(2) A convenient and accurate method has been given for the determination of small quantities of hydrocyanic acid by the thiocyanate method, the potassium thiocyanate being leached out by means of acetone.

(3) Organic coloring matter can be removed from the thiocyanate solution by extraction with ethyl acetate.

HONOLULU, HAWAII.

THE SOLUBILITIES OF SEVERAL SUBSTANCES IN MIXED NONAQUEOUS SOLUTIONS.

BY J. W. MARDEN AND MARY V. DOVER.

Received January 19, 1916.

Introductory and Historical.—It is pretty generally agreed that the solubility of materials in mixed solvents is not as great as in one or other of the pure solvents. Mixtures of nonaqueous liquids are not infrequently recommended, however, for solution and separation. For example, the United States Pharmacopeia suggests the use of ether-chloroform for the extraction of quinine. Thorpe[1] suggests its extraction by means of a benzene-chloroform solution. In some cases the second solvent is used for the purpose of excluding undesirable materials. This can scarcely always be the case.

The solubilities of a number of substances have been determined in mixed aqueous solutions and a number of irregularities noted. The solubility of acetanilide,[2] for instance, has been shown to be greatest in 90% ethyl alcohol at 25°. If the concentration of the alcohol is either increased or decreased, the solubility is lowered. According to Müller,[3] the solubility of strychnine at 20° in water is 0.021 g. strychnine per 100 g., while in ether it is 0.0342 g. In water saturated with ether the solubility is 0.0166 g., which value is lower than in either solvent.

Dunkelski[4] has determined the solubilities of certain mercuric salts in given mixed nonaqueous solvents at different temperatures in an effort to show that chemical combination takes place between the solvent and solute in molecular proportions, much as we have the formation of hydrates in aqueous solution.

Bruner[5] has determined the solubilities of iodine in various mixed solutions of nonaqueous solvents. Bruner's work shows that the solubility of iodine is less than proportional to the percentage composition of the solvent. The curves given in his paper are not smooth, but there are no very sharp breaks which might indicate the presence of various solution

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[1] "Dictionary of Applied Chemistry," Vol. V, p. 677, Longmans, Green & Co., New York.

[2] Holleman and Antusch, *Rec. trav. chim.*, **13**, 293 (1894).

[3] *Apoth. Ztg.*, **18**, 258 (1903).

[4] *Z. anorg. Chem.*, **53**, 327 (1907).

[5] *Z. physik. Chem.*, **26**, 145 (1898).

compounds. Bruner gives an arbitrary formula by which he calculates the solubility of the iodine. In some cases the calculated values are very far from even approximating the observed values. He acknowledges that the temperature conditions under which his work was done were not carefully regulated.

This paper is the result of the first portion of a larger piece of work now under way to furnish some accurate data on the solubility of certain substances in mixed nonaqueous solvents, and to answer some of the questions resulting from a study of the meagre literature now existing on the subject.

Theoretical Considerations.—It has been shown algebraically[1] that the fractional precipitation of substances follows the same general law as Bunsen's law for the washing of precipitates. If Bunsen's law is stated in terms of a fraction, the quantity of material which it is desired to remove still clinging to the precipitate, bears a constant ratio to the amount which is removed by each successive portion of wash liquid, provided that the quantity of wash liquid is always the same in each operation. When C_1, C_2, C_3, etc., represent the weights of undesirable material remaining with the precipitate, after 1, 2, 3, etc., washings, the law can be expressed in the following manner:

$$\frac{C - C_1}{C} = \frac{C_1 - C_2}{C_1} = \frac{C_2 - C_3}{C_2} = K$$

When stated in this way, K represents the fraction of the total material (before the operation) which is removed by a given portion of wash liquid. It is evident, however, that if the expression gives a constant, the expression

$$\frac{C - C_1}{C_1} = \frac{C_1 - C_2}{C_2} = \frac{C_2 - C_3}{C_3} = K$$

should also give a constant (or nearly a constant) which has a somewhat higher numerical value.

The constant of distribution between two immiscible solvents is usually expressed in the latter way, in order to show the equilibrium relationship between the concentrations of the solute in the two solvents.

The value of K in the fractional expression $\frac{C - C_1}{C}$ = etc., has been calculated in the first four tables of results for each 10% change of the composition of the solvent (where the mixed liquid is considered the solvent) using the values C, C_1, C_2, etc., as the differences between the observed solubilities and the solubilities in the poorer solvent. As this indicates, if K is a constant, it represents the fraction of the total precipitable material removed by any 10% change in the composition of the solvent.

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[1] Blackman, *J. Phys. Chem.*, 13, 436 (1909).

When the percentage composition of the solvent is plotted against the solubility on the rectangular system, the curve is exponential in form. (Fig. 1*a*.—Acetanilide in chloroform-ether.) There are various ways in which the curves of a ternary system of this kind may be plotted.

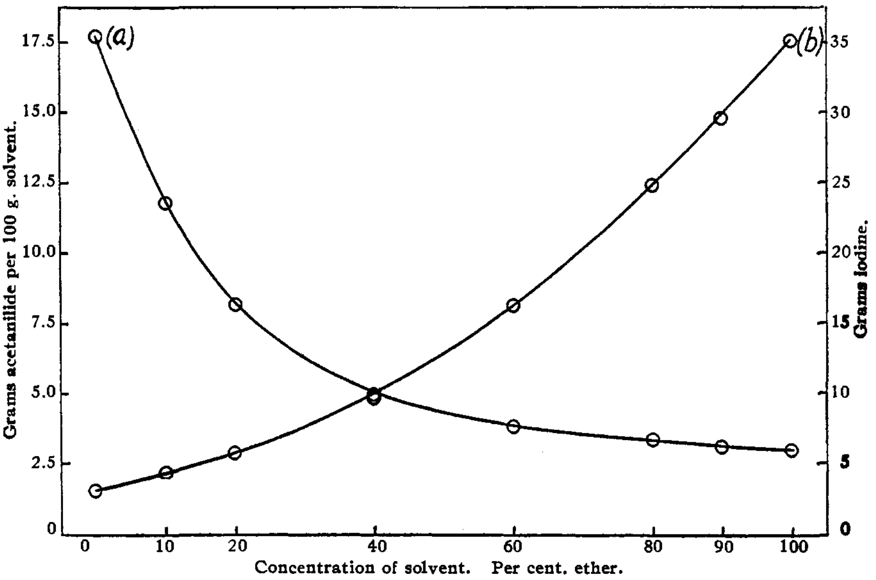

Fig. 1.

While the triangular system is convenient in many ways, the curves obtained by the rectangular system show the slope better for analytical purposes and for this reason are given here.

The fact that the curve is exponential in form may also be proved by applying the test of an exponential equation. If the log $(C - C_1)$, $(C_1 - C_2)$, etc., is plotted against the log $(1/C)$, $(1/C_1)$, etc., the result (Fig. 2*a*) is a straight line. It may also be seen from the slope of this curve that the exponent (n) is nearly equal to one. Two points have been disregarded here because the solubility change was less than 0.3 g. and the experimental error was consequently large.

If K is a constant, a formula can readily be developed by which the solubility for any percentage composition of solvent can be calculated from the average experimental value of K. Since K represents the fraction of the total amount of material (which may be precipitated by the poorer solvent) that is precipitated by any 10% portion of the poorer solvent, $(1 - K)$ represents the fraction still in solution. $(1 - K)^n$, then, represents the fraction of material still in solution after the addition of (n) 10% portions of the poorer solvent. If we let A equal the solubility in the better solvent and B equal the solubility in the poorer solvent, the formula, by the use of which the solubility may be calculated, is as follows:

$$[(1 - K)^n (A - B)] + B = \text{Solubility}$$

As will be seen in the cases of acetanilide and strychnine in chloroform-ether solutions, this relationship holds fairly well. When benzoic acid and iodine were tried in the same way K was far from a constant. It was found, too, that the curves, though smooth, were different from those obtained before. (Fig. 1*b*.—Iodine in chloroform-ether solutions.) When the log $(C - C_1)$, $(C_1 - C_2)$, etc., is plotted against the log $(1/C)$, $(1/C_1)$, etc., however, a straight line is obtained (Fig. 2*b*), the exponent (n) equalling very nearly two. From this, the expression $\frac{(C - C_1)}{\sqrt{C}} =$, etc., should give a constant.

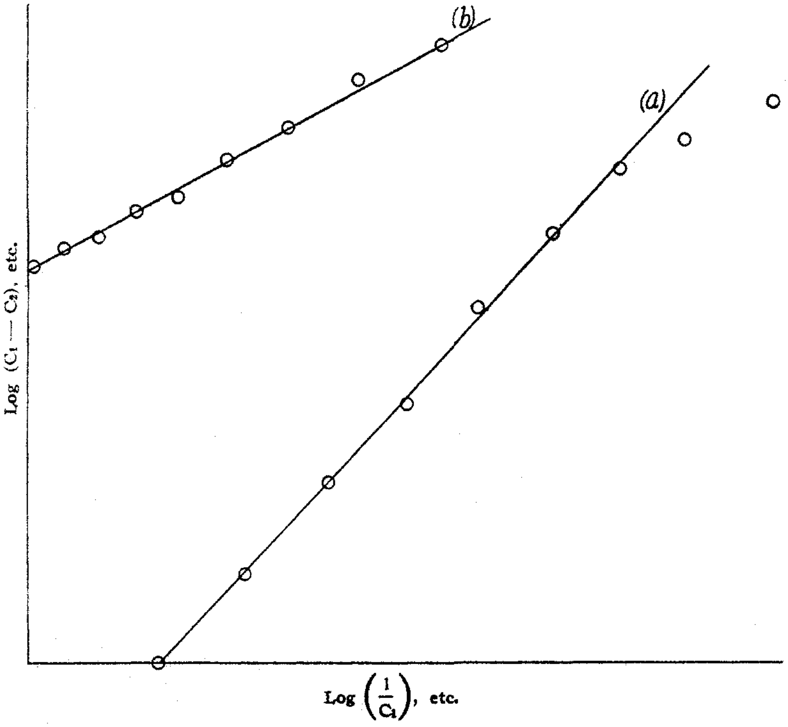

Fig. 2.

Other cases were found where the curves were broken, showing changes in the composition of the solute. The curves for acetanilide in acetone-benzene, benzoic acid in acetone-benzene and the same material in ethyl acetate-benzene solutions are given in Fig. 3*a*, *b* and *c*, respectively. No constant relationship could be developed to cover such curves.

Methods of Determination.—The solubilities as recorded in this paper were determined by shaking the mixed solvents with a large excess of the solid material for twelve to twenty hours in a thermostat, which regulated at 25° within one-tenth of one degree. The bottles had ground glass stoppers which were protected by a coating of beeswax and rosin, over which was tied a piece of rubber sheeting.

The saturated solutions were forced from the bottles upward with air pressure, through a glass-wool filter, into an especially constructed weighing pipet. This pipet is very similar to that described by Hall[1] but was in use before his publication. This type of pipet is not only convenient for weighing out such solutions, but if the small neck at the upper end of the apparatus be calibrated, the densities of the solutions can be determined in weighing out the liquids for the solubility determinations.

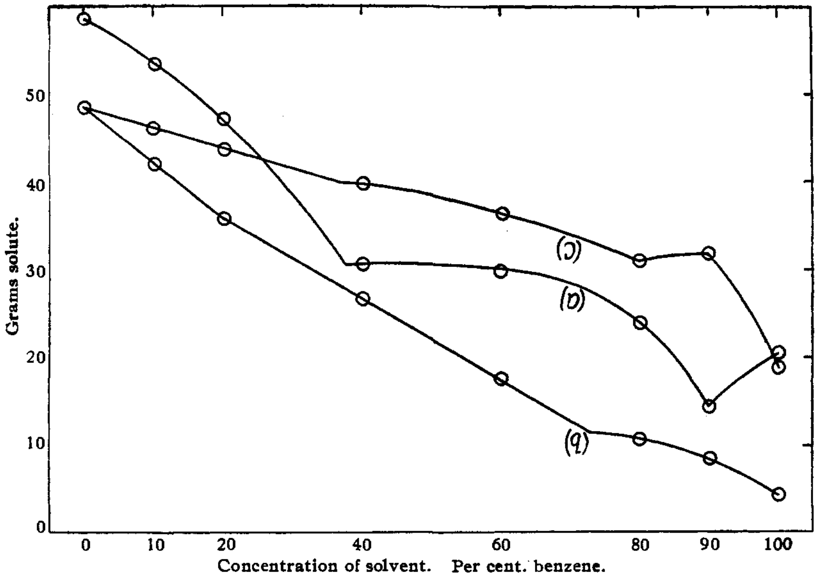

Fig. 3.

Most of the substances were determined by distilling off the solvent, drying in a sulfuric acid desiccator and weighing directly at ordinary temperatures. The iodine, however, was titrated immediately after having been weighed out, with carefully standardized sodium thiosulfate solution.

Purity of Materials.—The chloroform was Kahlbaum's best grade, the specific gravity of which was 1.479 at 25°. Linebarger[2] gives the specific gravity of pure chloroform at 25° as 1.4806. The ether was Merck's which had been distilled over sodium. It showed an average

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[1] This Journal, **37**, 2062 (1915).

[2] *Am. Chem. J.*, **18**, 442 (1896).

specific gravity of 0.709. Linebarger gives the specific gravity of ether at 25° as 0.7094. These solvents conformed in every respect to the tests for purity given by the United States Pharmacopeia and Krauch.[1]

The ether-chloroform solutions which were carefully weighed together are listed below in terms of percentage by weight with the specific gravities of the solutions.

TABLE I.

No.	% chloroform.	% ether.	Sp. gr. at 25°.
1	100	0	1.479
2	90.04	9.96	1.342
3	79.8	20.2	1.225
4	59.7	40.3	1.047
5	40.8	59.2	0.915
6	19.8	80.2	0.797
7	10.2	89.8	0.752
8	0	100	0.709

The acetone-benzene solutions were made from the best purified material available. The specific gravities of these solutions together with their percentage compositions are given in Table II.

TABLE II.

No.	% acetone.	% benzene.	Sp. gr. at 25°.
1	100	0	0.792
2	90	10	0.800
3	80	20	0.808
4	60	40	0.824
5	40	60	0.841
6	20	80	0.857
7	10	90	0.866
8	0	100	0.876

The specific gravity of acetone is given by Saposchnikow,[2] D_4^{15}, as 0.79705. The specific gravity of benzene at 25° is given by Linebarger as 0.87661.

The specific gravities of ethyl acetate-benzene solutions are stated in the same way.

TABLE III.

No.	% ethyl acetate.	% benzene.	Sp. gr. at 25°.
1	100	0	0.896
2	90	10	0.894
3	80	20	0.892
4	60	40	0.887
5	40	60	0.883
6	20	80	0.879
7	10	90	0.8775
8	0	100	0.876

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[1] "Testing of Chemical Reagents," D. Van Nostrand & Co., New York (1902).

[2] *J. Russ. Phys. Chem. Gesellschaft,* **28,** 229 (1896).

The specific gravity of ethyl acetate is given by Linebarger as 0.89156 at 25°. There seems to be some difference between this value and the value obtained in this work. This sample showed a boiling point of 77.5° on a standardized thermometer. By a comparison with the values given by other authors for the specific gravity of this substance at several different temperatures, the value given by Linebarger appears to be somewhat low.

The acetanilide conformed to the standards of the U. S. P. Two grams of the material left no weighable residue when ignited. The melting point was 113°. The determination of the nitrogen by the Kjeldahl method gave a value within 0.02% of the calculated percentage.

The strychnine, in addition to the requirements of the U. S. P., was tested for other impurities which might be in such a sample. None were found. There was no weighable residue left by the ignition of 2 g. of strychnine. This sample gave a melting point of 284°.

The iodine, which was resublimed, showed no test for any of the impurities described by the U. S. P. or by Krauch. The iodine was further carefully tested quantitatively by titration with sodium thiosulfate solution which had been standardized by means of an especially prepared potassium dichromate solution. The average weight of iodine, calculated from the volume of thiosulfate solution, was almost exactly that taken for analysis and considerably below the errors of titration.

No impurity was found by the tests described in the U. S. P. for benzoic acid. The melting point was 122°. Weighed samples were dissolved in hot water and titrated with tenth-normal sodium hydroxide solution, using phenolphthalein in the hot solution; 0.2000 g. of the acid gave an average weight by titration of 0.2002 g.

It might be pointed out here, however, that even though quite pure, these reagents may vary a small amount in their content of certain objectionable materials and yet conform to our standards of purity. A small amount of water or alcohol, for example, may be present in some of the liquid solvents and escape detection, which may have a marked effect on the solubility of some substance in it. This may explain, partly, at least, why some of the solubility results obtained here do not in all cases check those of previous observers. As an example of such discrepancies, the case of mercuric chloride might be cited. Four authors[1] give its solubility at 25° varying from 22.2 g. to 40 g. per 100 g. of ethyl acetate. In acetone at the same temperature, also, the solubility varies from 37.4 g. to 61.7 g. per 100 g. of solvent.

The Solubility Data.—In stating the data, the solubility of the solid substance is given in terms of grams per 100 g. of the mixed solvent, the

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[1] Seidell, "Solubilities of Inorganic and Organic Substances," D. Van Nostrand & Co., New York (1907).

percentage composition of the solvent being given. The results are listed in this way to show the decrease in solubility with the change in composition of the liquid mixture.

TABLE IV.

Acetanilide in ether-chloroform solutions at 25°.

Composition of solvent. % chloroform.	Observed solubility.	K = $\frac{C - C_1}{C}$.	Calculated solubility.
100	17.7	...	...
90	11.7	0.405	12.2
80	8.2	0.398	8.8
(70)	(6.2)	0.378	6.5
60	4.95	0.378	5.1
(50)	(4.25)	0.341	4.3
40	3.8	0.333	3.8
(30)	(3.5)	0.333	3.46
20	3.25	0.417	3.26
10	3.05	...	3.13
0	2.9	...	...
Average....................		0.373	

The values given in the above table in parenthesis have not been determined experimentally but read from curves (Fig. 1*a*). It will be noticed that K has a value that is very nearly constant. Speyers[1] has found the solubility of acetanilide in chloroform at 25° as 14.5 g. per 100 g. of the solvent.

TABLE V.

Strychnine in ether-chloroform solutions at 25°.

Composition of solvent. % chloroform.	Observed solubility.	K = $\frac{C - C_1}{C}$.	Calculated solubility.
100	15.3	...	..
90	7.1	0.538	7.1
80	2.77	0.612	3.3
70	(1.5)	0.462	1.5
60	0.65	0.574	0.7
50	(0.35)	0.476	0.47
40	0.27	...	0.18
30	(0.21)	...	..
20	0.15	...	..
10	0.09	...	..
0	0.02	...	..
		Average = 0.532	

Only the first few values given here are calculated for K. The reason for this is that when the solubilities get much below 0.3 g. the error of determination becomes large. The solubility of strychnine in chloroform and in ether at 25° is given by Müller[2] as 16.6 and 0.0182 g. in 100 g. of solvent, respectively.

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[1] *Am. J. Sci.*, [4] **14**, 294 (1902).

[2] *Apoth. Ztg.*, **18**, 258 (1903).

TABLE VI.

Benzoic acid in ether-chloroform solutions at 25°.

Composition of solvent. % chloroform.	Observed solubility.	$K = \frac{C - C_1}{C}$.	$K = \frac{C - C_1}{\sqrt{C}}$.
100	38.4	...	...
90	34.0	0.188	0.910
80	30.1	0.205	0.897
70	(26.6)	0.232	0.902
60	23.2	0.293	0.995
50	(20.8)	0.293	0.840
40	18.6	0.380	0.916
30	(16.8)	0.500	0.947
20	15.6	0.667	0.895
10	15.2	0.667	...
0	15.0	...	...
		Average =	0.913

The solubility of benzoic acid in chloroform at 25° is given by Bourgoin[1] as 14.3 g. in 100 g. chloroform and 31.35 g. in 100 g. of ether. It will be noticed here how very nearly constant are the values of K in this table.

TABLE VII.

Iodine in ether-chloroform solutions at 25° (Fig. 1*b*).

Composition of solvent. % chloroform.	Observed solubility.	$K = \frac{C - C_1}{C}$.	$K = \frac{C - C_1}{\sqrt{C}}$.
0	35.1	...	...
10	29.6	0.172	0.973
20	24.8	0.181	0.932
30	(20.2)	0.212	0.990
40	16.3	0.230	0.934
50	(12.7)	0.272	0.992
60	9.83	0.299	0.925
70	(7.5)	0.342	0.900
80	5.73	0.402	0.843
90	4.31	0.539	0.877
100	3.10	...	...
		Average =	0.931

Bruner gives the solubility of iodine in chloroform at about 15° as 3.02 g. per 100 cc. of solution. Molecular-weight determinations of iodine by the boiling-point method in ether indicate that it has a diatomic molecule.

Each set of data which has been given thus far, when plotted as in Fig. 1, gives smooth curves in which no breaks have been observed. It will be recalled that the values for acetanilide in ether-chloroform solutions give a constant for the simple relationship $K = \frac{C - C_1}{C}$. In acetone-benzene solutions, acetanilide gives a curve (Fig. 3*a*) not unlike the curves

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[1] *Ann. chim. phys.*, [5] 13, 406 (1878).

obtained when the solubilities of certain hydrates are plotted against temperature. Two other cases where broken curves have been obtained are cited below.

Table VIII.
Acetanilide in acetone-benzene solutions at 25°.

Composition of solvent. % benzene.	Observed solubility.
0	39.4
10	45.7
20	36.0
30	(33.0)
40	30.5
50	(30.0)
60	29.2
70	(20.0)
80	13.0
90	6.78
100	1.36

Table IX.
Benzoic acid in acetone-benzene solutions at 25°. (Fig. 3*b*.)

Composition of solvent. % benzene.	Observed solubility.
0	55.6
10	51.3
20	49.2
30	(47.0)
40	42.2
50	(37.0)
60	33.5
70	(31.0)
80	24.1
90	18.3
100	11.6

Table X.
Benzoic acid in ethyl acetate-benzene solutions at 25°. (Fig. 3*c*.)

Composition of solvent. % benzene.	Observed solubility.
0	41.2
10	28.1
20	29.0
30	(26.5)
40	23.9
50	(22.0)
60	20.4
70	(20.0)
80	16.5
90	14.0
100	11.6

A glance at the curves shows that no such expressions could be used on this curve as were used to calculate K in the data above.

Conclusions.

1. The solubilities of several substances have been determined in nonaqueous solutions.

2. It has been found that the solubilities of substances tried in ether-chloroform are exponential functions of the percentage composition of the solvent. The law which governs the fractional precipitation may be stated, if so desired, in the same way as the law of distribution or Bunsen's law for the washing of precipitates.

More cases of this kind have been observed and will be given in a later contribution.

3. The curves show only one case where the solubility in mixed solvents is greater than in either of the pure liquids. This is the case of acetanilide in a solvent made up of 10% benzene and 90% acetone.

4. It has been pointed out that the molecular weight of iodine in ether at its boiling point corresponds to Formula I_2, and it is well known that the molecular weight of benzoic acid in certain nonaqueous solvents is not greater than that which would correspond to a double molecule. If the formula $K = \frac{C - C_1}{\sqrt{C}}$ is true in ether-chloroform solutions, however, there must be a dissociation when the solid material is precipitated. The reason for this is the same reason that we use to explain the similar square-root relationship in the distribution of benzoic acid between benzene and

water.[1] It is quite unlikely that a substance going from solution to the solid form should dissociate. By analogy we should rather expect the reverse process.

The data for mercuric chloride, which are not given above because a small amount of moisture was found in the sample after the determinations were made, are interesting on this point. Mercuric chloride gives a normal molecular weight corresponding to the formula $HgCl_2$ by the boiling-point method in ether and yet the data show that the relationship $K = \frac{C - C_1}{\sqrt{C}}$ holds very closely.

We have no better explanation to offer at present than to say that perhaps solution compounds similar to the hydrates which we have in aqueous solutions are formed in some cases. These compounds are not stable, however, at the boiling point of the solvent any more than hydrates are at 100° and are decomposed when the solid material is precipitated by the addition of the poorer solvent.

Compounds of mercuric chloride and certain nonaqueous solvents have already been isolated by Dunkelski.[2]

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ON THE DIGESTIBILITY OF BREAD. I. SALIVARY DIGESTION IN VITRO.

[PRELIMINARY PAPER.]

By J. C. Blake.

Received March 14, 1916.

Summary.

The rate of digestion *in vitro* of the starch of bread can be followed readily and accurately by means of the polariscope, the only optically active substance entering the solution under the conditions herein stated being maltose. A rather large array of subsidiary findings surrounds this main observation, such as confirmation of the specificity of the starch of different plants, a clearer identification of some of the ingredients of the starch of the common cereals and the products of their hydrolyses (including two new substances), the variation of the activity of salivary amylase with the dilution and with the temperature, a comparison of amylases of different origin, and a comparison of the salivary digestibility of a number of standard breads. This paper is a report of progress rather than a finality.

[1] Nernst, "Theoretische Chemie," 483 (1903).

[2] *Loc. cit.*