gram of adsorbent to remove the original paraffin completely from the first step, then

$$\frac{V_s c_a}{Q_{va}} b$$

is the volume of displacing liquid required in the first step. If c_a' is the concentration in volume fraction of aromatic hydrocarbon in the displacing solution,

$$\frac{V_s c_a}{Q_{va}}\left(\frac{b c_a'}{1-c_a'}\right)$$

is the volume of aromatic hydrocarbon to be adsorbed. If Q_{va}' is the adsorptive capacity of the adsorbent for a solution of the concentration c_a', the quantity of adsorbent required in the second step is

$$\frac{V_s c_a}{Q_{va}}\left[\frac{c_a'}{Q_{va}'}\left(\frac{b}{1-c_a'}\right)\right].$$

The total quantity of adsorbent required for all steps is

$$y=\frac{V_s c_a}{Q_{va}}\left[1+\frac{c_a'}{Q_{va}'}\left(\frac{b}{1-c_a'}\right)+\frac{c_a' c_a''}{Q_{va}' Q_{va}''}\left(\frac{b}{1-c_a'}\right)\left(\frac{b}{1-c_a''}\right)+\cdots\right] \tag{3}$$

Assuming that $c_a'=c_a''=c_a'''= \ldots$ and that $Q_{va}'=Q_{va}''=Q_{va}'''= \ldots$, and substituting k for c_a'/Q_{va}', there is obtained

$$y=\frac{V_s c_a}{Q_{va}}\left[1+k\left(\frac{b}{1-c_a'}\right)+k^2\left(\frac{b}{1-c_a'}\right)^2+\cdots\right]=\frac{V_s c_a}{Q_{va}}\left[\frac{1}{1-\frac{kb}{1-c_a'}}\right]$$

$$=\frac{V_s c_a}{Q_{va}}\left[\frac{1-c_a'}{1-c_a'-kb}\right]. \tag{4}$$

In determining values to be used for k and b, it is desirable to consider separately the case of solutions with greater than 20-percent aromatic content from the case of those with less, for the reasons indicated below.

With pentane as the displacing liquid and with the natural rate of flow obtained, using well-packed silica gel of 28 to 200 mesh, the aromatic content of the displacing liquid is usually less than about 15 volume percent for all concentrations of the original solution above about 20 volume percent. To be safe, however, c_a' may be taken as 0.20 and the corresponding value 0.18 taken for Q_{va}', so that $k=c_a'/Q_{va}'$ becomes about 1.1. In addition to the simple volume displacement of the original solution, the displacing liquid must also desorb and substitute itself for any of the original paraffins and naphthenes which have been adsorbed. The quantity of displacing liquid required for this purpose depends on the equilibrium between the displacing liquid and the original paraffin and naphthene, and on how closely this equilibrium is approached in the desorption process. This in turn depends on the rate of filtration. With pentane as the displacing liquid, and with the natural rate of flow obtained with well-packed silica gel of 28 to 200 mesh, an allowance of 0.35 to 0.40 ml of pentane per gram of silica gel usually suffices to remove the original paraffins and naphthenes and to carry them into the filtrate (see section VIII–1). That is to say, b may be taken as equal to 0.35 ml/g. Substituting the values for k, b, and c_a' in equation

5 for all solutions with an aromatic content greater than about 20 volume percent, the quantity of silica gel required becomes

$$y=2\frac{V_s c_a}{Q_{va}}. \tag{5}$$

For original solutions containing less than about 20 volume percent of aromatic hydrocarbon, the difference between the concentration of aromatics in the original solution and in the displacing liquid (*n*-pentane) is much less than for solutions containing more than about 20 percent by volume of aromatic hydrocarbon, and in the absence of any better method for estimating the concentration of aromatic hydrocarbon in the displacing liquid, c'_a may be taken as equal to c_a, and Q'_{va} may be taken as equal to Q_{va}. Thus for solutions containing less than about 20 volume percent of aromatic hydrocarbons, the required quantity of silica gel is

$$y=\frac{V_s c_a}{Q_{va}}\left[\frac{1-c_a}{1-c_a-kb}\right]. \tag{6}$$

It should be emphasized that equations 5 and 6 will give approximately the quantity of silica gel required only for silica gel of 28 to 200 mesh, in well-packed columns of comparatively narrow diameter (2.5 to 5 cm). With columns of wide diameter the rates of flow at various distances from the periphery are likely to differ appreciably. Thus the boundaries of the zones will not be substantially normal to the walls of the column but may be concave, convex, or irregular in shape. A greater quantity of adsorbent will therefore be required. For silica gel of larger particle size, with which the rate of flow (when not controlled) is rapid, a greater volume of displacing liquid will be required, and the concentration of aromatic hydrocarbons in the displacing liquid may be considerably below the values given in this section.

VI. APPARATUS AND MATERIAL

1. THE ADSORPTION TUBE

The only apparatus specifically required for the adsorption method is a cylindrical tube of a volume sufficient to hold the quantity of adsorbent required for the given separation. The ratios of length to diameter of the tubes prepared in this laboratory are generally not less than 30 to 1. The adsorption column may be made out of any material that will not react with the hydrocarbons or the displacing or desorbing liquids. Some arrangement for retaining the adsorbent within the column must also be provided. In the case of the Pyrex glass columns used in this laboratory, the adsorbent is retained with a small plug of glass wool fitted into the bottom of the adsorption column, which is drawn down and sealed to a tube of smaller dimensions. It is desirable to include a stopcock in the small tube at the bottom of the column, so that the flow of filtrate may be interrupted when it is desired to change the receiver. In the filtration process, there is a rise in temperature due to the heat of adsorption, and it is desirable to prevent loss by evaporation by refrigerating the receiver. Precautions should also be taken to prevent loss by evaporation at the top of the column, as by venting through a capillary tube if the operation is performed at atmospheric pressure.

If it is desired to reactivate the adsorbent in the column used for the adsorption, the column should preferably be constructed of some metal such as stainless steel. In this case, additional equipment for maintaining the column at the desired temperature, for introducing steam and air or an inert gas and for condensing the excess desorbing liquid must be provided.

2. THE ADSORBENT

Any solid adsorbent which selectively adsorbs aromatic hydrocarbons may be used. Practically, however, it is desirable that the adsorbent have as large an adsorptive capacity per unit volume as possible, in order that the size of the adsorption column may be kept at a minimum. For this particular work, silica gel appears to be better than the other adsorbents tested (section IV–5). The 28- to 200- and the 28- to 42-mesh sizes of silica gel have substantially the same adsorptive capacity (section IV–5), but the rate of filtration (unless auxiliary control is provided) is many times greater with the silica gel of larger particle size. As already mentioned, the more rapid the rate of filtration the greater the volume of pentane required, and the greater the tendency to produce irregularly shaped zones. For these reasons, the 28 to 200 mesh appears preferable for laboratory work, whereas for large-scale operation, where time is a major consideration, a larger size may be more desirable.

3. THE DISPLACING LIQUID

Any paraffin or naphthene hydrocarbon in the liquid phase with a boiling point well removed from that of the material under investigation may be used to displace the original paraffins and naphthenes. With hydrocarbons of the gasoline fraction, *n*-pentane, *n*-butane, or *n*-propane may be used. When the method is used on a laboratory scale, *n*-pentane is the most convenient displacing liquid.

4. THE DESORBING LIQUID

Almost any polar liquid which does not react with the hydrocarbons, the adsorbent, or the material of the adsorption tube may be used to desorb the aromatic hydrocarbons. For work on a laboratory scale, it is desirable that the desorbing liquid dissolve and carry the aromatic hydrocarbons in solution into the filtrate. It is also desirable that the desorbing liquid be completely soluble in water and preferentially less soluble in the hydrocarbon, in order that its removal from the hydrocarbon may be readily effected by extraction with water. Methanol, acetone, and water have been used as desorbing liquids in this laboratory.

Water readily effects the desorption of aromatic hydrocarbons, but they remain entrapped within the macroscopic interstices of the adsorbent. In this case, if the aromatics are not too high-boiling, they can be removed by the passage of steam. While this procedure may have some merit for large scale operation, it is inconvenient for laboratory work. Acetone also desorbs aromatic hydrocarbons, but a number of washings with water are required to remove completely the acetone from the hydrocarbon portion.

Methanol is more satisfactory than water or acetone, since it dissolves the aromatic hydrocarbons and since a single extraction with water removes it almost completely from the hydrocarbon portion.

VII. PROCEDURE

The fraction by volume of aromatic hydrocarbon, c_a, and the volume of aromatic hydrocarbon, Q_{va} adsorbed per gram of adsorbent are determined for the petroleum fraction or mixture of hydrocarbons to be separated. The quantity of adsorbent required for the separation of a given volume of solution is then estimated (section 5), and this is charged into an adsorption column of the proper size. The mixture of hydrocarbons is allowed to filter through the adsorbent, and, as soon as the last of this material has entered the top layer of adsorbent, *n*-pentane is added and allowed to filter. It is desirable to use a substantial excess of pentane over that quantity which was estimated as sufficient to remove all the paraffins and naphthenes and which was used to estimate the quantity of silica gel required. As soon as the requisite amount of pentane has passed through the top layer of adsorbent, methanol is added to the column and allowed to filter. Fractions of filtrate are collected and their refractive indices determined. In figure 3 the refractive indices of the fractions resulting from a typical experiment are plotted with respect to the total volume of filtrate. This figure shows the decrease in refractive index from

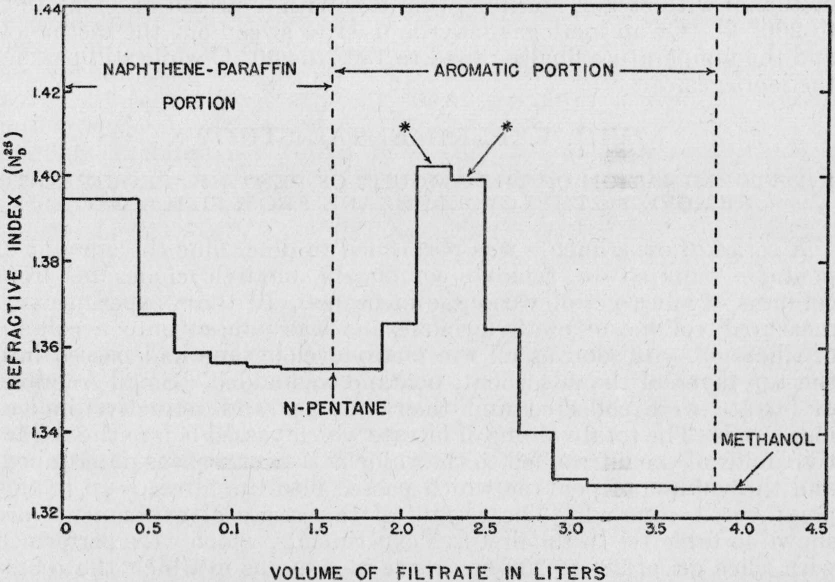

FIGURE 3.—*Results on the quantitative separation of the aromatic hydrocarbons in a known mixture of 17 pure hydrocarbons.*

The scale of ordinates gives the refractive indices of the fractions of filtrate, and the scale of abscissas gives the total volume of filtrate.

that of the original naphthene-paraffin portion to that of pentane, then the increase as aromatic hydrocarbons appear in the filtrate, and finally, when all the aromatic hydrocarbons have been removed, the decrease nearly to the refractive index of methanol (see section VIII–3).

If a definite portion with the refractive index of *n*-pentane is not obtained, the operation is a failure and should be repeated with more pentane, or more silica gel, or both.

The naphthene-paraffin portion is distilled to remove the *n*-pentane. The aromatic portion is extracted once with water to remove the methanol and then distilled to remove *n*-pentane. If a small amount of methanol remains after the extraction, it will be removed as an azeotropic distillate with the *n*-pentane.[11]

At the end of an operation, the adsorbent contains only methanol and is readily reactivated. This can be done by sweeping out the methanol with steam, and following this with a stream of air at 180° to 200° C. Or an inert gas may be used to sweep out the methanol, and the temperature finally raised to 180° to 200° C while still passing the inert gas.

VIII. EXPERIMENTAL STUDY

1. DETERMINATION OF THE AMOUNT OF PENTANE REQUIRED TO REMOVE METHYLCYCLOHEXANE FROM SILICA GEL

A series of experiments was performed to determine the amount of pentane required to remove completely methylcyclohexane from columns of silica gel of various dimensions. In these experiments a measured volume of methylcyclohexane was poured onto a column of silica gel. As soon as all the methylcyclohexane had passed into the top layer of the adsorbent, pentane was added. Small fractions of filtrate were collected and their volumes and refractive indices measured. The total volume of filtrate which passed before the refractive index of the filtrate fell to the value of *n*-pentane was determined, and the volume of pentane which passed into the filtrates up to this point was computed. The results of this series of experiments are shown in table 1. In the first five experiments, which were performed with silica gel of 28- to 200-mesh size in columns in which the diameter varied between 4.27 and 1.03 cm and the ratio of length to diameter between 11.7 and 70.2, substantially the same ratio of pentane to silica gel, namely 0.28 to 0.33 ml per gram, was required. In experiments 6 and 7, silica gel of 28- to 42-mesh size was employed and a much higher ratio of pentane to silica gel was required, namely 0.60 to 0.76 ml per gram. The larger quantity required in this case is associated with more rapid filtration. In experiments 8 and 9, a stopcock at the bottom of the column was used to reduce the speed of filtration to a small fraction of the free rate. In this case the amount of pentane was reduced, and the values 0.35 and 0.48 per ml per gram were obtained. Unless the adsorption column has been provided with equipment to control the rate of filtration and unless the influence of this factor has been evaluated for the apparatus in question, adsorbent of 28- to 200-mesh size should be used for laboratory work.

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[11] It is interesting to note that methanol displaces a small amount of water from the silica gel in the column, and this causes the appearance of two phases in certain of the filtrate fractions. The fractions indicated with asterisks in figure 3 contained two phases. (See also section VIII–3.)

TABLE 1.—*Amount of pentane required to remove methylcyclohexane*[a] *from silica gel*

Experiment number	Particle size of silica gel	Mass of silica gel	Volume of pentane	Dimensions of the column			Ratio: volume of pentane to mass of silica gel
				Length	Diameter	Ratio: $\frac{\text{length}}{\text{diameter}}$	
	Mesh	*g*	*ml*	*cm*	*cm*		*ml/gm*
1	28 to 200	31.08	9.00	50	1.03	48.5	0.29 ±0.03
2	28 to 200	65.10	18.7	50	1.52	32.9	.29 ± .03
3	28 to 200	170.4	56	50	2.43	20.6	.33 ± .03
4	28 to 200	485.0	154	50	4.27	11.7	.32 ± .03
5	28 to 200	108.4	30.5	99	1.41	70.2	.28 ± .03
6	28 to 42	29.9	18	50	1.03	48.5	.60 ± .05
7	28 to 42	62.9	8.3	50	1.52	32.9	.76 ± .05
8[b]	28 to 42	63.0	22	50	1.52	32.9	.35 ± .03
9[b]	28 to 42	158.8	76	50	2.43	20.6	.48 ± .03

[a] A sufficient amount of methylcyclohexane was used in each experiment, so that the first portion of the filtrate contained only methylcyclohexane.

[b] In experiments 8 and 9, the rate of filtration was reduced below that of free filtration by means of a stopcock at the bottom of the adsorption column.

2. RECOVERY OF METHYLCYCLOHEXANE-HEPTANE MIXTURE FROM SILICA GEL

A mixture of 365.3 g (505.9 ml), consisting of 47.33 percent by weight of *n*-heptane and 52.67 percent by weight of methylcyclohexane, was added to a column containing 2,000 g of silica gel.[12] This column of silica gel was 120 cm long and 5 cm in diameter. Pentane was added after all the heptane-methycyclohexane mixture had passed into the top layer of the adsorbent. After 1,125 ml of filtrate had been collected, the refractive index of the filtrate had fallen to that of *n*-pentane. (This corresponds to 619 ml of pentane in the filtrate, or 0.31 ml of pentane per gram of silica gel.) The pentane was separated from the heptane-methylcyclohexane mixture by distillation in an appropriate column, and the heptane-methylcyclohexane mixture siphoned from the still pot into a cold bottle. The still was washed with methanol and the heptane-methylcyclohexane recovered from the washings by removal of the methanol by extraction with water. The total mass of heptane-methylcyclohexane recovered was 362.9 g. The loss was 2.4 g, which corresponds to 0.7 percent of the original mass.

3. DETERMINATION OF THE AMOUNT OF METHANOL REQUIRED TO REMOVE TOLUENE AND "DIETHYLBENZENE" FROM SILICA GEL

Three filtration experiments were performed with 200 g of silica gel [13] in a 60-cm column 2.3 cm in diameter. In the first and second experiments, 15 ml of "diethylbenzene" and 15 ml of toluene, respectively, were added and allowed to percolate into the gel, and then methanol was added. In the third experiment, methanol alone was allowed to filter through the adsorbent. The results of these experiments are shown in figure 4, in which curves I, II, and III refer, respectively, to experiments 1, 2, and 3, and in which the refractive

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[12] No. 859528–2000, see footnote 5.

[13] No. 859528–2000, see footnote 5.

indices of the individual filtrate fractions are plotted with respect to the volume of filtrate.

Curves I and II show that after a volume of filtrate of about 30 ml was obtained the refractive index of the filtrate fell nearly to the refractive index of methanol. The fractions representing that portion of the filtrate beyond 30 ml were free from hydrocarbon. The failure to reach the refractive index of methanol immediately after the re-

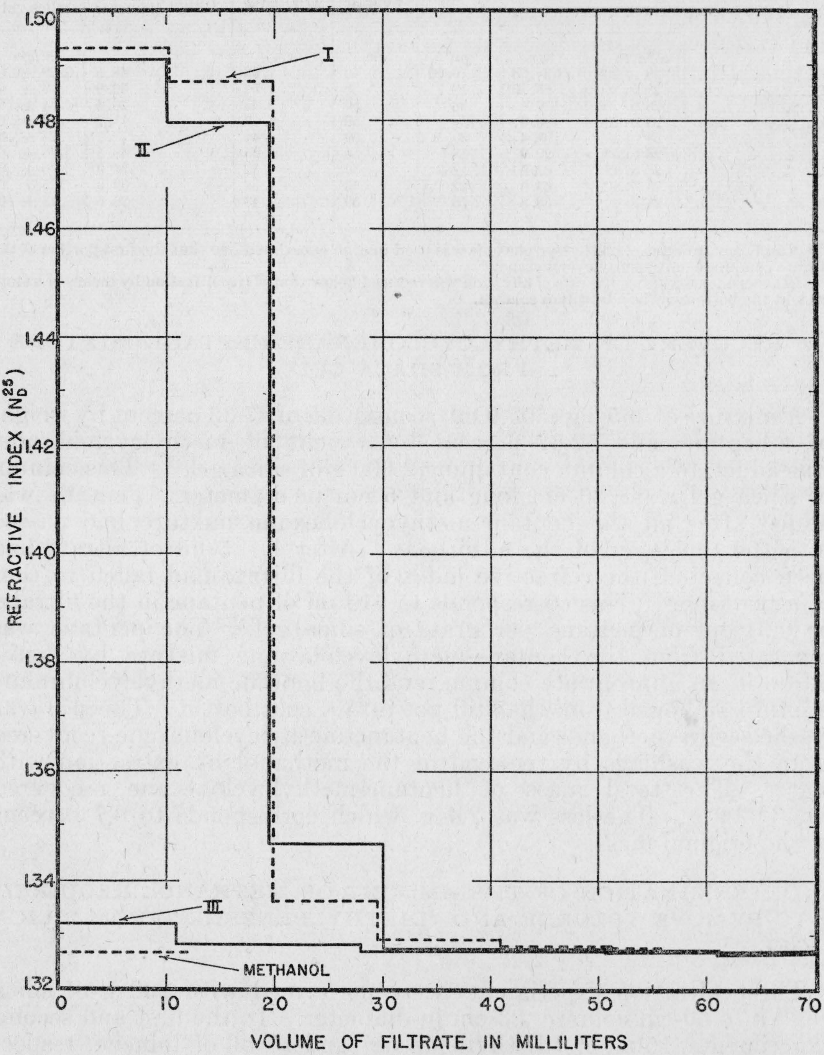

FIGURE 4.—*Results of experiments on the recovery of toluene and "diethylbenzene" from silica gel.*

The scale of ordinates gives the refractive indices of the frations of filtrate and the scale of abscissas gives the total volume of filtrate. Curves I and II refer to experiments in which "diethylbenzene" and toluene, respectively, were added to the adsorbent column and then methanol was added. Curve III refers to an experiment in which only methanol was added.

moval of the hydrocarbon was found to be due to the continued displacement of small amounts of water from the silica gel. The presence of water was evident in the second fractions from the first two experiments, in which two phases were observed. In experiment 3, in which methanol alone was filtered, the refractive index (n_D^{25}) of the first fraction was 1.3319, which may be compared with the values 1.3266 and 1.3325 for methanol and water, respectively. In general, fractions with refractive indices below about 1.329 are unlikely to contain hydrocarbon, but should in any case be tested by extraction with water.

4. RECOVERY OF TOLUENE FROM SILICA GEL

A weighed amount of toluene (approximately 15 ml) was added to a column containing 200 g of silica gel.[14] After all the toluene had passed into the top layer of silica gel, methanol was added. The filtrate was allowed to run into a weighed 125-ml separatory funnel containing 30 ml of water. After 30 ml of filtrate had collected, the total volume of water in the separatory funnel was brought to 85 ml, the separatory funnel was shaken and placed in a centrifuge, and the mixture centrifuged. The bulk of the aqueous solution was drawn off, the mixture again centrifuged, and the remainder of the aqueous solution drawn off. In this manner a sharp separation between the phases was obtained, and the walls of the separatory funnel were entirely free from water globules. The recovered toluene was weighed. The results of three such experiments, together with those of three blank experiments in which the same volumes of toluene, methanol, and water were shaken together in a separatory funnel and the toluene recovered and weighed, gave the following results: Loss of toluene in both adsorption and recovery, mean of three experiments, 0.35 ± 0.05 percent by weight; loss of toluene in the blank experiments, mean of three experiments, 0.14 ± 0.02 percent by weight; loss of toluene in the adsorption process alone, mean 0.21 ± 0.05 percent by weight.

5. SEPARATION AND RECOVERY OF A KNOWN MIXTURE OF AROMATIC HYDROCARBONS FROM A KNOWN MIXTURE OF NAPHTHENES AND PARAFFINS

A mixture of the 17 known hydrocarbons shown in table 2 was prepared quantitatively by weight. This mixture (about 2.3 liters in volume) was divided into four nearly equal portions, each of which was filtered through 4,200 g of silica gel,[15] contained in a 250-cm column, 5 cm in diameter. This was followed by the addition of 1,800 ml of *n*-pentane and then by the addition of methanol. The refractive indices of the fractions resulting from the filtration of one of these portions are shown in figure 3. The naphthene-paraffin portions and the aromatic portions from the four experiments were combined to make one naphthene-paraffin portion and one aromatic portion. The pentane and methanol were removed from each portion as described in section VII, and the remainder of each portion was distilled separately in a column of high separating efficiency. The values of boiling point and refractive index of the fractions of distillate as a function of the

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[14] No. 859528-2000, see footnote 5.
[15] No. 859528-2000, see footnote 5.

volume and mass showed in each case excellent accord with the known composition of the material.[16] An indication of the completeness of the separation and of the material lost during the processes of adsorption and distillation is given in table 3.

The percentages of the total product recovered constituted by the aromatic portion and by the naphthene-paraffin portion recovered are 35.97 and 64.05, respectively, whereas the corresponding percentages representing the composition of the original material are 35.69 and 64.31. That is to say, the percentage by weight of the aromatics in the material recovered differs from that in the material charged by only 0.3 percent.

TABLE 2.—*Data on the 17 pure hydrocarbons used in making up the known "test" mixture*

Compound	Boiling point	Mass		
		Paraffin	Naphthene	Aromatic
	°C	g	g	g
2-Methylpentane	60.3	57.79		
n-Hexane	68.7	97.39		
Benzene	80.1			86.46
Cyclohexane	80.7		158.90	
n-Heptane	98.4	132.97		
Methylcyclohexane	100.9		141.47	
Toluene	110.6			94.10
n-Octane	125.7	105.64		
Ethylcylohexane	131.8		62.17	
Ethylbenzene	136.2			87.40
p-Xylene	138.4			89.44
m-Xylene	139.1			88.94
o-Xylene	144.4			73.80
n-Nonane	150.8	110.46		
Isopropylbenzene	152.4			104.77
n-Propylcyclohexane	156		115.19	
n-Decane	174.0	144.03		
Total		648.28	477.73	624.91

TABLE 3.—*Results on the quantitative separation and recovery of the aromatic hydrocarbons in a known mixture of 17 pure hydrocarbons*

Material	Charged		Recovered		Loss	
	Mass	Percentage	Mass	Percentage	Mass	Percentage
	g		g		g	
Aromatics	624.91	35.69	617.71	35.28	7.20	0.41
Paraffins+naphthenes	1,126.01	64.31	1,099.66	62.80	26.55	1.51
Total	1,750.92	100.00	1,717.37	98.08	33.55	1.92

IX. DISCUSSION OF THE SEPARATION OF HYDROCARBONS BY ADSORPTION

The method of separating aromatic hydrocarbons from naphthenes and paraffins by adsorption has the following desirable features: (a) the simple type of the apparatus required; (b) the quantitative nature of the separation which can be obtained; and (c) the applicability of the method to material of very wide boiling range, such as the entire gasoline or kerosine fractions of petroleum.

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[16] A report on the analysis of the fractions from this distillation is given elsewhere [15].

The separation of aromatic hydrocarbons from naphthenes and paraffins is only one of several separations which, by the choice of proper conditions, can be accomplished by the use of the adsorption method. Winterstein and coworkers [3, 5] have shown that various polynuclear aromatic hydrocarbons may be separated from each other. These authors have found that for aromatic hydrocarbons consisting of condensed rings arranged linearly those with the greater number of rings are the more strongly adsorbed, while for other aromatic hydrocarbons consisting of condensed rings, the arrangement of the rings influences the order of their adsorption. Thus they found that naphthacene, with four rings per molecule arranged linearly, is more strongly adsorbed than 1,2-benzpyrene with five rings per molecule arranged nonlinearly. The presence of olefinic linkages also influences the order of adsorption; in general the greater the number of olefinic linkages, other things being equal, the more strongly the substance is adsorbed [3]. Observations made in this laboratory show that monoolefins are selectively adsorbed from naphthenes and paraffins of corresponding molecular weight [7, 11]. The results of these investigations may be summarized by the statement that, with certain limitations on the type and configuration of the aromatic rings, and with the restriction to compounds of approximately equal molecular weights, the arrangement of hydrocarbons in order of their decreasing adsorbability is as follows: 4-, 3-, 2-, and 1-ring aromatic hydrocarbons, diolefins, monoolefins, naphthenes, and paraffins.

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