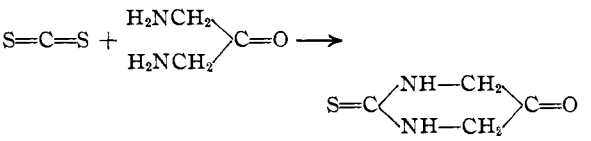
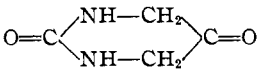


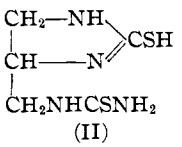
Diaminoacetone dihydrochloride was dissolved in hot alcohol and hot alcoholic sodium hydroxide then added in sufficient quantity to neutralize all hydrochloric acid. An equivalent amount of carbon disulfide was then poured into the solution, causing a vigorous reaction. A brown precipitate formed immediately, which was filtered off and dried at 110°. This compound gives a white precipitate with silver ions which decomposes into silver sulfide upon standing.[8] The compound decomposes without melting at about 150°.

Chloroformic ester was added to a hot alkaline solution of diaminoacetone, yielding a white precipitate which Rügheimer and Mischel[9] say is probably a derivative of urea having the formula

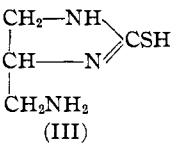


This compound gives a white precipitate with silver ions.

According to Pyman[10] two products are obtained when diaminoacetone is treated with potassium thiocyanate



(II)



(III)

Diaminoacetone dihydrochloride was heated on a water-bath for ninety minutes with the theoretical amount of potassium thiocyanate causing the formation of a white precipitate. The two products were separated by heating with water in which most of the precipitate dissolved leaving only a small residue. This residue, which melts at 212° with decomposition, is only very slightly soluble in acetone and alcohol. In acid solution, however, it gives a yellow precipitate with silver ions. This seems to be compound (II).

If the aqueous solution is allowed to crystallize, another compound is obtained which darkens at 240° but does not melt even when heated to 350°. This compound gives a white precipitate with silver and presumably is compound (III).

It is apparent from the reactions of the various compounds with silver ions that those with simpler structures give white or light colored precipitates and that only compound (I) gives a highly colored precipitate and hence is the most sensitive reagent for silver.

Rhodanine, which is closely related to these compounds, behaves in an analogous manner. Thus, Feigl[11] found that the condensation product of rhodanine with *p*-dimethylaminobenzaldehyde gave a more highly colored precipitate with silver ions than did rhodanine itself.

Acknowledgment.—Our thanks are expressed to Professors Robert E. Lutz and Alfred Burger for helpful suggestions during the course of this investigation.

Summary

2-Thio-5-keto-4-carbethoxy-1,3-dihydropyrimidine has been prepared by a modification of the Sheppard and Brigham method. Several related compounds have also been made. The reactions of these compounds with silver ions have been studied; only the former is a sensitive reagent for silver.

(8) Sheppard and Brigham[1] also prepared this compound by another method and report this reaction with silver.

(9) S. E. Rügheimer and E. Mischel, *Ber.*, **25**, 1562 (1892).

(10) F. L. Pyman, *J. Chem. Soc.*, **99**, 668 (1911).

(11) F. Feigl, *Z. anal. Chem.*, **74**, 380 (1938).

UNIVERSITY, VA. RECEIVED MARCH 31, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS]

Adsorption of Organic Compounds. I. Adsorption of Ampholytes on an Activated Charcoal*

BY VERNON H. CHELDELIN AND ROGER J. WILLIAMS

During recent years charcoal adsorption has become an important operation in the purification of materials of biological importance. It has been especially useful in the concentration and isolation of several of the water-soluble vitamins, the wound hormone traumatin[1] and the amino acid methionine.[2]

Amino acids as a class might be expected to be adsorbed considerably less than the parent carboxylic acids, due to their salt forming properties and high water solubilities. A few experiments by Phelps and Peters[3] and Bartell and Miller[4] indicate that glycine and alanine are not adsorbed at all on Norite or sugar charcoal, and that aspartic acid and glutamic acid are only slightly adsorbed, with a maximum near the isoelectric point. Ito[5] observed marked adsorption of the

* Original manuscript received August 5, 1941.

(1) English and Bonner, *J. Biol. Chem.*, **121**, 791 (1937).

(2) Mueller, *Proc. Soc. Exptl. Biol. Med.*, **18**, 14 (1921).

(3) Phelps and Peters, *Proc. Roy. Soc.* (London), **124A**, 554 (1929).

(4) Bartell and Miller, THIS JOURNAL, **45**, 1106 (1923).

(5) Ito, *J. Agr. Chem. Soc., Japan*, **12**, 204 (1936); through *Chemical Abstracts*, **30**, 6265[2] (1936).

basic amino acids lysine, histidine and arginine. Wunderly[6] obtained adsorption isotherms for phenylalanine, leucine, alanine, serine and aspartic acid on animal and sugar charcoals.

Further information regarding the charcoal adsorption of organic ampholytes is lacking. It was therefore decided to begin a systematic study of the problem by obtaining adsorption isotherms for thirty-three amino acids, vitamins and related compounds on one charcoal, with emphasis upon discovering differences in adsorption produced by constitutive differences within the molecules of the different adsorbates.

Experimental

Adsorbent.—The adsorbent used in the present investigation was Darco G-60, a commercial grade lignite charcoal which is in general a very effective adsorbent.[6a] Its ash content (practically all non-leachable) is 4% and the charcoal was used as received since information was first desired with respect to an adsorbent which finds common laboratory and commercial use. Adsorption studies using other charcoals will be discussed in another communication.

Method of Measuring Concentrations.—Measurements of all amino acid solutions and some of the others were made by the interferometric method.[7] The instrument used was of the Zeiss portable water type and was calibrated for each adsorbate by obtaining readings of several solutions of known concentrations. After adsorption and centrifuging, readings were made and the residual concentrations were calculated by comparison with the standards. The inorganic constituents of the charcoal were not leached away by this procedure, so that it was possible to detect concentration changes as small as 10 mg. per liter.

The lower concentrations of calcium pantothenate, β-alanine, biotin, pyridoxin and thiamin after adsorption were determined by microbiological assay methods developed in this Laboratory.[8,9]

Duplicate determinations were made for each experimental point. The number of duplicate experiments ranged from three to ten for each substance tested, averaging five or six.

Procedure.—Samples of the adsorbent were weighed into 50-cc. Erlenmeyer flasks. To these were added the desired volumes of various concentrations of a given solution. The amounts varied from 25 ml. to 2 liters per gram of carbon, depending upon the solute used. The flasks were stoppered and shaken for thirty minutes, after which the solutions were centrifuged, decanted and their concentrations determined in the interferometer.

Experiments were run at room temperature, which was usually about 25° but at times rose to 35°. Other workers[10] have found little change in adsorption over this temperature range.

Preliminary experiments with asparagine showed that adsorption was essentially complete in a very few minutes. This is in line with general experience in so far as adsorption is a reversible process.

The substances tested were adsorbed from pure solutions with no special effort being made in most instances to control their *p*H, since ampholytes in solution tend to maintain *p*H values near their isoelectric points. Comparison of the *p*H values of many amino acid solutions before and after adsorption revealed relatively little change in *p*H (Table I). In the cases of pantothenic acid and biotin dilute solutions of aspartic acid (0.0025 *M*) were added to buffer the systems near the isoelectric points of these substances.

Treatment of Adsorption Data.—Any attempt to reduce adsorption behavior to a simple mathematical expression usually results in the adoption of the well-known Freundlich equation.[11] In almost all cases in the present study the Freundlich equation was found applicable. The Langmuir equation[12] has been found in our work to be less useful.

Data and Results

The data obtained for each adsorbate are listed in Table II. The values of $1/n$ and k were determined from adsorption isotherms (not shown) derived from the experimental data.

It may be observed from Table II that, contrary to previous reports,[3,4] glycine and alanine are definitely adsorbed, although only slightly. The amounts adsorbed are less than for the parent carboxylic acids, but increase with increasing members of a homologous series. This is in accordance with adsorption experience in general.

The introduction of an amino group into the carboxylic acid molecule more than doubles the values of $1/n$ in the Freundlich equation. The

TABLE I

*p*H OF AMINO ACID SOLUTIONS BEFORE AND AFTER ADSORPTION

Substance	Maximum concn., g./l.	*p*H Before adsorption	*p*H After adsorption	Minimum concn., g./l.	*p*H Before adsorption	*p*H After adsorption
Serine	13.4	6.0	6.2	0.84	6.1	6.7
Aspartic acid	7.2	3.3	3.3	.90	3.4	3.8
Threonine	14.6	5.7	5.5	.91	5.6	6.0
Glycine	50.0	5.8	5.7	3.1	6.1	5.9
Nicotinic acid	1.00	3.4	3.4	0.250	3.6	3.7
Valine	3.94	6.2	6.2	.246	6.6	6.4
Creatine	5.00	7.1	6.8	.313	6.9	6.2
Leucine	2.50	5.9	5.8	.156	6.2	5.8

(6) Wunderly, *Helv. Chim. Acta*, **17**, 523 (1934).

(6a) Thanks are extended the Darco Corporation for their donations of materials used in this work.

(7) Bartell and Sloan, THIS JOURNAL, **51**, 1637 (1929).

(8) Williams, Lyman, Goodyear, Truesdail and Holaday, *ibid.*, **55**, 2912 (1933).

(9) Williams, *et al.*, *The University of Texas Publications*, No. 4137 (1941).

(10) Yajnik and Rana, *J. Phys. Chem.*, **28**, 267 (1924).

(11) Freundlich, *Z. physik. Chem.*, **57**, 385 (1906).

(12) Langmuir, THIS JOURNAL, **40**, 1361 (1918).

TABLE II

ADSORPTION OF AMPHOLYTES ON DARCO G-60

Substance	Equilibrium concn., moles/liter Maximum	Minimum	Mg. carbon per cc. of solution	$1/n$	k	Average dev., %
Acetic acid	1.69	0.0070	20	0.34[e]	0.0032	±0.8[a]
Propionic acid	1.26	.0201	20	.31[e]	.0044	±0.5
Glycine	0.659	.082	50[b], 20	.76	.00023	±5
dl-Alanine	.225	.0145	20	.86	.00083	±2
β-Alanine	.394	.0000057	20[c], 40	.64	.00050	±7
dl-α-Aminobutyric acid	.280	.0168	20	.75	.0015	±1.7
dl-Norleucine	.0402	.00079	20	.45	.0048	±0.4
dl-Valine	.0276	.00156	20	.82	.0056	±1
dl-Leucine	.0124	.00051	20[d], 10	.50	.0054	±0.3
dl-Isoleucine	.137	.00092	20	.50	.0054	±0.5
dl-Serine	.125	.0076	20	.63	.00051	±8
dl-Threonine	.125	.0098	20	.83	.0014	±2
dl-Methionine	.0161	.00055	10	.61	.011	±0.4
l-Lysine	.0446	.00522	10	.68[e]	.0051	±2
l-Aspartic acid	.0414	.00315	20	.70	.0059	±0.8
	.0360	.00377		.66[f]	.0041	±0.1
l-Asparagine	.164	.00377	20	.64	.0022	±0.3
				.65	.0023	±2
Benzoic acid	.0081	.00042	2	.24	.013	±0.6
Aniline	.164	.0041	10	.26	.010	±0.2
o-Aminobenzoic acid	.0113	.00090	2	.16	.0071	±0.5
m-Aminobenzoic acid	.0125	.00145	2	.16	.0057	±0.3
p-Aminobenzoic acid	.0117	.00140	2	.12	.0045	±0.3
Nicotinic acid	.00593	.00067	1	.22	.0069	±3
dl-Phenylalanine	.0489	.00075	1	.10[e]	.0023	±1.3
l-Tyrosine	.00014	.000031	0.5	.30[g]	.011	±10
dl-Tryptophan	.00340	.00284	0.5	.10[e]	.0032	±0.3
Urea	.762	.0419	40	.66	.0021	±1
d-Glucose	.093	.0042	20	.54	.0033	±0.4
i-Inositol	.0570	.00536	20	.86	.0042	±1
l-Hydroxyproline	.0500	.00250	20	.79	.0032	±1
Caffeine	.0145	.00124	2	.10	.0033	±1
Creatine	.0367	.00170	1	.15	.0023	±4
Creatinine	.0862	.00448	1	.26	.0044	0
Calcium pantothenate (dextro)	.024	.00000019	0.5	.69	.39	±10
Calcium pantothenate (from liver extract)	.00334	.000000230	.5	.56	.026	±10
Biotin	.000000037	.000000000092	.1	.69	.53	±10
Pyridoxin hydrochloride	.00335	.00000097	2	.38	.0062	±15
Thiamin hydrochloride	.00107	.00000013	0.3	.66	.30	±10

[a] The per cent. average deviation is the average of the deviations obtained at all concentrations. [b] 50 mg. carbon per cc. solution in the first two cases, 20 mg. per cc. in the last three. [c] 20 mg. carbon per cc. solution for the five highest concentration levels, 40 mg. per cc. for the lower five. [d] 20 mg. carbon per cc. solution at the highest concentration, 10 mg. per cc. in the others. [e] In this case the logarithmic plot is not a straight line. The value of $1/n$ increases with dilution. [f] Duplicate determinations made nine months later with a different sample of charcoal. [g] This value does not fit in well with generalizations presented later, but is only very approximate due to experimental difficulties involved in obtaining sufficient data regarding a compound of such low solubility. In several similar cases the $1/n$ values increased with dilution.

higher homologous alpha amino acids have somewhat lower $1/n$ values compared to the lower members and branched chain amino acids seem to have higher $1/n$ values than the corresponding straight chain acids. The position of the amino group appears to be important, for β-alanine has a lower $1/n$ value than either α-alanine or α-aminobutyric acid.

The introduction of additional functional groups causes at most a slight rise in the $1/n$ value. The effect of these additional groups on the *amount* of adsorption is in the opposite direction, however, as was the case with the monoamino monocarboxylic acids mentioned above.

Striking differences exist between aromatic and

aliphatic compounds, both in the values of $1/n$ and in the amounts adsorbed.

While the difference in $1/n$ for the representative carboxylic acids (acetic, benzoic) is not large, the difference becomes much greater when amino groups are introduced; for whereas among aliphatic acids the $1/n$ values are increased by the presence of polar groups, the effect of these groups when placed on the aromatic nucleus is to *lower* the $1/n$ values. The difference in $1/n$ for alanine and phenylalanine is most striking, and illustrates the influence of the benzene nucleus on adsorption.

The relation between the amounts of adsorption and the trend in $1/n$ values is opposite in aromatic compounds to that found among the aliphatic compounds.

The adsorption data for various nutrilites is as varied as might be expected on the basis of the structures of the nutrilites themselves.

Calcium pantothenate, β-alanine, thiamin hydrochloride and inositol are all non-aromatic compounds with several polar groups. Their $1/n$ values are high (above 0.6) in accordance with the previous discussion. The aromatic compounds nicotinic and *p*-aminobenzoic acids and pyridoxin hydrochloride have low $1/n$ values (below 0.4). Biotin, the structure of which is unknown, on this basis would be expected to be non-aromatic ($1/n = 0.69$), provided of course that the extrapolated curve is valid over the extremely wide range for which as yet no experimental data are available.

It is worthy of note that the adsorption data for several of the nutrilites follow the Freundlich equation through extremely wide concentration ranges. By using microbiological tests it has been possible in some cases to measure adsorption from solutions far more dilute than has hitherto been possible in dealing with organic compounds. The application of the Freundlich equation through a wide range is somewhat contrary to results obtained with certain other substances studied within a much narrower range.

Summary

1. Adsorption isotherms have been obtained for thirty-three amino acids, vitamins and related substances using Darco G-60 as the adsorbent. The experimental data fit the equation commonly known as the Freundlich adsorption isotherm.

2. Several generalizations have been evolved from the data which show certain trends (based upon structure) in adsorption and in the $1/n$ values of the Freundlich equation. The presence and position of polar groups and the presence or absence of aromatic nuclei are important factors.

AUSTIN, TEXAS RECEIVED MARCH 23, 1942

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

Studies on High Molecular Weight Aliphatic Amines and their Salts. VII. The Systems Octylamine–, Dodecylamine– and Octadecylamine–Water

BY A. W. RALSTON, CHARLES W. HOERR AND EVERETT J. HOFFMAN

Previous studies upon the behavior of aliphatic amines in water have been concerned only with amines of low molecular weight, and the literature pertaining to the higher homologs in water is confined to statements regarding their solubility. Preceding papers of this series have reported some aspects of the behavior of the hydrochlorides and acetates of primary aliphatic amines containing from 8 to 18 carbon atoms in the paraffin chain. This paper reports the behavior of octyl-, dodecyl- and octadecylamines in water. Since these three amines represent a cross-section of the series of normal primary aliphatic amines, a comparison of their water systems illustrates the effect of increased length of the alkyl chain upon such systems.

The applicability of the phase rule to colloidal systems has been demonstrated with respect to soap phases by McBain and his co-workers.[1] While they have shown that the phase rule can be applied in its usual form without the introduction of any new variable, they point out several of the assumptions and interpretations which must necessarily be made to fit the phase rule to some of the phenomena encountered in colloid chemistry. Of course, the original Gibbs deduction of the phase rule specifically excludes the effects of surface and boundary forces which are so important in connection with colloidal behavior; hence, in some cases certain observations must be omitted

(1) McBain, Vold and Vold, THIS JOURNAL, **60**, 1866 (1938).