portions of boiling water, and the original filtrate and wash waters evaporated to 100 ml. This solution was acidified (pH 3) with hydrochloric acid and the organic acids extracted with tributyl phosphate (three 20-ml. portions). The acids were recovered from the phosphate solution by extraction with dilute potassium hydroxide, which was then evaporated to dryness. The residue was taken up in a little water, acidified with hydrochloric acid (total volume 10 ml.) and extracted with ether. Evaporation of the ether under reduced pressure also removed the trifluoroacetic acid (b. p. 72.4°). The residual crude caproic acid was converted to the potassium salt (0.9 g.) and then to the anilide, m. p. 93.5–94.5°, which did not depress the m. p. of known caproic anilide.

(b) **Hydrogenation.**—An 0.542 g. sample of the olefin in alcohol over Raney nickel absorbed the calculated amount of hydrogen at room temperature and atmospheric pressure, in sixty minutes, and absorption then ceased.

(c) **Bromination.**—To a standardized solution of bromine in chloroform (0.00217 mole of bromine) there was added 0.5298 g. (0.00319 mole) of olefin, and the solution was allowed to stand on the desk in a glass stoppered flask. A similar sample of the bromine–chloroform solution (without olefin) was also allowed to stand. At the end of eleven days both solutions were titrated with 0.1055 N thiosulfate solution. The blank required 24.98 ml., the solution containing olefin required 10.90 ml. From this it can be determined that the olefin used up 23.3% of the amount of bromine required to saturate the double bond.

The olefin (0.547 g., 0.00329 mole) and 25.0 ml. of an aqueous bromine–potassium bromide solution (0.4012 N) were allowed to stand in a glass-stoppered flask in the dark for forty hours. The remaining bromine required 84.5 ml. of 0.1055 N thiosulfate, indicating that the olefin consumed 17% of the calculated amount of bromine.

(d) **Nucleophilic Reagents.**—A mixture of 1,1,1-trifluoro-2-octene (7.4 g.) and excess diethylamine (14 ml.) was refluxed for seven days. From the amount of diethylamine (84%) and olefin (93%) recovered little or no addition could have occurred.

Equimolar amounts of trifluoroöctene and sodiomalonic ester were refluxed in benzene for twenty-five hours. Most of the olefin and malonic ester were recovered unchanged, and no addition product could be found.

A mixture of equimolar amounts of trifluoroöctene and sodium methoxide in dry methanol was refluxed for two hours. The solvent was removed by distillation and the residue taken up in aqueous hydrochloric acid. The aqueous solution gave a positive test for fluoride ion, but no definite products could be isolated.

1,1,1-Trifluoro-2-octene was refluxed for twenty-four hours with an excess of t-butylmagnesium chloride in ether. Most of the olefin (82%) was recovered on working up the reaction mixture in the usual way.

Summary

1. The reaction of aliphatic Grignard reagents with esters of trifluoroacetic acid has been investigated. With the larger Grignard reagents (n-propyl and n-hexyl) only the secondary alcohol was obtained; with ethylmagnesium bromide both the secondary and the tertiary alcohol were formed.
2. 1,1,1-Trifluoro-2-octanone was reduced to the secondary alcohol by propylmagnesium bromide and no addition occurred.
3. When trifluoroacetyl chloride was treated with dihexylcadmium in benzene solution a low yield (22%) of the expected ketone was obtained. When the reaction was carried out in ether, the only product isolated was the tertiary alcohol, trifluoromethyldihexylcarbinol.
4. 1,1,1-Trifluoro-2-octene and 1,1,1-trifluoro-2-pentene were prepared by pyrolysis of the corresponding secondary acetates.
5. Some addition reactions of 1,1,1-trifluoro-2-octene have been investigated.

NOTRE DAME, INDIANA RECEIVED APRIL 27, 1950

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA, NO. 1402]

An Adsorption System for the Fractionation of Nitrocellulose with Respect to Molecular Weight[1,2]

BY MARVIN C. BROOKS[3] AND RICHARD M. BADGER

This paper describes a study of the adsorption of nitrocelluloses on starch from several binary solvent mixtures. The results indicate the feasibility of the molecular weight fractionation of nitrocellulose by elution chromatographic procedures. One chromatographic experiment is described which demonstrates the application.

The fractionation of high polymers by chromatographic methods has been attempted by several workers. The first report to the best of our knowledge, was made in 1936 by Mark and Saito[4] who demonstrated that cellulose acetate was adsorbed on blood charcoal selectively on a molecular weight basis. Levi and Giera[5] also studied the adsorption of cellulose acetates on charcoal. More recently Landler[6] has reported on the adsorption of GR-S, Perbunan, and Vistanex on charcoal from mixtures of toluene and methanol. Claesson[7] has made a preliminary report on the use of the chromatographic method of frontal analysis. Fractionation of a high polymer by this method does not appear practical, though some information can be obtained regarding molecular weight distribution.

The investigations just mentioned appear to show that charcoal is not likely to be a very useful

---

(1) This paper is based on work supported by the Bureau of Ordnance and done under contract with the Office of Naval Research. Contract N6-ori-102, Task Order VI.

(2) Presented before the High Polymer Forum at the Atlantic City meeting of the American Chemical Society, September 19, 1949.

(3) General Laboratories, U. S. Rubber Co., Passaic, N. J.

(4) H. Mark and G. Saito, *Monatsh.*, **68**, 237 (1936).

(5) G. R. Levi and A. Giera, *Gazz. chim. ital.*, **67**, 719 (1937).

(6) I. Landler, *Compt. rend.*, **225**, 629 (1947).

(7) S. Claesson, *Arkiv Kem. Mineral. Geol.*, **26A**, No. 24 (1949).

adsorbent for the fractionation of cellulose derivatives by elution chromatography. It seems evident that the adsorption is not adequately reversible, and the attainment of equilibrium appears to be slow. The fact that starch has been widely used for chromatographic separations of a variety of substances of moderate molecular weight suggested its possible applicability in the fractionation of nitrocellulose. Our earlier attempts to use this material were, however, abortive which led us temporarily to abandon its further investigation and to develop a fractionation procedure based on partition between two phases.[8] We have recently discovered that the earlier failures resulted at least in part from inadequate preparation of the adsorbent. By the use of appropriate pretreatment and of suitable solvent systems we have been able to obtain absorption which is reversible and rapidly attained, and can be controlled within rather wide limits. This control depends upon the addition of suitable co-solvents to the basic solvent which in all cases was acetone. The adsorption can be increased by non-polar substances such as cyclohexane, but is decreased by hydrogen bonding solvents such as methanol.

Experimental

Materials.—Two varieties of starch have been used: corn starch manufactured by the Argo Products Refining Co. and potato starch manufactured by Morning Star-Nicol Inc. and distributed by the Amend Drug and Chemical Co. It is necessary that the starch be dried completely before being used in an adsorption experiment. Following Stein and Moore,[9] who used starch in chromatographic separations of amino acids, we have treated the starch used in our experiments with a solution of 8-hydroxyquinoline to complex with and thereby make possible the removal of trace impurities of metals. Approximately 1 mg. of 8-hydroxyquinoline was used for each gram of starch. It was added to a slurry of starch in water and a dark green color of the complexes appeared immediately. After settling, the supernate was poured off and the starch washed by reslurrying and again removing the supernate. The volume of distilled water was approximately 10× the volume of the starch; the process was repeated 8×. The wet starch was then placed on a sintered glass filter and about 8× its volume of acetone was passed through the starch bed. Finally, the starch was placed under vacuum for one week. When attempts were made to use shorter drying times, adsorption results were not reproducible, indicating that traces of moisture still remained.

The nitrocelluloses were unfractionated commercial polymers: NC No. 17, 10.98% N, $[\eta] = 5.1$, $M_w = 164{,}000$, obtained from cotton linters; NC No. 18, 10.96% N, $[\eta] = 0.71$, $M_w = 23{,}000$, obtained from cotton linters; NC No. 19, 10.93% N, $[\eta] = 1.62$, $M_w = 52{,}000$, obtained from cotton linters; NC No. 39, 12.52% N, $[\eta] = 5.3$, $M_w = 145{,}000$, obtained from wood pulp; NC No. 41, 11.99% N, $[\eta] = 0.85$, $M_w = 24{,}500$, obtained from wood pulp. The weight average molecular weight values which are given were not determined by direct methods but have been estimated from viscosity data by use of relations given by Doyle, *et al.*[10] Likewise, the intrinsic viscosity values for NC No. 17 and NC No. 39 were estimated from determined values of 20 and 22 Hercules smokeless seconds, respectively, again by relations of Doyle, *et al.*[10] Although the results of direct measurements would have been preferred, the requirements of accuracy in the present studies did not seem to justify the work of making the additional measurements. All of the intrinsic viscosity values given above apply to the butyl acetate solvent system.

Methods.—The adsorption isotherms which are reported were determined from a set of adsorption experiments carried out in a manner similar to that employed in the partition experiments described in a previous paper.[8] To obtain adsorption equilibrium, the tubes containing the adsorbent and solution were allowed to shake for ten minutes at 180 cycles per minute, which is shown to be adequate by data given below.

The column used for the elution chromatographic experiment was 30 mm. inner diameter and 40 cm. long. The development was initiated with a weak developer, *viz.*, a co-solvent mixture of cyclohexane and acetone relatively rich in cyclohexane; thereafter, the concentration of cyclohexane was decreased gradually and development was completed with an acetone–methanol co-solvent mixture. The rate of flow of the developer was controlled by adjusting the height of the head of the developing solvent; and on the average was 12 ml. per hour. The elute was collected in fractions of 50–100 ml. and the concentrations of nitrocellulose within each fraction were determined colorimetrically.[8] Successive elute fractions were then combined and concentrated by vacuum distillation over a hot water bath to give "combined" fractions of approximately equal size suitable for characterization. The method of molecular weight characterization was a diffusion method developed especially for this application.[11]

Results and Discussion

The Effect of Molecular Weight Variation on the Extent of Adsorption of Nitrocellulose on Starch.—In Figs. 1 and 2 are shown the adsorption isotherms for nitrocelluloses of three different molecular weights on two different types of starch. The polymers had nitrogen contents very nearly equal. It is evident that the adsorption depends significantly upon molecular weight and increases with increasing molecular weight.

The Effect of Starch Type on the Adsorption of Nitrocellulose on Starch.—Figures 1 and 2 were purposely drawn on the same scale to allow the convenient comparison of the adsorption properties of corn starch and potato starch. It is evident that the adsorption is stronger for corn starch, but the curvature of the adsorption isotherm is also greater. To obtain the optimum separation by a chromatographic method it is important that the adsorption isotherm be linear or nearly so. A curvature of the isotherm causes a "tailing" of the fraction in the elute. Consequently, potato starch appears to be preferable to corn starch for use in chromatographic separations. It is likely that the greater adsorption on the corn starch is due simply to the smaller size of the corn starch particles compared to those of potato starch.

The Rate of Equilibration of Nitrocellulose Adsorption on Starch.—The necessity of rapid adsorption and desorption if a system is to be adapted to elution chromatographic methods

---

(8) M. C. Brooks and R. M. Badger, THIS JOURNAL, **72**, 1705 (1950).

(9) W. H. Stein and S. Moore, *J. Biol. Chem.*, **176**, 337 (1948).

(10) G. J. Doyle, G. Harbottle, R. M. Badger and R. M. Noyes, *J. Phys. Colloid Chem.*, **51**, 569 (1947).

(11) M. C. Brooks and R. M. Badger, *ibid.*, **52**, 1390 (1948).

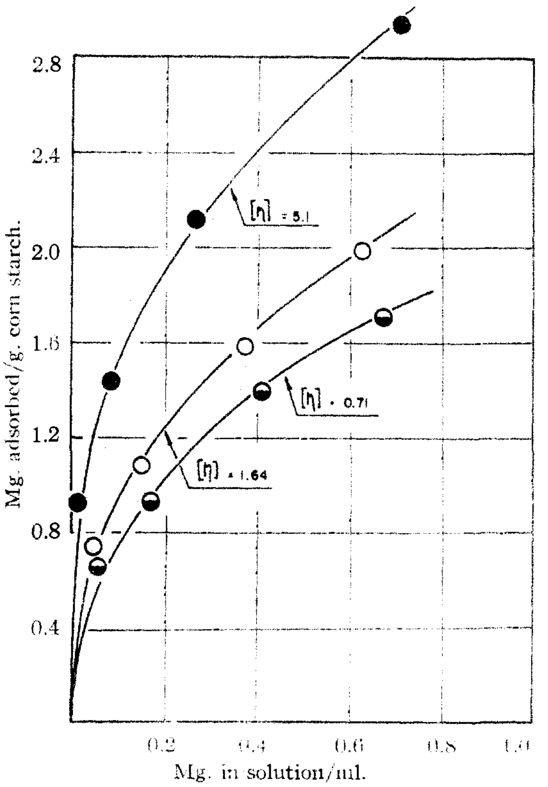

Fig. 1.—Adsorption isotherms of nitrocelluloses of several different molecular weights on corn starch. All adsorptions determined for system consisting of 1 g. corn starch suspended in 3 ml. cyclohexane and 4 ml. acetone: ●, NC No. 17; ○, NC No. 19; ◒, NC No. 18.

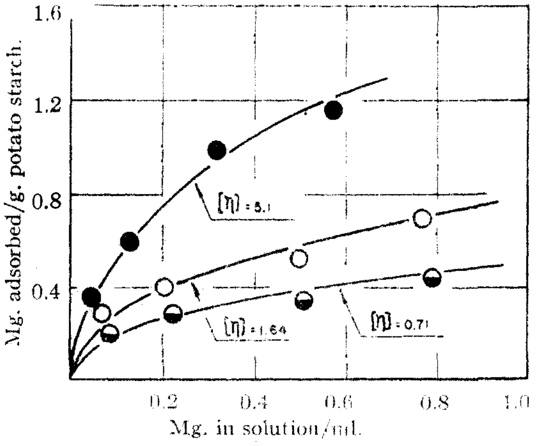

Fig. 2.—Adsorption isotherms of nitrocelluloses of several different molecular weights on potato starch, all adsorptions determined for system containing 2 g. potato starch suspended in 3 ml. cyclohexane and 4 ml. acetone: ●, NC No. 17; ○, NC No. 19; ◒, NC No. 18.

has been pointed out. In order to demonstrate that the rate of equilibration for the potato starch–acetone–cyclohexane system is rapid, adsorption isotherms have been determined by approaching equilibrium from both directions. It was found that ten minutes is adequate to obtain the same steady state independent of the direction of approach. The results are shown graphically in Fig. 3.

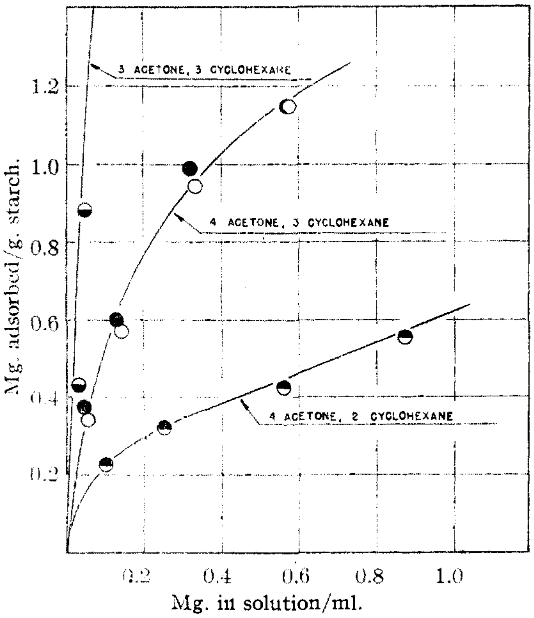

Fig. 3.—Adsorption isotherms of NC No. 17 indicating reversibility and speed of attaining equilibrium: ◒, 2 g. potato starch, 3 ml. acetone, 3 ml. cyclohexane, extent of adsorption after 10 min. shaking; ●, 2 g. potato starch, 3 ml. acetone, 3 ml. cyclohexane; 10 min. on shaker and then allowed to stand 2.75 hr., 1 ml. additional acetone added, extent of adsorption after 10 min. further shaking; ◓, 2 g. potato starch, 4 ml. acetone, 2 ml. cyclohexane, extent of adsorption after 10 min. shaking; ○, 2 g. potato starch, 4 ml. acetone, 2 ml. cyclohexane; 10 min. on shaker and then allowed to stand 2.75 hr., 1 ml. additional cyclohexane added, extent of adsorption after 10 min. further shaking.

The upper and lower curves represent the adsorption obtained from two different solvent mixtures on 2 g. of potato starch after ten minutes of shaking. After further standing, acetone and cyclohexane, respectively, were added to these systems in appropriate amounts to produce two new systems of the same composition. After ten minutes of shaking the adsorption is essentially identical in the two cases, as is shown by the points lying near the middle curve.

The Effect of Solvent Composition on the Extent of Adsorption of Nitrocellulose on Starch.—In Fig. 4 are shown representative isotherms giving the adsorption of a high molecular weight nitrocellulose, NC No. 17, on potato starch from a number of solvent mixtures. In all experiments the ratio of solvent to adsorbent was very nearly the same.

The addition of cyclohexane to acetone is seen greatly to increase the nitrocellulose adsorption. On the other hand, methanol considerably reduces

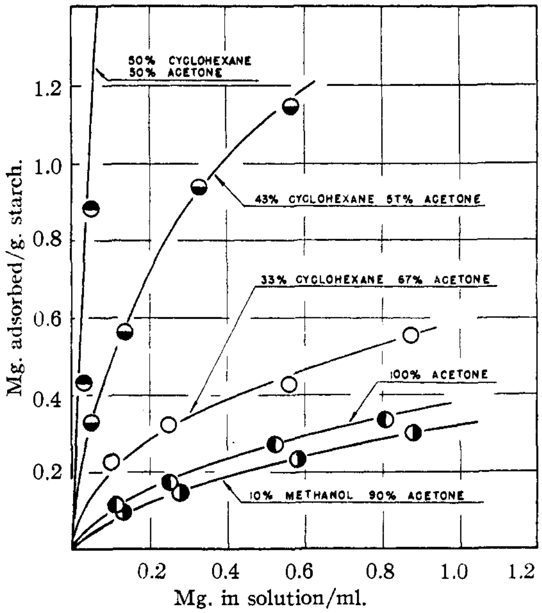

Fig. 4.—Adsorption isotherms of NC No. 17 showing effect of variations in solvent composition.

it. This may possibly result from the competition of solvent and solute for adsorption sites.

The effect of the addition of small amounts of alcohols and of water in reducing the extent of adsorption of nitrocellulose on starch is shown further in Table I. In all of the experiments here reported 2 g. of potato starch was shaken with 7 ml. of solvent mixture which initially contained 2.17 mg. of NC No. 17. It is particularly striking that small amounts of water, a good precipitant for nitrocellulose, cause essentially all of the nitrocellulose to go into solution.

TABLE I

THE EFFECT OF HYDROGEN BOND FORMING SOLVENTS IN DECREASING THE ADSORPTION OF NITROCELLULOSE ON STARCH

Volume per cent. of co-solvent	Ratio of nitrocellulose concentration in solution (mg./ml.) to amount adsorbed (mg./g. starch) Co-solvent with acetone		
	Ethanol	Methanol	Water
0.00	0.49	0.49	0.49
0.72			.56
1.43			.66
2.86			1.4
7.2	0.87	0.91	160
14.3	1.3	2.5	
28.6	3.2	7.5	

The Effect of Variation of the Nitrate Content of Nitrocellulose on the Extent of Adsorption on Starch.—Unfortunately nitrocellulose specimens having different nitrogen contents but exactly the same molecular weight were not available. Consequently the effect of degree of nitration on adsorption must be shown indirectly. In Fig. 5 the dashed isotherms refer to specimens having the same nitrogen content (10.95%) and different molecular weights. The solid curves refer to two specimens of higher nitration. It is quite evident that the latter specimens were adsorbed much less strongly than should be expected for nitrocelluloses of the same molecular weights but of 10.95% nitrogen content. Fractionation of a nitrocellulose with respect to molecular weight by the methods here discussed can clearly only be successful if the material is very homogeneous in nitration.

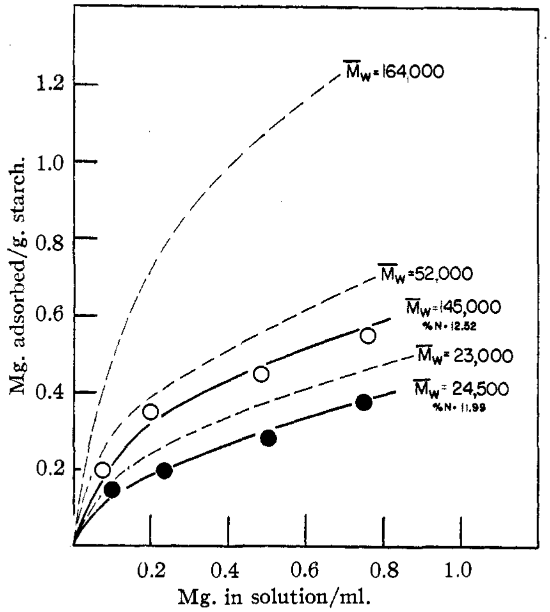

Fig. 5.—Adsorption isotherms of several nitrocelluloses showing the effect of variation of degree of nitration. Dashed isotherms are for nitrocelluloses of about 10.95% N (see Fig. 2). Solid isotherms are for nitrocelluloses of higher nitrogen content as indicated: ○, NC No. 39; ●, NC No. 41.

Elution Chromatographic Fractionation of Nitrocellulose.—A high molecular weight nitrocellulose, NC No. 17, has been fractionated by elution chromatographic methods using corn starch as the adsorbent. The high molecular weight polymer was chosen to furnish a critical test of the method. The choice of corn starch rather than potato starch was probably an unfortunate one but the chromatographic experiment was started before the studies reported above on the shapes of the adsorption isotherms for corn starch and potato starch systems had been completed, and the choice was based simply on the relative strengths of adsorption of nitrocellulose on the two types of starch.

It has been pointed out that sharp fractionation can be secured only if the adsorption isotherm over the concentration range obtaining in the column is essentially linear. For the system being considered, it was consequently necessary to stay in the low concentration range. Therefore, only 160 mg. of polymer was fractionated. In Table II are summarized the analytical data of the fractions obtained. Unfortunately, fraction II was destroyed in an accident during the vacuum distillation procedure for concentration. The diffusion constants reported are relatively low, and the method of measurement is not very sensitive in the low diffusion constant range. However, the trend of decreasing diffusion constant, *e. g.*, increasing molecular weight, with volume of solution eluting, certainly indicates that molecular weight fractionation did occur. Very roughly, the determined values of 8.0–4.4 for the diffusion constants in acetone correspond to intrinsic viscosities in butyl acetate of 2.8–7.3. The intrinsic viscosity of unfractionated NC No. 17 was 5.2.

Table II

Characterization of Fractions Obtained in an Elution Chromatographic Experiment

Combined fraction no.	Serial % of polymer eluted	Average composition[a] of developer	Diffusion constant, (cm.^{2} sec.$^{-1}$ × 10^7)
I	0–17.1	10 Cyclohexane	8.0
II	17.1–32.0	0	...
III	32.0–50.6	5 Methanol	6.0
IV	50.6–65.2	10 Methanol	5.3
V	65.2–76.5	15 Methanol	4.7
VI	76.5–91.7	25 Methanol	4.4

[a] Reported as the volume % of the co-solvent of acetone.

Summary

The absorption of nitrocellulose on starch from solutions of acetone admixed with several co-solvents has been studied. The extent of adsorption has been found to increase with molecular weight, to decrease with degree of nitration of the nitrocellulose, and to decrease as the hydrogen bonding character of the solvent mixture is increased. The rate of adsorption is high and the adsorption is reversible. A chromatographic experiment is reported which demonstrates that the dependence of the extent of adsorption on molecular weight makes possible the fractionation of nitrocellulose according to molecular weight.

Pasadena, California Received March 11, 1950

[Contribution from the University of Michigan]

The Adsorption of Aliphatic Amine Vapors by Silica Gel[1]

By F. E. Bartell and Donald G. Dobay[2,3]

Work in this Laboratory had shown that solids of an acidic nature, as silica, will preferentially adsorb from solution basic materials such as quinoline, etc.[4] It seemed probable that silica gel would serve as an active adsorbent for various amines and it further appeared probable that such adsorption would be of the chemisorption type. In that case it would be of interest to determine how well the theory of Brunauer, Emmett and Teller would apply. In the present investigation an attempt was made to extend earlier work but with the difference that adsorption would be caused to occur from the vapor phase. Adsorption isotherms at 25° were obtained using activated silica gel with diethylamine, *n*-butylamine and di-*n*-butylamine.

Experimental

Materials

The amines were of the highest commercial purity and were further purified by distillation from potassium hydroxide or from sodium through a column of ten theoretical plates. The middle fractions were collected over potassium hydroxide, each fraction having a boiling range of less than 0.1°. These were redistilled under reduced pressures. These twice distilled samples were found to have identical physical properties with those of the first distillates, indicating the absence of azeotropes. Before use the amines were redistilled directly into the sample tubes immersed in liquid air and sealed under vacuum to avoid contamination.

The silica gel was prepared by the method of Bartell and Fu[5] from redistilled silicon tetrachloride. It did not contain any chloride and left no residue after treatment with hydrofluoric acid. The specific area of this gel was found to be 320 sq. m. by the BET nitrogen adsorption method, using 16.2 sq. Å. as the molecular area of nitrogen. The results were highly consistent; values from six separate determinations deviated from the mean by no more than 1%. After one and one-half years the area still remained the same. The apparent density of this gel, determined by weighing the amount of mercury displaced, was found to be 0.653 g./ml. Assuming the density of the silica framework to be 2.2[6] an internal pore volume of about 1.1 ml./g. is indicated.

Apparatus.—The adsorption isotherms were determined gravimetrically by means of McBain–Bakr balances,[7] a sketch of the apparatus used is given in Fig. 1. It differs from previous designs in that a Stock valve (F) and a reference rod (D) were introduced. The former enabled convenient control of pressure in the adsorption chamber over long periods of time, and the latter served to correct for any alteration of the position of the adsorption chamber with respect to the cathetometer. There were no stopcocks between the liquid sample and the adsorbent. Any contaminants such as the stopcock and vacuum greases were eliminated by surrounding the trap P with

---

(1) The data in this paper are from a dissertation submitted to the Horace H. Rackham School of Graduate Studies by Donald G. Dobay in partial fulfillment of the requirements for the degree of Doctor of Philosophy, September, 1948.

(2) Holder of the Allied Chemical and Dye Corporation Fellowship, 1945–1946, 1946–1947.

(3) Linde Air Products Company, Tonawanda, New York.

(4) Benner and Bartell, "Fundamental Research on Occurrence and Recovery of Petroleum," published by American Petroleum Institute, 1943, p. 79.

(5) Bartell and Fu, *J. Phys. Chem.*, **33**, 676 (1929).

(6) Shapiro and Kolthoff, *J. Phys. and Colloid Chem.*, **52**, 1022 (1948).

(7) McBain and Bakr, This Journal, **48**, 690 (1926).