Joyner's data show, in some cases, an experimental error of 200 p.p.t. Much of this is undoubtedly due to his method of sampling.

A large scale plot was carefully constructed and used in determining the equation for the straight line which results. The equation which has been found to hold satisfactorily is $\log_{10} N = -1074.2(1/T) + 0.501$. The rounded solubility values in Table VI were obtained from this large plot. The calculated values in Table VI are those obtained using the above equation; the agreement is seen to be quite satisfactory.

In the analysis of the amalgams, it was found that distillation at 0.1 mm. and 200° yielded a residue of the approximate composition Ag_3Hg_4. As has been mentioned above, increasing the vacuum to 0.003 mm. and using flame temperatures, a residue composed of about 1 atom of Hg to 50 of Ag was obtained. There is every reason to believe that with a further decrease in pressure in distillation, results found by weighing the residues as silver would be fully as accurate as most wet methods for the determination of silver in the presence of mercury.

The authors wish to thank Professor Willard R. Line of the University of Rochester for his help in the analytical phase of the work.

Summary

1. A method of preparing and analyzing silver amalgams has been described which yields results uniformly only 2 p.p.t. low.

2. A tube has been developed of general applicability to solubility work, which permits of sampling without removal of the equilibrium mixture from the thermostat or the introduction of sampling devices.

3. This tube has been used to determine the solubility of silver in mercury up to 200°, over fifty determinations having been made.

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[Contribution from the Chemical Laboratory of the University of Oregon]

THE ADSORPTION OF ORGANIC COMPOUNDS ON HYDROUS OXIDES AND FULLER'S EARTH

By Donald P. Grettie with Roger J. Williams

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Adsorbents have not infrequently been used in the separation of materials of biological importance from extracts of tissues containing them. They have been used in this Laboratory for work of this nature where attempts are being made to isolate a "bios" from yeast extracts. The desire to use adsorbents as intelligently as possible made it desirable to have data on the adsorption of various organic compounds by different adsorbents under comparable conditions. The particular question which appeared most interesting to us was whether the adsorption of various compounds would take place in accordance with the acidic and basic properties of the adsorbent and adsorbate, and to what extent one might expect the adsorption to be specific and unpredictable.

Because data of this sort were not available the work here reported was done. This consisted in a study of the adsorption from solution of a series of pure organic compounds on the hydrous oxides of silicon, iron and aluminum and (because of its previous use as an adsorbent for organic bases) fuller's earth.

Preparation of Adsorbents.—The behavior of the hydrous oxides as adsorbents depends largely on the method of their preparation. Impurities on the adsorbents and the heat treatment of the adsorbents affect greatly the extent of adsorption on them. The adsorbents used in the work here reported were prepared according to methods previously used by other workers.

The silica was prepared by precipitating silicic acid and ferric hydroxide together by adding a solution of ferric chloride to a diluted solution of water glass After the precipitate was dried the ferric hydroxide was dissolved out by treatment with 6 *N* hydrochloric acid. The remaining hydrated silica was then washed by decantation with water until the water in which the silica had soaked for several hours gave no precipitate with silver nitrate. When this silica was dried and heated to 120° for several hours a very superior adsorbent resulted. Before use it was ground fine enough to pass through a 200-mesh sieve. This method of preparation was devised by Holmes and Anderson.[1]

The alumina was prepared according to the method described by Willstätter[2] for the preparation of his type B. A solution of aluminum sulfate was added slowly to a strong (20%) solution of ammonium hydroxide. The precipitate was washed four times by decantation with water and was then treated with ammonium hydroxide again, after which it was washed by decantation and then by filtration until free of sulfate ions. The product was dried at 120° for an hour and then ground and passed through a 200-mesh sieve.

The hydrous ferric oxide was prepared in a manner analogous to that used for the preparation of the alumina except that ferric chloride was used instead of aluminum sulfate.

The fuller's earth used was similar in appearance and general behavior as an adsorbent to the English earth marketed by Eimer and Amend, but its exact history is unknown.

Choice of Compounds for Adsorption.—An attempt was made to select a group of organic compounds of widely different chemical properties, both as to acidic and basic strengths and also as to molecular structure and complexity. The choice of compounds for this study was limited to those which are sufficiently soluble and to those which were available in pure form. Eighteen organic compounds, listed in the table, varying in acidic and basic strengths from aspartic acid, having a dissociation constant of $k_a = 1.4 \times 10^{-4}$, to piperidine, having a dissociation constant of $k_b = 1.2 \times 10^{-3}$, were finally chosen. Most of these substances are of biological importance. All except glucose contain nitrogen.

Carrying Out of Adsorption and Analysis.—Solutions of eighteen organic compounds in 0.01 *M* concentration were prepared and 25cc. samples of these solutions were shaken in a mechanical shaker for five minutes

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[1] Holmes and Anderson, *Ind. Eng. Chem.*, **17**, 280 (1925).

[2] Willstätter, *Ber.*, **56**, 149 (1923).

with 0.5 g. of the dried adsorbent which had been ground and passed through a 200-mesh sieve. The solution was then filtered from the adsorbent through filter paper in a Gooch crucible and analyzed for the amount of the compound left in the solution. The methods of analysis were different for the different types of compounds studied. Those compounds which were not volatile at 100°, the temperature of the drying oven, were analyzed simply by evaporating 10 cc. of the filtrate to dryness in a weighed crucible and weighing the non-volatile material. Any of the adsorbent that might have come through the filter was taken account of by igniting the material and weighing the crucible plus the non-combustible residue. Those compounds which are distinctly acidic or basic could be titrated and this method was used wherever possible. Some of the nearly neutral compounds were volatile at the temperature of the oven and the solutions of these compounds could not be analyzed by either of the two above methods. Since all of these compounds contained nitrogen the filtrates were analyzed as to their nitrogen content by means of the micro-Kjeldahl method as modified by Koch and McMeeken[3] in which hydrogen peroxide is used as an oxidizing agent.

Whenever results were doubtful or unexpected they were checked at least approximately by using more than one method of analysis. Control experiments showed that adsorption by the small filter used was too small to affect the results detectably, and evaporation during the filtration was shown to be too small to change the results appreciably. Bacterial contamination of the solutions was avoided by using only fresh solutions in case of compounds which might be attacked by micro-organisms. The adsorbents were kept in stoppered containers and the parallel adsorption experiments were all carried out within a short time so that the adsorbents would be uniform for the different tests.

Results and Discussion.—In Table I are given the results obtained in these experiments. The *P*H values listed were determined directly in the case of the more nearly neutral compounds and were calculated from the ionization constants in the case of the stronger acids and bases. The values apply to the 0.01 *M* solutions of the pure substances used in the experiments. The following facts should be noted from a consideration of the results: (1) the adsorption by silica seems to be roughly proportional to the basic strength of the compound adsorbed. This is in keeping with the acidic character of silica. The negative adsorption noted in several cases was due to the selective adsorption of water and the consequent increase in concentration of the solution. (2) Adsorption by alumina is most marked in the case of the acidic compounds, though the most basic substance, piperidine, is also adsorbed very appreciably. These results are not unexpected in view of the well-known amphoteric charac-

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[3] Koch and McMeeken, This Journal, **46**, 2066–2069 (1924).

ter of alumina. (3) Although the hydrous iron oxide used was apparently an excellent absorbent, the adsorption was very irregular, being strongest in the case of acid substances, as might be expected, but also taking place markedly in the case of certain of the neutral and basic compounds. (4) The adsorption by fuller's earth parallels very roughly the adsorption by silica. One striking exception appears in the case of caffeine. Approximately eight times as much of this substance is adsorbed by fuller's earth as by silica. (5) All of the adsorbents chosen have, rather surprisingly, adsorbent properties of about the same order, in spite of their different characters and sources.

TABLE I

RESULTS OF ADSORPTIONS

Substance	PH	By silica, %	By alumina, %	By iron oxide, %	By fuller's earth
Piperidine	11.46	94.5	5.7	25.2	73.8
Nicotine	10.6	87.3	1.5	2.2	43.7
Arginine	9.5	72.5	1.2	34.2	31
Quinoline	8.6	47	2	1	71.2
Adenine	8.4	10.6	2	60	21.2
Caffeine	7.8	11.2	0.5	0.0	87
Creatine	7.2	4.7	1.3	3	7.42
Betaine	7.5	5.5	0	0.0	5.08
Acetanilid	7.2	2.37	1.8	12.3	3.05
Urea	7.1	1.9	2.94	0.3	5
Acetamide	7.1	1.1	3.7	1	5.4
Glucose	7.1	0.7	1.0	11.0	0.0
Succinimide	6.0	.7	0.5	0.0	.5
Glycine	6.1	.7	3.0	15.85	.0
Vicine	6.0	.7	13.85	20.25	2.86
Asparagine	5.4	.7	10.95	44.77	.0
Glutamic acid	3.2	.6	74.3	81.6	.0
Aspartic acid	3.1	.0	84.5	87.5	.0

In order to throw some light on the irregularity of adsorption by hydrous iron oxide, another sample was prepared, using an entirely different method. Ferric chloride, which is not obtainable in very pure form, was used for the preparation of the sample used above. For a second iron oxide preparation, pure electrolytic iron was oxidized by ozone in the presence of water, using a piece of platinum foil as a catalyst. The oxidation proceeded slowly but eventually a sample of hydrous iron oxide was obtained. This was heated and screened as in the former cases and tested on several solutions similar to those used above.

The results indicated in Table II show that the second sample of hydrous oxide was not, in general, as good an adsorbent as the precipitated hydrous oxide. This result is not surprising, but it is surprising to note that there is no parallelism in the behavior of the two samples toward the compounds tested. The large differences obtained emphasize the difficulty and irregularities which are liable to be encountered because of the variation in the quality of the adsorbent.

TABLE II

RESULTS WITH SECOND IRON OXIDE SAMPLE

Compound adsorbed	Adsorbed by Sample No. 1, %	Adsorbed by Sample No. 2, %
Piperidine	25.2	19.6
Nicotine	0.2	2.7
Arginine	34.2	15
Quinoline	1	22.9
Glutamic acid	81.6	15.53
Aspartic acid	87.5	14.9

Further experimentation on the effects of different factors on adsorption of organic compounds is contemplated for the future.

Summary

The extent to which eighteen pure organic compounds are adsorbed from 0.01 *M* solutions on the hydrous oxides of silicon, aluminum and iron and on fuller's earth has been determined. It is found that the extent of adsorption on silica of the compounds used is roughly proportional to their basic strengths, and roughly proportional to their acidic strengths in the case of adsorption on alumina. Adsorption by hydrous iron oxide was very irregular, possibly due to impurities on the adsorbent. The extent of adsorption by fuller's earth was somewhat similar to the adsorption by silica, but in a few cases there was no parallel.

EUGENE, OREGON

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF STANFORD UNIVERSITY]

THE INTERNAL PRESSURE OF LIQUID CARBON DIOXIDE FROM SOLUBILITY MEASUREMENTS

BY ELTON L. QUINN[1]

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In a previous paper[2] on the surface tension of liquid carbon dioxide it was found that carbon dioxide had an internal pressure much the same as carbon tetrachloride, toluene and chloroform. This was determined by comparing the total energy of surface formation with the values found for these compounds, according to the method of Hildebrand.[3] It seemed desirable to check these results with the solubility data of liquid carbon dioxide but it was found that the few determinations[4,5] of a quantitative

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[1] On sabbatical leave from the University of Utah.

[2] Quinn, THIS JOURNAL, **49**, 2704 (1927).

[3] Hildebrand, "Solubility," Chemical Catalog Company, New York, **1924**, p. 111.

[4] Thiel and Schulte, *Z. physik. Chem.*, **96**, 328 (1920).

[5] Büchner, *ibid.*, **54**, 665 (1906).