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.$^{-1}$ $\times 10^7$)
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

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[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).

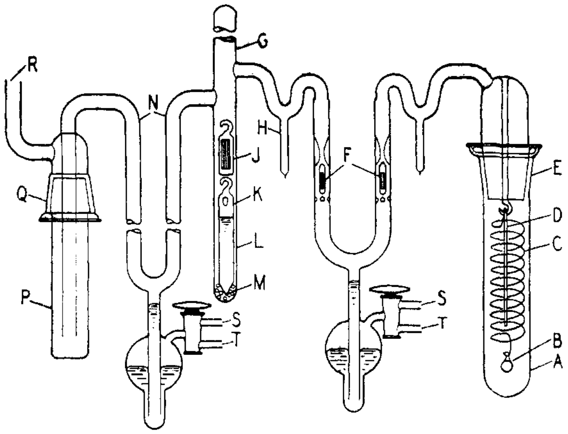

Fig. 1.—General sketch of the adsorption apparatus. An air thermostat (not shown) surrounded the adsorption chamber and spring (Parts A to E).

liquid air. Two quartz springs were used. The sensitivity of the first spring was 25.5 cm. per gram load, and that of the second 15.3. Typical sample loads were about 0.15 to 0.3 g. The second spring was housed in a separate chamber and was provided with a second Stock valve. Changes in the elongation of the springs were determined by a cathetometer which could be read directly to 0.01 mm. The temperature of the thermostat surrounding the adsorption chambers was controlled to ± 0.1°.

Treatment of the Gel.—After approximate weights of gel had been attached to the quartz springs, heaters were placed around the adsorption chambers and heating and evacuating started. The samples were brought to 200–215° and evacuation of 10^{-5} mm. or better was maintained for sixteen to twenty hours, the system being protected by liquid air traps at all times. The mercury cut-offs were raised while the samples were still hot. After cooling to room temperature the true weights of the gel were obtained from the elongations of the springs which had been calibrated previously. This treatment removed water and adsorbed gases and brought the samples to a uniform and reproducible condition. It has been shown by Bartell and Almy[8] that in driving off water from silica gel at 220°, only a very small amount of water was left after the first few minutes.

Data

The data from composite runs for the adsorption of amines by silica gel are shown in Figs. 2–4. For no point was the time of observation less than five hours, and in a few cases it was prolonged to over one hundred hours. A condensed form of the data, given in round numbers, interpolated from the smoothed curves, is given in Table I. It may be remarked that for the low pressure range the accuracy of the data depends primarily on the sensitivity of the spring, while for that pressure range within which the isotherms rise very rapidly the accuracy depends chiefly on the temperature control of the bath in which the liquid samples are immersed.

Discussion

All the isotherms obtained in this investigation have the following general characteristics. At relative pressures p/p_0 below 0.01, the curves rise very steeply. At about this pressure the isotherms exhibit a sharp change in slope and the rise becomes much more gradual so that the pressure must be increased fifty-fold or more in order to double the amount adsorbed at $p/p_0 \cong 0.01$. At relative pressures of about 0.5 the curves turn upward very sharply and the rate of increase does not slacken until p/p_0 reaches above 0.8.

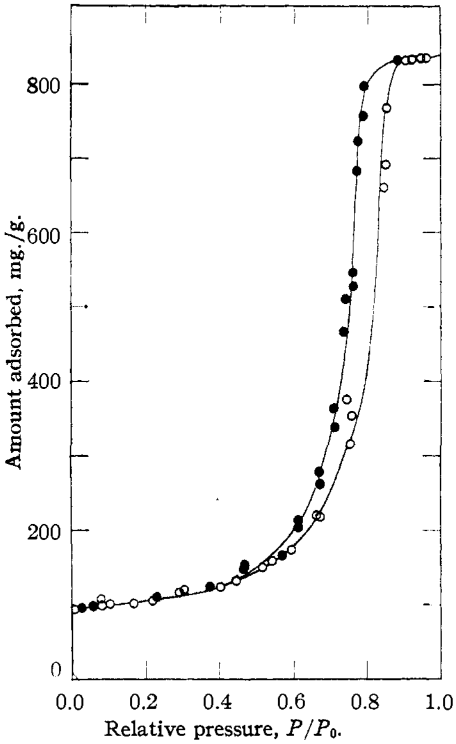

Fig. 2.—Isotherm for the adsorption of diethylamine by silica gel at 25°.

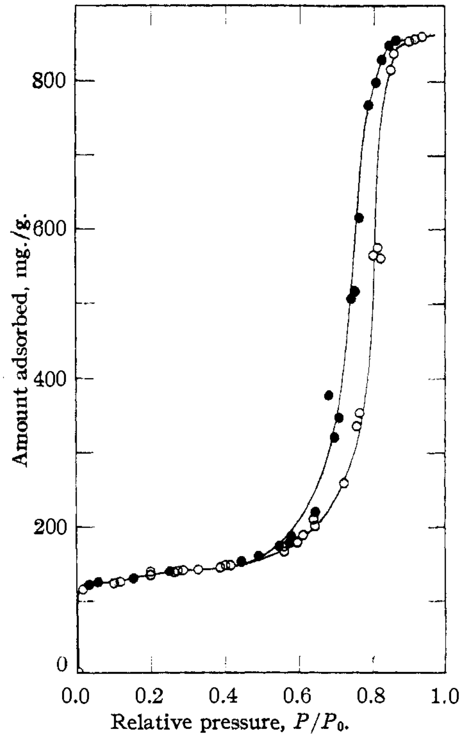

Fig. 3.—Isotherm for the adsorption of *n*-butylamine by silica gel at 25°: adsorption, ○; desorption, ●.

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[8] Bartell and Almy, *J. Phys. Chem.*, **36**, 475 (1932).

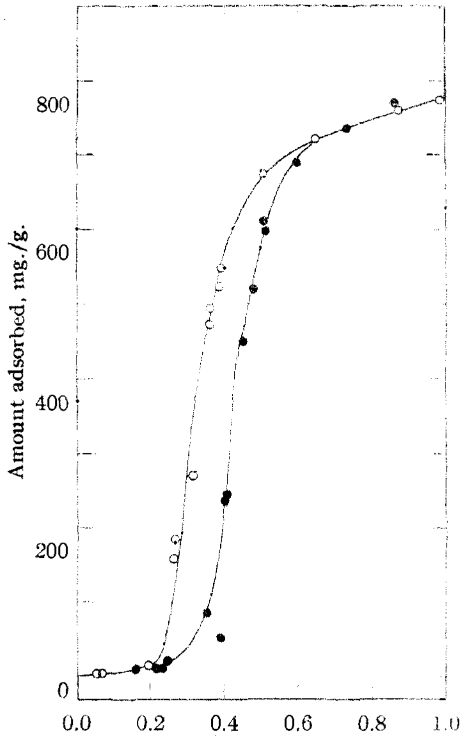

Fig. 4.—Isotherm for the adsorption of di-*n*-butylamine by silica gel at 25°: adsorption, ○; desorption, ●.

The rate of rise within this pressure range is much greater than has generally been reported in the literature. The extent of this rise is much greater than the initial rise at lower pressures. The major fraction of the amines is adsorbed by the gel within this pressure range. It may be noted that hysteresis also occurs within this pressure range. At relative pressures higher than about 0.9, the curves become almost horizontal and the adsorption and desorption isotherms coincide.

Low Pressure Region.—One surprising feature of these isotherms is the range of applicability of the simplified form of the BET equation. Usually, this equation is applicable within the relative pressure range of about 0.05–0.35. In the systems here studied, it holds only up to $p/p_0 \backsimeq 0.12$, but the lower limit is about $p/p_0 \backsimeq$ 0.002. Therefore, on the relative scale the range of applicability of the two-constant BET equation for these systems is about nine times greater than that for the systems hitherto investigated. This phenomenon may be accounted for as follows: The failure of the BET equation at very low pressures has been commonly attributed to the heterogeneity of the solid surface. If that were the case, the heat of adsorption of the first layer would have different values at different adsorption sites. Since the heat for purely physical adsorption is usually not high, the relative variation would be very large. This, then, would violate the assumption of a single E_1 value used in the derivation of the equation. If, on the other hand, due to the nature of the adsorbent and the adsorbate, the interaction between them is very strong, then the heat of adsorption of the first layer would be very high and its relative variation at different sites would become much less significant. The situation will then conform more closely to the assumption and, consequently, the range of applicability of the BET equation is extended to much lower pressures. Further evidence for this explanation will be presented in a later paper.

Table I

Condensed Absorption Isotherm Data

Relative pressure, p/p_0	Amount adsorbed, mg./g. Diethylamine	*n*-Butylamine	Di-n-butylamine
0.005	88	117	126
.01	91	118	128
.02	93	121	129
.03	94	123	131
.04	95	124	132
.05	96	126	133
.10	100	132	140
.15	103.5	135	147
.20	106	138	154
.25	110	141	160
.30	115	145	170
.35	119	148	180
.40	126	151	192
.45	134	155	210
.50	144	162	232
.55	157	171	275
.60	173	189	340
.65	200	210	450
.70	245	243	600
.75	310	292	800
.80	415	475	885
.85	725	800	892
.90	823	850	896
.95	830	858	897
(1.00)	831	860	898

If it is assumed that the BET equation can be legitimately applied to the present systems, and for this we can see no objection, then $(x/m)_m$, the amount of amines required to form a complete monolayer, can be obtained from the BET plot (Fig. 5). The values $(x/m)_m$ and the corresponding relative pressures are shown in Table II.

Table II

Amine	$(x/m)_m$ in mg./g.	Corresponding relative pressure	n
Di-ethyl	90	0.008	2.5
Di-*n*-butyl	126.3	< .01	2.3
n-Butyl	119.4	.011	2.0

These relative pressures are unusually low. Evidences for the validity of the above $(x/m)_m$ values will be given in a future communication. Considering the nature of the adsorbent and the adsorbates and the fact that the completion of the monolayer occurs at such low pressures, it might

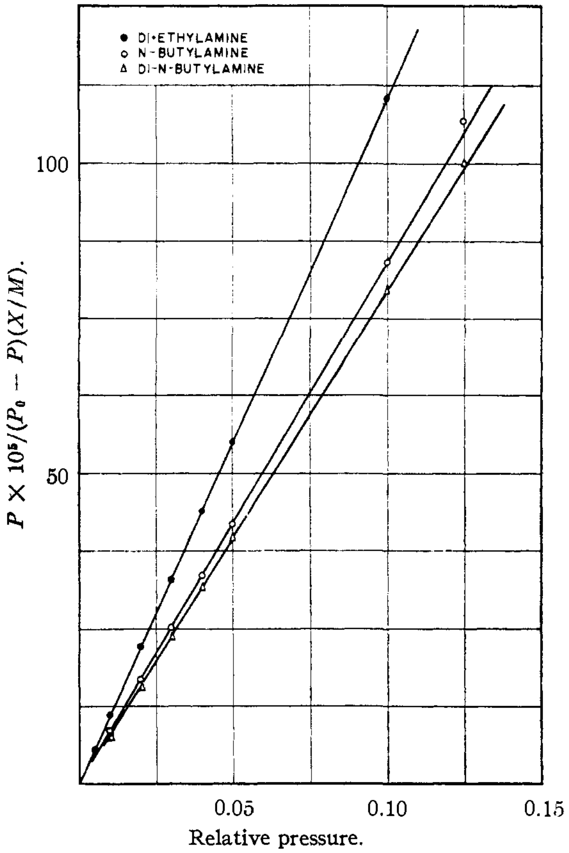

Fig. 5.—B. E. T. plot for low pressures.

be suspected that the adsorption may not be strictly physical, yet the BET equation, which was derived primarily for physical adsorptions, seems to hold surprisingly well. This leads us to conjecture that the original BET theory probably can be applied to the case of chemisorption without elaborate modification.

Intermediate and High Pressure Ranges.—At relative pressures above about 0.12 it became necessary to use the three constant BET equation.[9] To evaluate the third constant, n, large scale plots were made according to the method of Joyner, Weinburger and Montgomery.[10] The n values so obtained are given in Table II. It may be noted that these values are much smaller than those to be expected from the total amounts of amines adsorbed. It was originally thought that the constant n represents the maximum number of layers of adsorbate that could be accommodated by the surface. Obviously, this interpretation must be viewed with some reserve. If it were true, then the total quantity of amines adsorbed should amount to only about one-fourth of the values actually observed, even assuming that the gel surface be spread out as a plane and not composed of curved capillary surfaces. This conclusion is in agreement with those reached by Joyner, Weinburger and Montgomery,[10] Hansen,[11] and Smith and Bell.[12] A tentative interpretation of the constant n will be given in a later section of this paper.

At relative pressures higher than about 0.4, the three-constant equation no longer holds. The amount actually adsorbed is much higher than that prescribed by the equation. The extent of deviation may be as high as 300% (Table III).

TABLE III

SATURATION ADSORPTION VALUES, $(x/m)_s$

Amine	n	$(x/m)_s$ calcd., mg./g.	$(x/m)_s$ obs., mg./g.	Diff., mg./g.
Di-ethyl	3	181	831	650
n-Butyl	2	178	860	682
Di-n-butyl	3	274	898	624
	2	208	898	690

The non-conformity of data to theory can be brought out in an even more striking manner when the data are plotted to high pressures according to the two-constant equation, *i.e.*, taking n as infinity (Fig. 6). In general, the experimental values are lower than predicted by the equation, as

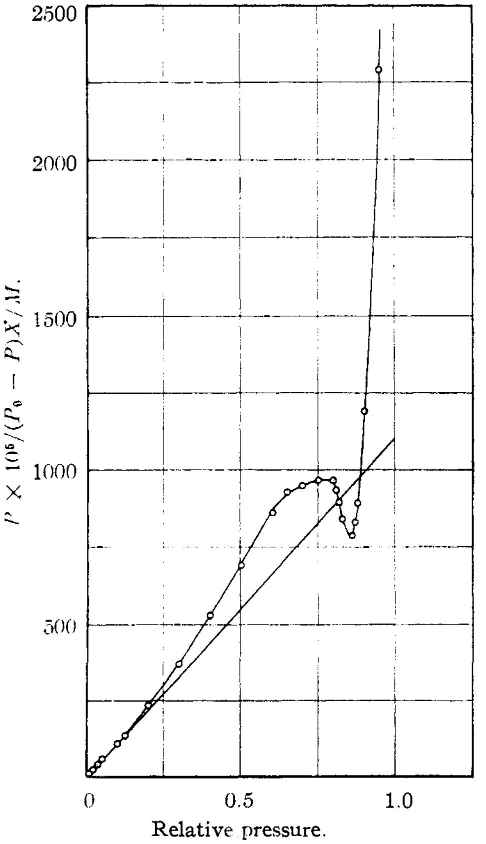

Fig. 6.—B. E. T. plot to high relative pressure.

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(9) Braunauer, Emmett and Teller, THIS JOURNAL, **60**, 309 (1938).

(10) Joyner, Weinburger and Montgomery, *ibid.*, **67**, 2182 (1945).

(11) Hansen, Thesis, University of Michigan, 1948.

(12) Smith and Bell, *Nature*, **162**, 109 (1948).

is to be expected. But there is a small range in which the observed values are higher than the calculated. In a limited portion of the curve within this range, the slope even becomes negative, a fact which defies physical interpretation. It should be pointed out, however, that neither the calculation of the saturation adsorption values by means of the three-constant equation nor the extension of the BET plot to such high pressures is legitimate because both of these equations were derived explicitly for adsorption alone, while in the systems under investigation both adsorption and capillary condensation are taking place.

Capillary Condensation.—Greatly enhanced adsorption was observed in the region of the isotherm exhibiting hysteresis. This has been generally attributed to the condensation of vapors at pressures lower than the normal condensation pressure due to the effect of the low radius of curvature on the vapor pressure of the liquid in the capillary. Brunauer, Deming, Deming and Teller(13) have elaborated the original BET theory to include cases ordinarily attributed to capillary condensation. Even though their equation is the most comprehensive equation of adsorption ever proposed, as it contains all adsorption types known to date as special cases, and, furthermore, has the beauty of interpreting all adsorption phenomena from a unitary point of view, the model they adopted in deriving their equation was highly artificial. It seems unlikely, because of its artificial nature, that the BDDT equation will be able to describe more than qualitatively adsorption phenomena observed with adsorbents which are radically different from their model. For instance, the curves in Fig. 2–4 are much too steep to be embraced by this theory. As a matter of fact, they are more akin to the hypothetical curve precluded by these authors. Even in those cases where it has been fairly successfully applied, the interpretation is not always unambiguous.(14) In view of the fact that one of the constants, c, in their equation cannot be accurately evaluated for the present systems and some of the predictions of their theory have not been confirmed by this investigation, as will be discussed in another paper, it seems preferable to approach the problem in another way.

Years ago Lord Kelvin derived thermodynamically the relationship between vapor pressure lowering and pore radius

$$\ln (p/p_0) = \pm 2\gamma M/rdRT$$

where M, d, and γ are, respectively, the molecular weight, density and surface tension of the condensed liquid, and the sign depends on the curvature of the liquid surface in the capillary of radius r. This equation, or one of its modifications, has been generally used for the calculation of the capillary radii of porous substances.(15,16,17,18) When it was applied to the desorption isotherms of the three amines at the point of inflection, the results in Table IV were obtained:

TABLE IV

RADII CALCULATED ACCORDING TO THE CAPILLARY CONDENSATION THEORY

		Amine	
	Di-ethyl	*n*-Butyl	Di-*n*-butyl
Surface tension, dynes/cm.	19.1	22.9	23.6
Molecular weight	73.1	73.1	129.2
Density, g./ml.	0.6972	0.7735	0.7556
Vapor pressure (mm.) at 25°	238.4	95.0	2.51
p/p_0 at desorption inflection point	0.75	0.73	0.57
Kelvin radius, Å.	56	58	58
Pore radius, Å.	67	68	70

These results are very satisfactory when it is considered that a difference of 0.01 relative pressure unit will alter the calculated radius by 2 Å. It might have been suspected that because of a possible complication from the probable chemisorption, the Kelvin equation might not be applicable to the present systems. However, recent work in our laboratory with aliphatic alcohols, for which the probability of chemisorption is admittedly much less, gave similar results. Furthermore, the results given above can be checked approximately in the following manner. In a previous section the BET constant n has been calculated for the present systems. If one assumes that n represents not the total number of layers in the capillaries but the number of BET layers, *i.e.*, layers due to multilayer adsorption as postulated by Brunauer, Emmett and Teller, then the true radius of the capillaries should be at least equal to the sum of the Kelvin radius and the thickness of the BET layers. The thickness of a single layer in Å. is given by

$$t = (x/m)_{\mathrm{m}} \text{ in grams}/d \times 320 \text{ sq. m. (in Å. units)}$$

With the pertinent data recorded previously the results in the last line of Table IV were obtained. If one further assumes these radii represent the average radius of the capillaries in the gel, then the specific area of the gel is given by the geometric relation $A = 2V/r$, assuming the pores to be circular. The pore volume as calculated from the amount of amines taken up by the gel at saturation pressure is about 1.17 ml./g. With this value an area of 340 sq. m. was obtained. Considering the number of assumptions made and the fact that we are under-correcting the pore radius the agreement with the BET nitrogen value is very satisfactory. Thus the application of the

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(13) Brunauer, Deming, Deming and Teller, THIS JOURNAL, **62**, 1723 (1940).

(14) Joyner and Emmett, *ibid.*, **70**, 2359 (1948).

(15) Emmett and Cines, *J. Phys. and Colloid Chem.*, **51**, 1248 (1947).

(16) Foster, *Discussions of the Faraday Society*, No. 3, **41**, (1948).

(17) Milligan and Rachford, THIS JOURNAL, **70**, 2922 (1948).

(18) Schull, *ibid.*, **70**, 1405 (1948).

Kelvin equation to the present systems is justified. We may conclude, therefore, that in the systems investigated capillary condensation is superimposed on multilayer adsorption. This concept is implied in the BDDT theory, though they preferred to designate it as "additional energy."

Acknowledgment.—The authors wish to acknowledge their indebtedness to Dr. Ying Fu of this Laboratory for his valuable assistance in the development of the work of this paper.

Summary

1. The adsorption isotherms over the entire pressure range for di-ethylamine, *n*-butylamine, and di-*n*-butylamine on silica gel have been determined at 25°. These isotherms were found to be unusual in that within the relative pressure ranges of 0 to 0.01 and about 0.5 to 0.8 the rates of increasing adsorption with pressure were very great. The completion of the monolayers occurred at the very low relative pressure of about 0.01.

2. The three-constant BET equation was found to be applicable in the approximate relative pressure range of 0.002–0.4. The constant *n* was found to be less than 3 in all cases. A tentative interpretation of the constant *n* has been proposed and applied to the data.

3. Highly concordant values for the capillary radius of the gel were obtained by the application of the Kelvin equation, indicating that to account for the experimental data capillary condensation must be taken into consideration in addition to the chemi- and to multilayer adsorptions.

ANN ARBOR, MICHIGAN RECEIVED JULY 14, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Absorption Spectra of Some Cobalt(III) Coördination Compounds

BY FRED BASOLO

There is at present no general method completely reliable for the determination of configuration of ions of the type $[\mathrm{Ma_4b_2}]$, $[\mathrm{Ma_4bc}]$, $[\mathrm{M(AA)_2b_2}]$ and $[\mathrm{M(AA)_2bc}]$[1] in solution. The work of Shibata[2] suggests that this can be accomplished by means of absorption spectra when b and c are negative ligands. Very recently[3] it has been shown that rotatory dispersion curves may be used to reveal the configuration of such ions in which the AA groups are optically active.

That geometric isomers of certain metallic complexes exhibit distinctly different colors has long been known.[4] It has likewise often been stated that the *cis* compounds are more highly colored than the *trans*, but the exceptions to this rule are so numerous that it is without value. These observations do suggest however that there may be some correlation between the configurations of these ions and their absorption spectra. To establish whether this is true and to define the differences existing between such geometric isomers, a number of spectra were determined in neutral or acid water solutions or in methanol–water solutions. The compounds studied were of known configuration with groups b and c being either neutral or negative.

Experimental

Spectral Measurements.—All measurements were made with a Beckman model DU spectrophotometer in silica cells having a 1 cm. light path. Extinction coefficients were calculated from the familiar equation

$$\epsilon = 1/cd \log_{10} (I_0/I)$$

Measurements were made at room temperature and a total operation time of approximately two hours was required. The complete spectrum was obtained from 625 to 220 mμ.

Compounds.—The compounds studied were prepared by the procedures described in the literature[5] and purified either by recrystallization or reprecipitation by the addition of ethanol–ether to a concentrated aqueous solution of the salt. All of the compounds were analyzed for either halogen or nitrogen. A few of the compounds used were kindly supplied by Professor John C. Bailar, Jr.

Solutions.—Distilled water and reagent grade methanol were used as solvents. The molar concentration of the solutions varied from 3×10^{-2} to 1×10^{-5}. The acid aqueous solutions were prepared from a stock solution of dilute acid so that in all cases blanks were the same sample of solvent used for dissolving the compound studied. The methanol solutions were prepared by the immediate transfer of an aliquot of a concentrated aqueous solution to absolute methanol. This methanol solution was used in the longer wave length regions and subsequent dilutions were made with absolute alcohol. The blanks were obtained by starting with the same amount of water as the aliquot of concentrated solution and carrying out the same dilutions with methanol. These solutions varied from 95–99% methanol by volume.

Results.—The data obtained are summarized in Table I and the more pertinent results are shown in Figs. 1 to 6. It is evident from these absorption curves that the isomeric ions do have different spectra; however, in some cases this difference is only very slight. It is further evident that this difference is shown either by a shift in the absorption maximum to other wave lengths or by a change of intensity or by both.

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[1] The following abbreviations are used: a, b and c = monodentate groups; AA = bidentate groups.

[2] Shibata, *J. Coll. Sci. Imp. Univ. Tokyo*, 37 (1915).

[3] O'Brien, McReynolds and Bailar, THIS JOURNAL, **70**, 749 (1948).

[4] Jörgensen, *J. prakt. Chem.*, **39**, 16 (1889).

[5] The literature references for the preparation of these compounds are given in Table I.