*p*H of 3.41–3.43, and the colloidal sol thus produced flocculates before the theoretical ratio of $3OH^-$ to $1In^{+++}$ is attained.

2. At 25° a mole ratio of $0.84OH^-$ to $1In^{+++}$ must be reached before indium hydroxide can be precipitated from sulfate or nitrate solutions. From a chloride solution, this ratio is only 0.02.

3. On the assumption that the ultimate precipitate is indium hydroxide, the solubility product constant at 25° is calculated to be of the order of 10^{-33} and the corresponding water solubility 2.2×10^{-9} g. moles of indium hydroxide per liter (slightly higher from chloride solutions).

4. In the temperature range 10 to 40°, the solubility of hydrous indium hydroxide in water trebles.

5. Variation in the initial indium ion concentration between 0.00500 and 0.02466 *M* has no effect on the *p*H at which precipitation begins.

6. When indium hydroxide is treated with excess sodium or potassium hydroxide, at least part of the indium hydroxide is peptized to a negative sol.

URBANA, ILLINOIS RECEIVED APRIL 21, 1941

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Chromatography of Solutions Containing a Single Solute

BY HAROLD G. CASSIDY AND SCOTT E. WOOD

The theory of chromatography proposed by Wilson[1] is based, as he has pointed out, on the assumption of instantaneous equilibrium between the solution and the adsorbent, and on the assumption that the effects of diffusion can be neglected. The theory might therefore be called one of ideal chromatography. It seemed of interest to compare the theory in a simple case with data which had been obtained in this Laboratory. Quite good agreement was found, on the whole, between experiment and theory in this comparison.

The outstanding predictions about the adsorbed zone according to the theory are that the leading and following edges of the zone will be infinitely sharp and that the adsorbed material will be in equilibrium with the solution at the original concentration, c_0. If the adsorption isotherm is written as $Q = Mf(c)$, where Q is the moles of adsorbed material per cm. length of column, M, the grams of adsorbent per cm. length of column, and c, the equilibrium concentration, then the length of the zone, x, in cm., after V cc. of solution have passed into the column is given by $x = Vc_0/(\alpha c_0 + Q_0)$. Here α is the interstitial volume per cm. length of the column, and $Q_0 = Mf(c_0)$. The rate in cm. per cc. of liquid passed into the column at which the edges of the zone move down the column when the same solvent is used for developing is given by $c_0/(\alpha c_0 + Q_0)$.

In these experiments the form of the zone was determined by analyzing the solution passing from the column. Sufficient solution of concentration c_0 was used so that the front edge of the zone attained the bottom of the column of adsorbent before all of the solution had been passed into the column. Under these conditions, and with the assumption that the molal volume of the solution is equal to the molal volume of the pure solvent, the volume, V_1 (Table I), of liquid which must pass through the column in order to bring the front edge of the zone to the bottom of the adsorbent is lQ_0/c_0, where l is the length of the column of adsorbent. The total volume, V_2, which must pass through the column to completely remove the entire zone of adsorbed substance is $V_0 + V_1$, where V_0 is the volume of the original solution.

Experiment.—The materials were the same as have been described in previous papers.[2] Solutions of lauric acid in petroleum ether were passed at room temperature through tubes, 1.3 cm. in diameter, packed with Darco G-60 carbon. In each case 1 g. of carbon was used, and in all cases but "b" (Table I) 1 g. of filter aid (which does not adsorb[2b]) was mixed with the carbon. Fresh solvent was added to the column just when the last of the lauric acid solution passed into the adsorbent. The liquid passing from the column was collected in fractions of varying sizes, depending on the exigencies of the experiment. The solvent was then evaporated from each fraction and the residue weighed.

Data for the chromatography of solutions of lauric acid of several concentrations are shown in Table I and Fig. 1. In the figure the solid lines show the experimental results; the broken lines indicate those predicted by the theory using the adsorption isotherm given below. It was ob-

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[1] J. N. Wilson, THIS JOURNAL, 62, 1583 (1940).

[2] H. G. Cassidy, *ibid.*, 62, 3073 (1940); (b) 62, 3076 (1940).

served that the rate of flow increased as the development of the column progressed.

TABLE I

Curve, Fig. 1	Acid, millimole	Solvent, cc.	Rate of flow, 100 cc. (min.)	Length of column, cm.	V_1, cc.
a	3.5	100	30	4.9[a]	51.7
b	6.0	200	35	2.5	57.3
c	5.0	200	23	4.7	64.9
d	4.0	200	25	4.9	75.3
e	3.0	200	28	5.2	91.5

[a] Assumed, not measured.

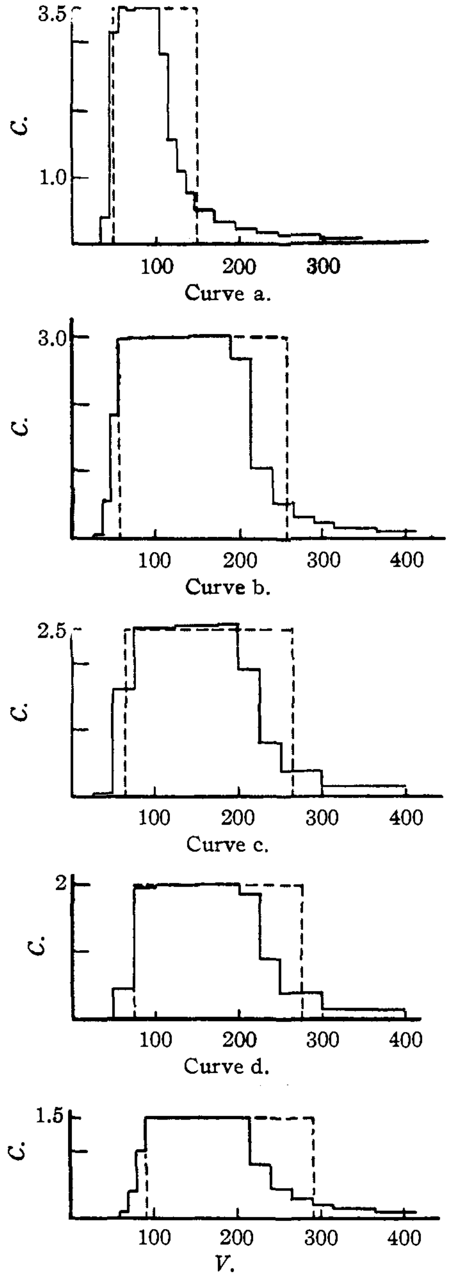
Discussion of Results.—The adsorption isotherm (2a, Fig. 1) of lauric acid was fitted to Freundlich's equation giving

$$\log q = 0.324 \log c + 0.081$$

In this equation q is the millimoles of acid adsorbed per gram of carbon in equilibrium with a solution containing c millimoles of acid per 100 cc. of solution. An equation of the Langmuir type did not give a good fit. The volatility of the petroleum ether made it impossible to obtain results of very great accuracy, but they are sufficiently accurate for these purposes. The assumption that the molal volume of the solution and that of the pure solvent are the same is also sufficiently accurate.

It can be seen from the curves that good agreement between experiment and theory is shown at the front of the zones. Lauric acid begins to appear in the percolate at about the calculated points. Each zone has a fairly sharp face over which the concentration of the percolate rises rapidly to that of the original solution. It is evident that the approach to equilibrium at the leading edge of the zone is quite rapid. As Wilson has pointed out, the effects of diffusion are probably not of much importance in this region. The slight irregularities in the horizontal portions, noticed in most of the curves, are due to evaporation of the solvent.

Agreement between experiment and theory is not good, however, for the rear portion of the zones. It is here that the assumption of instantaneous equilibrium shows itself most clearly in disagreement with the facts. The rate of approach to equilibrium on desorption must be very slow. It is probable that better agreement with the theory would have been obtained if the rates of flow had been slower. However, it is thought that there would still have been a discrepancy at the rear of the zones. Such tailing off has been observed in columns which flowed at the rate of 100 cc. in five hours. The effects of diffusion would be much larger when the rate of flow is slow.



Curve a.

Curve b.

Curve c.

Curve d.

Curve e.

Fig. 1.—Chromatography of lauric acid on a carbon column. C is the concentration of the percolate in millimoles of lauric acid per 100 cc. of liquid for each portion collected, V, the volume of the total percolate in cc. The solid lines show the experimental results. The broken lines indicate those predicted by the theory.

As has already been pointed out, these experiments were so arranged that the leading edge of the zone reached the bottom of the adsorbing material before all of the original solution had passed into the adsorbent. At this stage the entire column of adsorbent was in equilibrium with the solution of concentration c_0, and the zone was coextensive with the column. The situation would ordinarily be different under the normal conditions of chromatography, such as in the separation of two or more substances. Here the length of the zone should be small compared with the length of the column of adsorbent. In such cases the concentration of the emerging liquid might not reach c_0 and, therefore, there would not be a flat portion of the curve. Instead, diffuseness of both the leading and following edges of the zones would be expected, the effect being greater the slower the approach to equilibrium. Examples of such curves will be found in a later paper dealing with the separation of fatty acids by means of adsorption analysis. Experiments of the "liquid chromatogram" type might be useful in the study of rates of adsorption and desorption.

Summary

It has been shown in a simple case that the chromatography of a solution containing a single solute is in reasonable agreement with the theory.

New Haven, Connecticut Received July 11, 1941

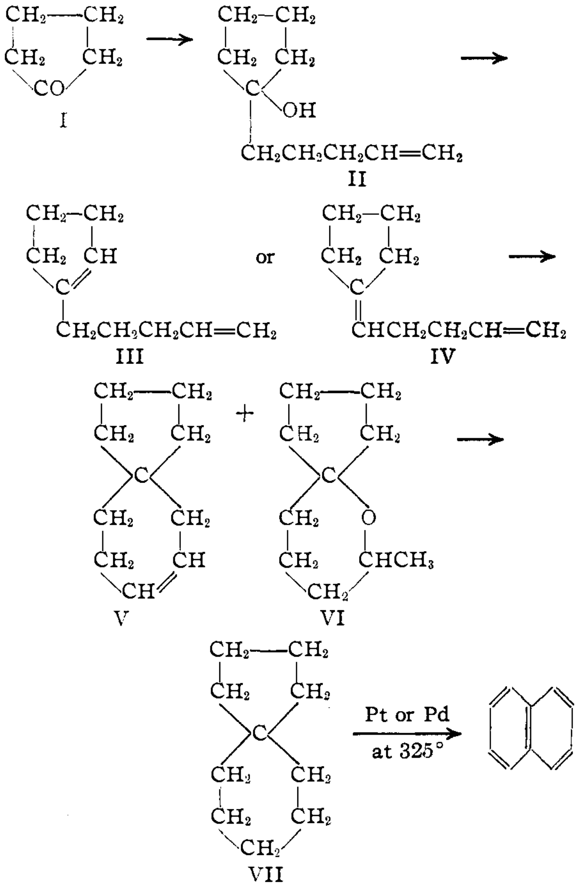
[Contribution from the Noyes Chemical Laboratory, University of Illinois]

The Preparation and Dehydrogenation of Spirodecane and 3-Methylspirodecane[1]

By C. S. Marvel and Lester A. Brooks

The possible formation of spirans as by-products in the cyclization of dienynes and the dehydrogenation of spirocyclohexane-1,1'-indane[2] to give phenanthrene and anthracene has led us to study the preparation and dehydrogenation of some simple spirans. The present work describes a new synthesis of spirodecane and 3-methylspirodecane based on the method which Hibbit and Linstead[3] have devised for the synthesis of 1,1-dimethyl-3-cyclohexene. Some studies of the dehydrogenation of these two spirans with platinum, palladium and selenium also have been made.

Condensation of cyclopentanone (I) with the Grignard reagent from 1-bromo-4-pentene gave the tertiary alcohol (II) which on distillation with a trace of iodine yielded 1-(Δ^1-cyclopentenyl)-4-pentene (III) or its isomer (IV). Cyclization of this diene with sulfuric acid produced spirodecene (V) contaminated with an oxygen containing by-product which was presumably a cyclic ether (VI). The exact position of the double bond in the spirodecene (V) was not determined. Reduction of the mixture of the spirodecene and the ether with hydrogen over Raney nickel[4] gave a mixture of spirodecane (VII) and the ether from which the latter could be removed by washing with concentrated sulfuric acid. The properties of our spirodecane are compared in Table I with its proper-



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[1] This is the twelfth communication on the cyclization of dienynes. For the previous article see, This Journal, 63, 2218 (1941).

[2] Levitz, Perlman and Bogert, *J. Org. Chem.*, 6, 105 (1941).

[3] Hibbit and Linstead, *J. Chem. Soc.*, 470 (1936).

[4] Covert and Adkins, This Journal, 54, 4116 (1932).