[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Adsorption of Low Molecular Weight Fatty Acids by an Activated Charcoal. Use of Chromatography to Obtain Adsorption Isotherms

BY F. H. MAX NESTLER[1,2] AND HAROLD G. CASSIDY

The possible advantages in knowing the adsorption behavior of each component of a system to be studied chromatographically have been pointed out in recent years by a number of investigators.[3,4,5,6] For reasons such as they have given, and also in order to systematically investigate the problem of mixed adsorption in greater detail with a view to an analytical separation method, the adsorption isotherms of the three saturated, aliphatic fatty acids, acetic, propionic and butyric, were measured over as wide range of concentration as was experimentally possible. Two types of isotherms were determined: (1) the static adsorption of each acid alone dissolved in water was found in the conventional manner by shaking a quantity of adsorbent and acid solution of known concentration together until equilibrium was established, whereupon the concentration was again determined, the difference in concentration being proportional to the relative amount of acid adsorbed on the charcoal; (2) the adsorption of an acid in the presence of the one next higher (with respect to number of C-atoms) in the homologous series was measured using the technique and theory of "frontal analysis."[3]

Comparatively few investigations of adsorption have been made over wide concentration ranges, and of these, the majority are not concerned with the lower aliphatic fatty acids adsorbed on charcoals. Schmidt-Walter[7] found acetic acid in water to be preferentially adsorbed over the range 0–100% acid. Though Ostwald and Schulze[8] measured the adsorption of acetic acid in water to only about 55% of acid, the shape of the curve is such that it would appear to predict the same results as found by Schmidt-Walter. In the work of Heymann and Boyé,[9] the isotherm for butyric acid in water was irregular and probably based on too few points to support with certainty the assumed slight negative adsorption of acid in the region 80–100 mole per cent.

The adsorption of the aliphatic fatty acids at low concentrations on carbon adsorbents is represented by extensive investigations, among which may be mentioned those of Wiegner, Magasanick and Virtanen,[10] Miller,[11] Wöhler and Wenzel,[12] Landt and Knop,[13] Linner and Gortner,[14] and Claesson.[3] The data of all of these workers[3–14] amply illustrate the generally accepted facts of the reversibility and rapidity of adsorption, the usually consistent behavior of an homologous series as embodied in Traube's rule, the effect of molecular structure and purity of charcoal on adsorption, and most important, the over-all inconsistency found when one attempts to compare the results obtained with one charcoal with those obtained with another. The non-uniformity of adsorbents which gives rise to the latter problem is of particular importance to chromatography, as recently pointed out by Zechmeister[15] and Deitz.[16] The use of an adsorbent of more reproducible properties[3,17] has been an important consideration in the present work.

Claesson,[3] using the technique and theory of frontal analysis to obtain adsorption isotherms for single pure solutes, and for the components of binary mixtures, has shown that the multiple solute Langmuir equation[18] may be applied qualitatively, and to a certain extent quantitatively, to the chromatographic adsorption analysis of mixtures of fatty acids, esters and alcohols. Unfortunately however, the greater proportion of data obtained for adsorption from solution can be expressed not by the Langmuir equation, but rather by that of Freundlich. And, there have been few systematic investigations of pure and mixed adsorption of an homologous series of substances, and especially for the case where the data follow only the Freundlich type of isotherm. Likewise, there has not been available an analogous exponential equation for mixed adsorption.

The results of the present investigation have allowed us to compare the adsorption isotherms for three members of an homologous series of substances, each separately obeying the Freund-

---

[1] Nutrition Foundation Post Doctoral Research Fellow, 1946–1948.

[2] Present address: Naval Research Laboratory, Chemistry Division, Washington 20, D. C.

[3] S. Claesson, *Arkiv for Kemi, Mineral. Geol.*, **23A** [1] (1946).

[4] D. DeVault, THIS JOURNAL, **65**, 532 (1943).

[5] D. Glueckauf, *J. Chem. Soc.*, 1321 (1947).

[6] H. G. Cassidy, THIS JOURNAL, **62**, 3076 (1940).

[7] D. Schmidt-Walter, *Kolloid Z.*, **14**, 242 (1914).

[8] Wo. Ostwald and H. Schulze, *ibid.*, **36**, 289 (1925).

[9] E. Heymann and E. Boye, *ibid.*, **63**, 154 (1933).

[10] G. Wiegner, J. Magasanick and A. J. Virtanen, *ibid.*, **28**, 51 (1921).

[11] E. J. Miller, *J. Phys. Chem.*, **36**, 2967 (1932).

[12] L. Wöhler and W. Wenzel, *Kolloid Z.*, **53**, 273 (1930).

[13] E. Landt and W. Knop, *Z. physik. Chem.*, **A162**, 331 (1932).

[14] E. R. Linner and R. A. Gortner, *J. Phys. Chem.*, **39**, 35 (1935).

[15] Conference on Chromatography, N. Y. Academy of Sciences, November 29 and 30, 1946. A topic which arose during the discussion following presentation of Dr. Zechmeister's paper. See H. G. Cassidy, *Ann. N. Y. Acad. Sci.*, **49**, 324 (1948).

[16] V. R. Deitz, *ibid.*, **49**, 315 (1948).

[17] The choice of adsorbent charcoal for this investigation is based on information from Dr. W. A. Helbig of the Darco Corporation (by private communication in 1946), that they could furnish at any time "reagent grade" Darco G-60 of the same quality as that sold in 1942.

[18] S. Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press, Princeton, N. J., Chapter XIV, 1943.

lich equation, with their respective adsorption isotherms when mixed together as binary systems. And, with the recent publication of Glueckauf's[5] binary Freundlich isotherm equation, the experimental data obtained have been used to determine to what extent the isotherm constants for single pure solute systems could be utilized to calculate the adsorption isotherms for corresponding binary mixtures. Except for those data of Claesson[3] on the higher saturated fatty acids (beginning with hexanoic) we know of no similar investigation dealing with adsorption of mixtures of two so chemically similar adsorbates as the lower saturated aliphatic fatty acids.

Adsorption isotherm data are treated by the empirical equation of Freundlich

$$x/m = q^0 = kc^{1/n} \tag{1}$$

where x is the weight of acid in grams adsorbed by m grams of dry adsorbent, q^0 is the specific adsorption (grams of acid adsorbed per gram of adsorbent), c is the equilibrium concentration in weight per cent., and k and $1/n$ are empirical constants. Theoretical interpretations of this equation as regards the effect of temperature and of quantity of adsorbent on the constants k and $1/n$, and limitations to its use, are given by Ostwald and de Izaguirre,[19] Wöhler and Wenzel[12] and Ostwald.[20]

The adsorption isotherms for each component of binary mixtures of the fatty acids studied were obtained using the technique and theory of frontal analysis. For a detailed discussion of this, and the other methods of chromatographic adsorption analysis, reference is made to Claesson[3] and to Weil-Malherbe.[21] In a frontal analysis, as carried out during the course of this work,[22] the solution to be analyzed was passed through the tube of adsorbent (filter), and the concentration of the solution (filtrate) leaving the bottom of the filter measured and plotted against the total weight of liquid which had passed through.

For a system containing one solute, pure solvent is obtained until the adsorbent is saturated, whereupon the concentration of the filtrate rises sharply to the equilibrium value, and passes through unchanged thereafter. The weight w of liquid passed up to this break point is called the threshold weight, and originally contained the amount of solute adsorbed in the filter. If the threshold weight is divided by the weight of adsorbent used, the specific threshold weight, w^0, is obtained. Thus per gram of adsorbent

$$q^0 = w^0 \times c \tag{2}$$

where q^0 is the specific adsorption, and c the equilibrium concentration (in weight per cent.) of the filtrate at the break-through point.

When a solution containing two solutes is analyzed by this means, two breaks (steps) are observed in the frontal analysis diagram, *e.g.*, Fig. 10. Again the filtrate obtained is pure solvent until the adsorbent is saturated with respect to the first, or less strongly adsorbed component. The solution between the two steps contains only solute 1, but after saturation of the adsorbent by component 2 also, the solution passes through at the original concentrations of both components. The equilibrium concentration of solute 1 in the first step ($c_{1,1}$) is not, however, equal to its initial concentration c_1. Rather, $c_{1,1}$ will be greater due to partial displacement of solute 1 from the adsorbent by the more strongly adsorbed solute 2. And, because of the competition between the two adsorbates for the available active adsorption sites, they mutually diminish their adsorption and, in this case, are adsorbed less than they would be from their respective pure solutions at corresponding concentrations.

The amounts adsorbed of 1 and 2 may be calculated from the diagram. Thus

$$q_2^0 = w_2^0 \times c_2 \tag{3}$$

since the adsorbent is saturated with solute 2 after the second step and the solution goes through unchanged. With the concentration expressed as weight per cent., q_1^0 may be calculated from the expression

$$q_1^0 = w_2^0 \times c_1 - (w_2^0 - w_1^0) \times c_{1,1} \tag{4}$$

where $w_2^0 \cdot c_1$ is the weight of solute 1 originally contained in w_2^0 grams of solution. After passing through the filter, w_2^0 contains only the amount of solute 1 in the first step, namely, $(w_2^0 - w_1^0) \times c_{1,1}$.

It is readily seen that, for systems containing a single solute, the equilibrium concentration, being that of the original solution, can be fixed beforehand. Such is also true for the more strongly adsorbed component of a binary mixture, but not so for the less strongly adsorbed one due to adsorption displacement. However, for a chemically similar series of compounds such as these three acids, the ratios of the equilibrium concentrations were found to be approximately constant (the ratios of the initial concentrations were held constant, but the total acid concentration varied), so that $c_{1,1}$ could be predicted roughly from c_2 after the first few frontal analyses of mixtures.

The determination of adsorption isotherms for the components of mixtures is limited in this method, however, to binary solute systems only, since for a larger number of components there are more unknowns than equations.

---

(19) Wo. Ostwald and R. de Izaguirre, *Kolloid Z.*, **30**, 279 (1922).

(20) Wo. Ostwald, *ibid.*, **43**, 268 (1927).

(21) H. Weil-Malherbe, *J. Chem. Soc.*, 303 (1943).

(22) It is generally more common in chromatographic adsorption analysis to first wash the column of adsorbent through with pure solvent before the solution to be analyzed is passed in. For our experiments, it was more convenient to use the filters initially dry. The several advantages are discussed later.

Experimental

Adsorbent.—Charcoal was obtained from the Darco Corporation, New York, N. Y., as a single shipment of twelve 1-lb. cartons of Darco G-60, reagent grade.[17] According to the manufacturer the particle size of the charcoal was such that approximately 90% passed through a 300-mesh sieve.

For the static adsorption experiments charcoal samples were dried individually. Moisture analyses, based on the weight of "air dry" charcoal taken, showed that it contained 12–14% adsorbed water.

For the frontal analyses the adsorbent used in the filters was a mixture (air-dried) of Celite 535[23,24] and Darco G-60 in the ratio 1:1, on a weight basis. The two were thoroughly mixed, then heated twice for two-hour periods at 110°. The percentage of charcoal in the dry mixture after correction for the amount of water lost by heating, was 46.08. It was later necessary to make up a second such mixture; the charcoal content was 46.35%.

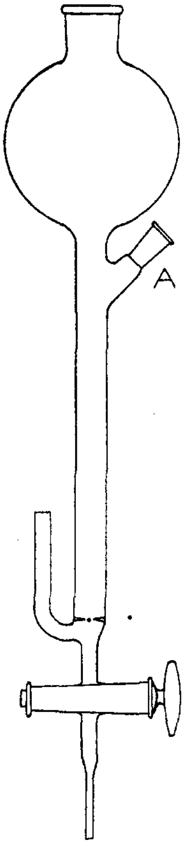

Fig. 1.—Diagram of adsorption tube.

Acids.—Each of the three acids was purified by careful fractional distillation through a glass-helix-packed column (1.5 cm. i.d. by 60 cm. of packing) after drying over Drierite. Purity of fractions was determined by freezing point and/or titration with standard base.

Solutions and Apparatus.—Solutions of fatty acids were made up with boiled distilled water, and carefully analyzed with standard barium hydroxide solutions. Exposure of apparatus and solutions to the atmosphere was minimized. A large water thermostat held at 25.00 ± 0.50° was used for all static isotherms measurements. Frontal analysis experiments were carried out at room temperature.

The adsorption tubes for frontal analysis were constructed from Pyrex glass as shown in Fig. 1. The diameter of tubing was nominally 15 mm. o.d.; several 13 mm. tubes were made for use with smaller amounts of adsorbent. The ground, standard taper side-tube A was added in connection with elution analysis studies.

Technique.—For static adsorption isotherm data vacuum corrections were applied to all weighings except where indicated otherwise. The adsorption flasks were left in the thermostat for about twenty hours, during which time they were shaken and/or rocked a number of times.

In making up filters for frontal analyses, an amount of dry adsorbent sufficient to give 1.00 or 2.00 g. of dry charcoal within ±0.5%, was transferred directly to the adsorption tube from a weighing bottle. The adsorbent was then firmly packed into the tube. In order to maintain approximately the same degree of firmness in the packed adsorbent, and to eliminate somewhat the possibility of a change in the frontal analysis diagram due to shape of the adsorbent column,[21] the diameter of the glass tubing was picked so that the ratio of the length to diameter of the column of adsorbent after compressing was always near 7.0. The acid solution was pipetted carefully on to the column, and pressure (20 ± 0.5 cm. above atmospheric) applied at the top of the tube by means of a rubber aspirator bulb. An open-end manometer, and a ballast volume of 2–3 liters were also connected to the system.

The quantity of solution initially added was generally such that it was not necessary to release the pressure until completion of the experiment. The flow rate with the above pressure varied between 0.30 and 0.40 g./min., depending on the column. The fractions of filtrate were weighed in air to the nearest milligram. The quantity of liquid taken per fraction was adjusted to the conditions of an experiment.

From curves shown later it will be seen that after the first few experiments, it was possible to predict approximately the points at which the "breaks" in the diagrams should occur. Furthermore, it was observed that the ratio of the two specific threshold weights (w_2^0/w_1^0) was approximately constant (though actually decreasing slightly with decreasing initial concentration), so that once w_1^0 was obtained, it was possible to calculate w_2^0 within about +10%. Thus, when the total weight of liquid collected was within about 5 g. of the predicted value, the size of fractions was reduced, the minimum weight being around 1.0 g. On the flat portions of the curve, larger fractions were taken.

Though the point at which the first component should emerge from the bottom of the column could be estimated fairly well, it was fixed more exactly by testing minute droplets of the filtrate with acid test paper, as the calculated break point was approached. In this way there was much less chance of both overshooting the point of emergence of the zone and, as was the case in a number of early experiments, of effectively missing the entire front by getting only one point on the steep portion of the curve. The second zone is much more diffuse at its leading edge, hence there was less chance of missing this portion of the chromatogram.

Early considerations showed that it would be more convenient if the columns could be started with the packing initially dry, in which case the reference point was the bottom of the column of adsorbent. By means of the side-tube and an attached rubber medicine dropper bulb, liquid which collected in the delivery tube below the packing could be blown out. The major inaccuracy in this method is the small amount of liquid retained in the cotton wad and hanging at the underside to the indentations. However, preliminary comparative experiments with columns of wet and dry adsorbent showed that the error introduced in this manner was about the same as that resulting when, with an initially wet column, the correction applied for the solvent held between the particles of adsorbent is an average value of the solvent retention per gram of adsorbent. In addition when a column is prewetted with solvent, it is necessary to maintain a column of liquid between the end of the delivery tube and the bottom of the packing; this amount must also be subtracted from the eluate weights as a correction. And if sufficient solvent had not been pressed through the filter to begin with, gas continuing to desorb from the adsorbent collects beneath the cotton wad, soon breaking the column of liquid, which then runs out, and the filter might just as well have been started dry.

Results

The experimental data for the static adsorption isotherms are shown in Fig. 2 for high acid concentrations, and by the points along curves A, P and B in Fig. 3 for low concentrations. Since the number of experimental points at the highest acid concentrations (98–100%) are too few in number, it was not possible to fit the data of Fig. 2 to an equation of the type utilized by Bartell and Sloan[25] in expressing their low con-

---

[23] Obtained from the Johns-Manville Corp.

[24] The Celite was added as the diluent in order to increase the rate of flow of liquid. In separate experiments dealing with elution analysis of binary mixtures of the same acids, the Celite introduced no changes in the curves as compared with those for pure charcoal. From this it is assumed that there was negligible adsorption of acid by the diluent.

[25] F. E. Bartell and C. K. Sloan, This Journal, **51**, 1643 (1929).

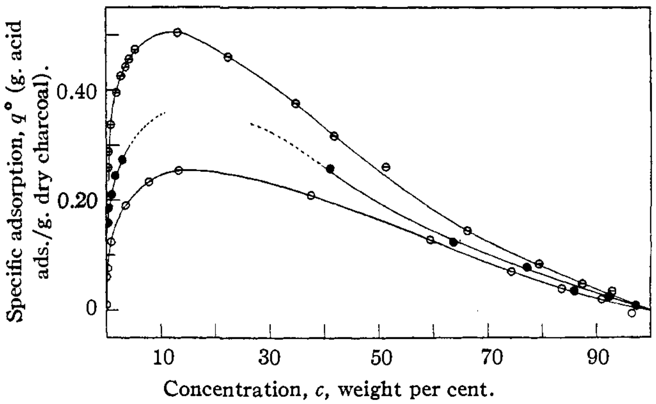

Fig. 2.—Adsorption of the fatty acids on charcoal from aqueous solution at 25°: O, acetic; ●, propionic; ⊖, butyric.

centration data.[26] However, the experimental curves obtained do serve to show that the three acids were preferentially adsorbed at all equilibrium concentrations. The one point showing negative adsorption of acetic acid is undoubtedly due to experimental error since the adsorption values at these very high concentrations of acid were of the same order of magnitude as the errors in the acid analyses.

The over-all shapes of the single solute isotherms (Fig. 3) are typical for the members of this homologous series adsorbed statically at low equilibrium concentrations on an activated carbon. The experimental data were plotted according to the linear (logarithmic) form of the Freundlich equation, $\log q^0 = \log k + 1/n \log c$, whereby the slope of the straight line and its intercept with the ordinate, give the constants $1/n$ and k, respectively. The graphs of the straight lines from which these constants were obtained, are shown in Fig. 4 by the curves A, P and B. Table I summarizes the values of k and $1/n$ and the solid lines in Fig. 3 illustrate the shapes of the isotherms calculated using these values substituted in equation 1, thus affording a comparison with the experimental data (the open and filled circles).

TABLE I

VALUES OF THE CONSTANTS k AND $1/n$ FOR THE ADSORPTION EQUATION $q^0 = kc^{1/n}$

Parentheses around an acid indicate that the data were obtained by frontal analysis of the mixture shown. Symbols are those used to represent the curves of Figs. 3 and 4.

Acid	Symbol	k	$1/n$	Mixture	a[a]
MeCOOH	A	0.136	0.494	....	0.0178
(MeCOOH)	A′	.041	.350	MeCOOH + EtCOOH	....
(EtCOOH)	P′	.190	.435	MeCOOH + EtCOOH	....
EtCOOH	P	.232	.419	....	0.0309
(EtCOOH)	P″	.060	.645	EtCOOH + PrCOOH	....
(PrCOOH)	B″	.293	.228	EtCOOH + PrCOOH	....
PrCOOH	B	.378	.339	....	0.0567

[a] k recalculated according to equation 6.

It is readily seen that the agreement between the calculated curve and the experimental points is good only up to about 0.5% acid, even though in the logarithmic plots the data fell on fairly good straight lines over a wider concentration range. This is contrary to the general behavior observed by others,[10,12,14] wherein the interval of fit was three or four times as wide. There is independent evidence, however, which indicates possibly that the lower aliphatic fatty acids when adsorbed on Darco G-60 from aqueous solution do not strictly follow a Freundlich type of adsorption isotherm. Thus Cheldelin and Williams[27] have published isotherm constants for acetic and propionic acids adsorbed on G-60, but attach the limitation that the log plots were not straight lines. Close examination of the trend of the points for curves A, and especially for P and B in Fig. 3, discloses a curvature; however, for

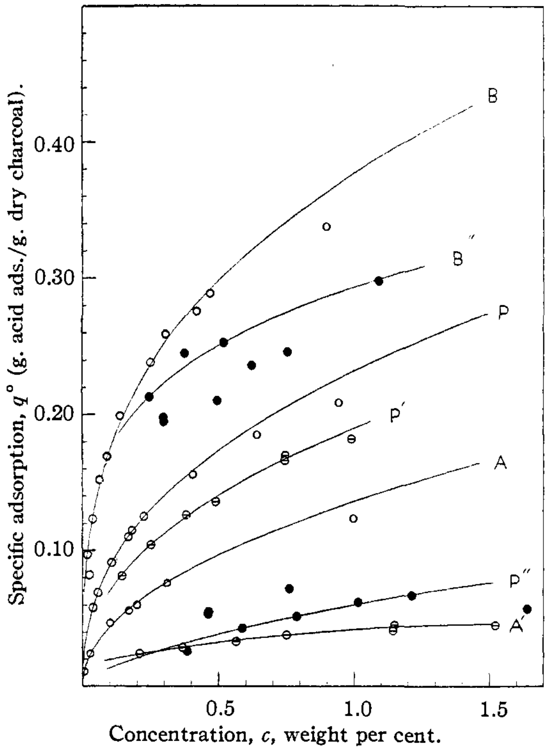

Fig. 3.—Adsorption of fatty acids (curves A, P and B, resp.) at low concentrations in water: O, static adsorption of pure acids at 25°; ⊖, frontal analysis of acetic + propionic mixtures (A′ and P′, resp.); ●, frontal analysis of propionic + butyric mixtures (P″ and B″, resp.). Solid lines computed from equation 1.

---

(26) In their investigations of the adsorption of benzene on carbon from ethyl alcohol as solvent, Bartell and Sloan looked upon the adsorption at high concentration of benzene as being equivalent to the adsorption of ethyl alcohol at very low concentrations in the other component as the solvent. They used two Freundlich equations to express the data at low concentrations for each adsorbate, and then by successive approximations, obtained one composite equation, capable of expressing the adsorption of one component over the full concentration range in the other as the solvent.

(27) V. Cheldelin and R. J. Williams, THIS JOURNAL, **64**, 1513 (1942).

the purposes of this investigation, the best average straight lines were drawn.

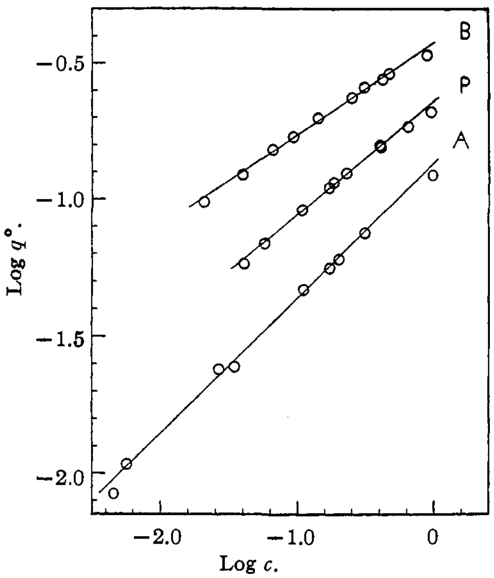

Fig. 4.—Static adsorption data plotted in the linear form of equation 1; symbols as in Fig. 3.

The extent to which the high concentration portions of the adsorption isotherms are affected by the use of charcoal which has not been previously dried is shown in Fig. 7 by data for acetic acid. For comparison the similar portion of the isotherm for acetic acid (Fig. 2) adsorbed on charcoal initially dry is drawn (solid line) with the experimental data for adsorption on "wet" charcoal superimposed. It is seen that the effect is chiefly one of dilution of the original acid solution, with, however, possibly some slight displacement of the adsorption curve due presumably to a slight alteration in the surface characteristics of the adsorbent as a result of the adsorbed water layer. The error introduced is particularly significant at very low adsorptions. That one should dehydrate the adsorbent before use is obvious, or at least correct the final results for the moisture introduced by the charcoal. Dobine[28] concluded that water so introduced resulted in a dilution effect only. Numerous qualitative statements may be found in the literature regarding the undesirability of having moisture in the adsorbent, though quantitative data supporting the opinions are generally lacking.

Since in a frontal analysis there is no complete separation of zones as may be possible in an elution analysis, it was more convenient to plot the concentration of each fraction of liquid emerging from the bottom of the column as an effective concentration, c', defined as cc. of standard base/g. of liquid. The abscissa is the total weight of liquid collected. From the resultant frontal analysis diagrams (examples of which are the curves of Figs. 10 and 11), w_1, $c'_{1,1}$ and w_2 were obtained by extrapolating as follows. The rate at which the effective concentration $c'_{1,1}$ changes in the diffuse front portion of the first zone was almost linear in nearly every instance; consequently it was possible to obtain w_1 by extrapolating this portion of the curve to the abscissa. A flat, straight line was drawn for the effective equilibrium concentration $c'_{1,1}$ and represented the average value for a number of points. It was only necessary then in order to convert from effective concentration to weight per cent. $c_{1,1}$ to multiply by the correct acid titer of the base. The threshold weight for the second component was obtained by drawing a straight line through the steep portion of the second step; the value (as read from the abscissa) of the point of intersection of this line with that of $c'_{1,1}$ extended was w_2. The specific values were computed in all cases from the actual weight of dry charcoal, and not from total weight of adsorbent packing.

Adsorption isotherms obtained by frontal analysis of binary acid mixtures are given in Fig. 3, where the respective isotherms for each of the acids in the mixture acetic and propionic are represented by points along the curves A′ and P′, and for the mixture propionic and butyric by points along P″ and B″. As previously for static adsorption data, the solid lines were calculated using equation 1 and constants (Table I) obtained by plotting the experimental data in the linear form of the Freundlich equation (as drawn in Fig. 5). The straight lines for curves P″ and B″ are open to some question, drawn as shown. However, the choice of points to which to give greater weight was based on an evaluation of the individual experiments. The scatter is due to the decreased precision with which the threshold weights could be obtained for the system propionic–butyric acids as a result of a number of unexplainable inconsistencies in the frontal analysis diagrams.

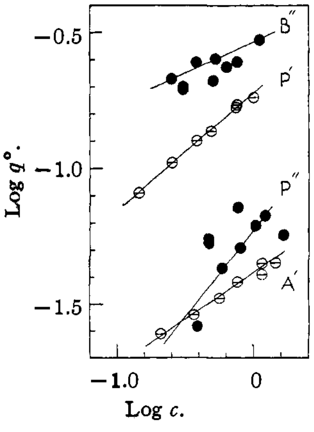

Fig. 5.—Adsorption data from frontal analysis plotted in the linear form of equation 1; symbols as in Fig. 3.

---

(28) M. Dobine, *Compt. rend.*, **212**, 155 (1941).

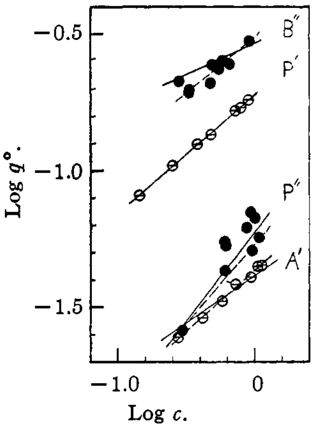

Fig. 6.—Comparison of experimental frontal analysis isotherm data (solid lines) with points calculated using equations 5a,b; symbols as in Fig. 3.

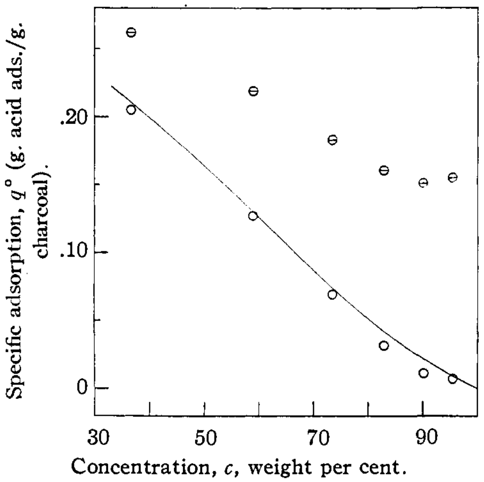

Fig. 7.—Influence of water adsorbed in the charcoal upon adsorption of acetic acid: solid line, dry charcoal (Fig. 2); ⊖, charcoal containing approximately 14% water; O, initial concentration corrected for water in the charcoal.

The frontal analysis data from which the individual isotherms were calculated have been tabulated in Tables II and III, and are shown graphically in Figs. 8 and 9, where the log of the specific threshold weight has been plotted as a function of the log of the initial concentration (log w_1^0 *vs.* log $c_{1,1}$, the equilibrium concentration, is included for comparison). It was interesting

TABLE II

FRONTAL ANALYSIS DATA FOR THE MIXTURE ACETIC ACID + PROPIONIC ACID

c_1	$(c_1 + c_2)$	$c_{1,1}$	w_1^0	$(w_2^0 - w_1^0)^a$
0.982	1.973	1.521	9.47	8.88
.759	1.502	1.145	11.05	11.3
.752	1.500	1.153	11.79	10.96
.503	0.995	0.751	14.24	13.46
.379	.761	.566	16.83	16.13
.251	.503	.367	20.75	20.6
.152	.298	.210	27.0	28.6

[a] Concentration and specific threshold weights are expressed in weight per cent. and grams, respectively.

TABLE III

FRONTAL ANALYSIS DATA FOR THE MIXTURE PROPIONIC ACID + BUTYRIC ACID

c_1	$(c_1 + c_2)$	$c_{1,1}$	w_1^0	$(w_2^0 - w_1^0)$
0.952	2.044	1.640	14.9	12.4
.763	1.522	1.214	17.6	14.8
.626	1.250	1.015	20.6	17.2
.483	1.003	0.788	25.4	23.2
.502	1.000	.764	23.9	18.3
.377	0.755	.588	30.1	33.2
.296	.598	.465	34.6	29.7
.297	.598	.462	35.5	30.3
.249	.497	.386	37.3	48.7

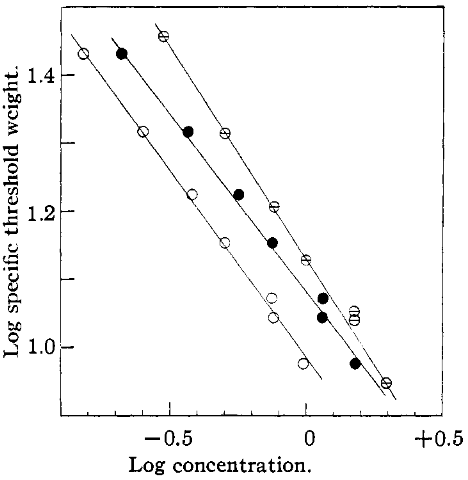

Fig. 8.—Specific threshold weights as a function of concentration for mixtures of acetic + propionic acids: O, log w_1^0 *vs.* log c_1; ●, log w_1^0 *vs.* log $c_{1,1}$; ⊖, log $(w_2^0 - w_1^0)$ *vs.* log $(c_1 + c_2)$; c_2/c_1 approximately 1.0.

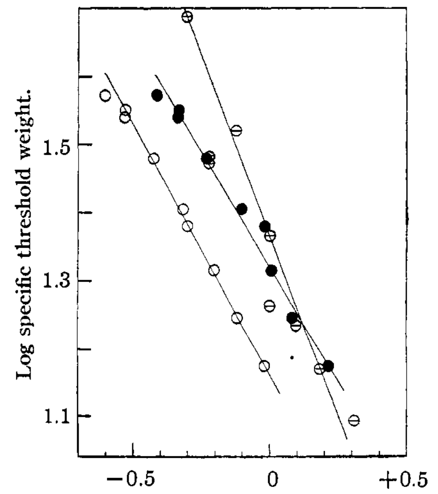

Fig. 9.—Frontal analysis data for mixtures of propionic + butyric acid plotted as in Fig. 8; c_2/c_1 approximately 1.0.

to find that the data fell on fairly good straight lines when so plotted, and could be represented by equations of the form $y = a + bx$, where y represented the log of the specific threshold values and x the concentrations. w^0 is thus seen to be exponentially dependent upon concentration, that is, for example, $w_1^0 = Ac_1^{-b}$ where $\log A = a$. The constants a and b were determined from the respective straight lines of Figs. 8 and 9, and are compiled in Table IV. The fact should be noted that, in carrying out all of the frontal analyses represented by the above data, the ratio of the initial concentrations of each acid was on the average 1.010 ± 0.012 for the acetic–propionic system, and 0.987 ± 0.018 for the propionic–butyric.

Table IV

Constants a and b for an Equation of the Form $y = a + bx$ Relating the Specific Threshold Values and Equilibrium Concentration Data Obtained by Frontal Analysis

	Fig. 7		Fig. 8	
	a	b	a	b
Log w_1^0 vs. log c_1	0.985	−0.520	1.161	−0.737
Log w_1^0 vs. log $c_{1,1}$	1.082	− .549	1.320	− .674
Log $(w_2^0 - w_1^0)$ vs. log $(c_1 + c_2)$	1.129	− .622	1.366	−1.244

The three curves shown in Fig. 10 for the system acetic acid–propionic acid are representative of those from which previous frontal analysis adsorption data were obtained. Variations in shape were chiefly a function of the total acid concentration. Little improvement in definition is found in the curves at higher concentrations; and, at lower values, irregularities become more numerous. For example, the horizontal separation between zones increases, but the vertical, *i.e.*, the concentration difference, decreases with a simultaneous decrease in the slope of that portion of the curve representing the front of the second zone. Consequently, the break in the curve where the more strongly adsorbed component emerges from the column is much less sharply defined at low concentrations. This loss in definition was greatest for mixtures of propionic and butyric acids, and accounts most for the scatter of the experimental points along the curves P″ and B″ in Figs. 3 and 5.

The degree to which the frontal analysis diagrams were affected by a change in the ratio of acid concentrations is shown by the three curves in Fig. 10 for the system acetic acid–propionic acid.

Practical limitations to the problem of a separation of fatty acids by means of frontal analysis are implied. From the alteration in the curves resulting when the acid ratio changes, it will be increasingly difficult to detect the presence of the more strongly adsorbed solute as it becomes a relatively smaller fraction of the mixture, and similarly as the total acid concentration decreases. Obviously increase of the amount of adsorbent in a column, in the hope of increasing separation, will not be the practical solution since both threshold weights will be proportionately increased. At the other end of the scale, smaller amounts of the less strongly adsorbed solute could probably be detected in the presence of the second acid because of the sharpening effect on the fronts resulting both from adsorption displacement and from the higher relative concentration of the latter component.

Chromatograms given in Fig. 11 for the four possible mixtures of the three acids show the displacements which occur. It is quite evident that such curves alone afford no means for quanti-

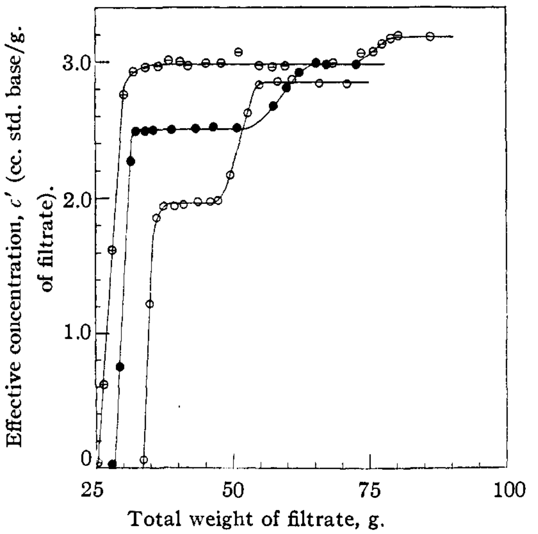

Fig. 10.—Chromatograms showing the alteration for acetic + propionic acid when the ratio of initial acid concentrations is changed. c_1/c_2 is: O, 1:3; ●, 1:1; ⊖, 3:1; $c_1 + c_2$ = 1.0%.

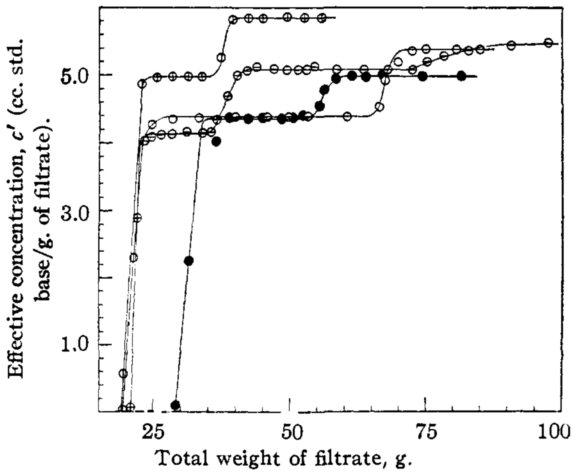

Fig. 11.—Frontal analysis diagrams for mixtures of fatty acids. c_3:c_2:c_1 approximately 1.0, and total c approximately 2.0%: ⦶, acetic + propionic acids; ●, propionic + butyric acids; O, acetic + butyric acids· ⊖, acetic + propionic + butyric acids.

tatively determining the composition of an unknown mixture.

Several columns were operated at higher flow rates (the applied external pressure being approximately double), and on several other occasions it was necessary to add more solution to a column; but, in both cases, the shapes of the resulting chromatograms were not significantly different from those obtained when columns, identically packed, were saturated with portions of the same acid solution. Similar conclusions may be drawn with respect to columns in which variations in the method of packing were introduced, or when a column of adsorbent was prewetted with solvent before adding the acid solution.

Dependence of Adsorption upon Amount of Adsorption.—In consideration of the foregoing data, and of the discussion to follow, a possible limitation in the results of this investigation is pointed out. Frontal analysis, especially for single solute systems, gives adsorption data at equilibrium concentrations equal to the initial concentrations whereas static adsorption methods do not. Therefore, the single solute constants a and $1/n$ used in equations 5a,b were not obtained under exactly the same experimental conditions as were the binary adsorption values q_1^0 and q_2^0 and the corresponding slope constants $1/n_1$ and $1/n_2$. In the case of the static adsorption data the ratio between the weight of solution and the weight of charcoal to which it was added was maintained constant at between 10 and 12 to 1. On the other hand, a frontal analysis may be likened to the situation in a static adsorption experiment where a large amount of solution is added to an amount of charcoal sufficiently small so that the initial and equilibrium concentrations are essentially the same.

In view of data published by Burgers,[29] there should be no difference between adsorption isotherms obtained by both methods since he found (for static adsorption of acetic acid in aqueous solution) that the specific adsorption was not dependent upon the quantity of adsorbent used. However, in a single experiment which was carried out with an acetic acid solution and in which six different quantities of adsorbent were added to equal weights of liquid, only two of the points fell on or near the isotherm (Fig. 2) for acetic acid. Furthermore, when q^0 was plotted as a function of the equilibrium concentration, curve B of Fig. 12 was obtained. q^0 is seen to increase as m increases (curve A), whereas Burgers was dealing with the opposite where q^0 decreases as m increases. Apparently our case was again one of the anomalies found in the course of the function $q^0 = \mathrm{f}(m)_{c_0, w}$ (c_0 and w are initial concentration and weight of solution, respectively). Certainly in this instance (Fig. 12) to ascribe the increasing values of q^0, as m increases, to depletion of the solution is not as reasonable as in Burgers' case.

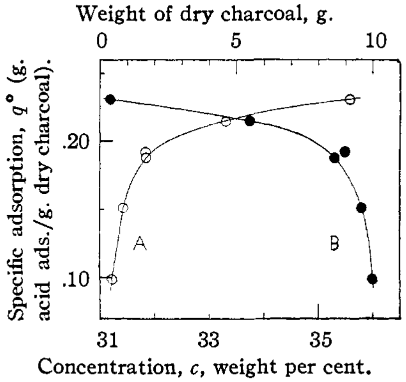

Fig. 12.—Variation in specific adsorption for 52.2 g. of 36.1% acetic acid solution: O, q° *vs.* weight of dry charcoal; ●, q° *vs.* equilibrium concentration.

In the absence of a greater quantity of experimental data dealing specifically with this problem for the charcoal used in the present investigation, we believe the aforementioned limitation exists, but does not appear to be serious.

Discussion

For adsorbates separately obeying the Langmuir adsorption isotherm equation it is sometimes possible to relate their behavior as mixtures by means of the multiple solute Langmuir equation.[3,18] Thus, Claesson[3] found that data for each component of various binary mixtures[30] when plotted according to the linear form of the multicomponent equation, gave straight lines which were parallel within the experimental error to those similarly plotted from data for the single solute isotherms.

Until recently, no analogous expression has existed for the adsorption of mixtures, the individual pure solutes of which followed a Freundlich isotherm. Glueckauf[5] however, has expressed the Freundlich equation in an empirical form suitable to the multiple solute problem. His equations as applied in this discussion to binary mixtures of fatty acids are

$$a_1c_1 = q_1^0(q_1^0 + \beta' q_2^0)^{n_1 - 1} \qquad (5a)$$

$$a_2c_2 = q_2^0(q_1^0\beta'' + q_2^0)^{n_2 - 1} \qquad (5b)$$

where the constants a_1,n_1 and a_2,n_2 (Table I) are those calculated from the isotherms (equation 1) of the single pure solutes, and q_1^0,c_1 and q_2^0, c_2 are the respective coexisting specific adsorption and equilibrium concentrations of each solute in a binary mixture analyzed by frontal analysis. The constants a and k are related as

$$k = a^{1/n} \qquad (6)$$

due to the Freundlich equation having been used in the form

$$q^0 = (ac)^{1/n} \qquad (7)$$

---

[29] W. G. Burgers, *Rec. trav. chim.*, **63**, 46 (1944).

[30] Binary mixtures of the following classes of substances were studied by adsorption analysis: normal and dibasic fatty acids, ethyl esters of normal acids, and normal fatty alcohols.

when equations 5a, b were derived. It is to be noted here that, as used by Glueckauf in his paper, $\beta' = \beta_2/\beta_1 = 1/\beta''$, and β_1 and β_2 referred to the surface area requirements of each of the adsorbates in the binary mixture (that is, β represented the amount of adsorbent occupied at saturation by 1 mole of the adsorbate).

Glueckauf's binary isotherm was tested using the data of this investigation. As is seen, the form of the equation is such that it is easier to compute values of the equilibrium concentration c, using the corresponding observed values of q_1^0 and q_2^0, and the constants $1/n$ and k (recalculated by means of equation 6) of the single pure solute isotherms. When this was done, very poor agreement was obtained regardless of the value of β_2/β_1 chosen. In particular it was found that when a so-called best value of β_2/β_1 was used in computing values for c_1, the concentrations then calculated for c_2 (using the inverse value of β_2/β_1) differed very considerably from the experimental, the deviations generally being either all positive or all negative.

In order to obtain any agreement, β in the present discussion is interpreted only as an empirical constant calculated from the observed values of the equilibrium concentration and specific adsorption. For each component of the two binary mixtures, values of the β-ratio (*i.e.*, β' and β'') were computed from each of the equilibrium concentrations by substituting the experimental values of c_1 and c_2, and the corresponding q_1^0 and q_2^0 in equations 5a,b; these are listed in Table V for coexisting concentrations, with average values for β' and β'' at the foot of each column.

TABLE V

VALUES OF THE β-RATIO (EQUATIONS 5a,b) CALCULATED FROM EXPERIMENTAL VALUES OF q^0 AND c OBTAINED BY FRONTAL ANALYSIS OF BINARY MIXTURES OF ACIDS

Acetic + propionic		Propionic + butyric	
MeCOOH β'	EtCOOH β''	EtCOOH β'	PrCOOH β''
1.65	1.66	2.53	1.35
1.97	1.66	1.67	1.44
2.20	1.62	1.64	1.66
2.33	1.74	2.00	0.95[a]
2.82	1.73	1.77	2.04
2.47	1.44	2.09	1.53
3.10[a]	2.02[a]	2.31	2.30
		2.38	2.43
		2.87[a]	2.60
2.24	1.64	2.05	1.92

[a] Omitted in the computation of the average β-value at the bottom of each column.

It is seen that there is not the relationship between β' and β'' suggested by Glueckauf. The above mentioned average values of β' and β'' were then used to recalculate equilibrium concentrations by means of equations 5a,b, and to compare these graphically in Fig. 6 with the experimental results.

In Fig. 6 for the binary acid system acetic–propionic, the solid lines A′ and P′ are those of Fig. 5 and the points were calculated by means of equations 5a,b using the average β-values, $\beta' = 2.24$ and $\beta'' = 1.64$. Comparison of the two figures shows some slight redistribution of the points along P′ and a greater change for those along A′ in the direction of increasing slope, which is shown by the dashed line redrawn through the calculated points.

A similar treatment was given the data for the system propionic–butyric acids, with results also shown in Fig. 6. The solid lines P″ and B″ again represent the experimental isotherms. The redistribution of points as a result of the calculations is much more apparent. For butyric acid (B″) the dashed line has an increased slope, while for propionic (P″) the slope has been decreased slightly, though the justification for redrawing the latter at all is open to some question, considering the precision of the observed data. The redrawn isotherm serves the purposes, however, of the discussion which follows.

The question early arose in this work as to what relationship the Freundlich isotherms for each component of a mixture would show with respect to the isotherms for the single pure solutes. We have seen that the behavior predicted theoretically by the multicomponent Langmuir equation, namely, that under certain conditions the linear form of the isotherms for the components of a mixture should have the same slopes as the corresponding isotherms for the pure solutes, has been verified experimentally by Claesson.[3] It appeared therefore to be not unreasonable to determine whether the linear form of the Freundlich equation could be fitted to the data in a similar fashion, even though there was no theoretical justification for such.

Comparison of the values of the slopes ($1/n$ in Table I) of the curves in Figs. 4 and 5 shows the extent to which the above reasoning applied to the experimental data. In only one instance were the lines approximately parallel (the slope of P′ being about 4% greater than that of P in the static adsorption measurements). On the other hand, however, it is interesting to note that when the experimental data were calculated according to equations 5a,b and replotted in the linear form, as was shown in Fig. 6, the straight lines (dashed) which could be redrawn through these points tended to be more nearly parallel to those of the pure acids than were the lines (solid) for the observed data. Thus, $1/n$ for A′ is 0.447, for P′ it equals 0.587, and for B″, $1/n$ is 0.411. These values should be compared with those in Table I for A, P and B. Considerably more data are needed for mixed adsorption in order to verify any postulations of parallelism in Freundlich adsorption analogous to that found where the Langmuir equations apply.

We conclude from the various calculations made that, though the pure acids separately follow Freundlich isotherms, they do not, as binary mixtures, obey the binary Freundlich isotherm equation proposed by Glueckauf. If, however, it is modified as previously described (that is, use separate β-ratio values determined from the observed results, for each component of a mixture) it gives reasonable agreement with the experimental data and appears to smooth out inconsistencies in the experimental points. But the agreement results only by virtue of the introduction of an empirical factor for one which previously bore a physical interpretation.

The authors wish to express appreciation to the Nutrition Foundation, Inc., for their generous support of this work.

Summary

1. Measurement of the adsorption isotherms of the aliphatic fatty acids acetic, propionic and butyric from aqueous solution and on a commercial activated charcoal, showed each acid to be preferentially adsorbed throughout the concentration range of 0–100% of acid by weight.

2. The experimental data could be fitted by the Freundlich isotherm equation over only a narrow concentration range of approximately 0.005 to 0.5%.

3. The technique of frontal analysis has been utilized in order to obtain data relating to the adsorption of binary mixtures of low molecular weight aliphatic fatty acids, with a view to an analytical method. By this means, the adsorption isotherms for each component of the binary acid mixtures, acetic plus propionic, and propionic plus butyric, have been determined for the equilibrium concentration range of approximately 0.3 to 1.5%. These data could be fitted also by the Freundlich equation.

4. The adsorption data for each acid obtained by static adsorption and from frontal analysis of mixtures, when plotted according to the linear form of the Freundlich equation, gave straight lines, corresponding ones of which appeared to be approximately parallel to each other.

5. Using the binary isotherm equation proposed by Glueckauf to express the adsorption data of mixtures, where the individual components follow the Freundlich equation, it was possible to obtain fair agreement between the observed data, and that calculated from his equation, but only when a modification was made in the interpretation attached to one of the constants in the equation.

6. The effect, upon the static adsorption isotherms, of moisture adsorbed in the charcoal, appeared to be one of dilution only.

7. Changes in adsorption, as evidenced by alterations in frontal analysis diagrams, were not observed when various experimental factors were varied. Thus, columns were packed differently, flow rate was increased by doubling the external pressure, a solid diluent was added to the charcoal in order to increase the rate of liquid flow and several columns were operated either initially dry, or prewetted with solvent before addition of the acid solutions.

8. The threshold values for each of the components of a binary mixture analyzed by frontal analysis are related exponentially to the respective initial or equilibrium concentrations.

9. The specific adsorption values in the static adsorption experiments were found to be dependent upon the quantity of adsorbent used, contrary to the findings of Burgers.[29]

WASHINGTON 20, D. C. RECEIVED[31] JULY 11, 1949

---

[31] Original manuscript received August 2, 1948.

[CONTRIBUTION NO. 166 FROM THE GOODYEAR TIRE AND RUBBER CO. RESEARCH LABORATORY]

Multilinked Polyamides[1a]

BY JOHN R. SCHAEFGEN AND PAUL J. FLORY[1b]

The synthesis of multichain polyamides having the general structure

$$\mathrm{R\{—CO[—NH(CH_2)_5CO—]_{\bar{y}}\ OH\}_{\mathit{b}}}$$

by reaction of ε-caprolactam with cyclohexanonetetrapropionic acid ($b = 4$) or with dicyclohexanoneoctapropionic acid ($b = 8$) has been described in a previous paper.[2] In the present investigation a technique has been developed for interlinking carboxyl end-groups of these multichain polymers by treating them with a reactive diamine under proper conditions. Using a quantity of the diamine which is stoichiometrically equivalent to the free carboxyl end-group content of the polymer, the interlinking of the carboxyl groups can be made nearly quantitative. Polymeric networks of definite structure may be prepared in this manner.

These interlinked multichain polyamides, which will be called "multilinked polyamides," exhibit an interesting combination of properties. At ordinary temperatures they behave like linear polyamides. Thus they are highly crystalline solids which, in the form of fibers, may be oriented by drafting to several times their initial lengths, resulting in an increase in strength and stiffness.

[1a] Presented before the High Polymer Forum at the Atlantic City Meeting of the American Chemical Society, September, 1949.

[1b] Present address: Department of Chemistry, Cornell University, Ithaca, New York.

[2] J. R. Schaefgen and P. J. Flory, THIS JOURNAL, **70**, 2709 (1948).