[CONTRIBUTION FROM KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

A METHOD FOR DETERMINING SMALL QUANTITIES OF WATER IN METHYL ALCOHOL[1]

BY MARY M. RISING AND JOSEPH S. HICKS

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The need has been felt for some time by research workers in this Laboratory for a short but accurate method of detecting traces of water in methyl alcohol and of measuring the amount of water present. Such a method could be used conveniently to follow the progress of dehydration of ordinary methyl alcohol by successive treatments with a suitable drying agent. The method would be of use further to demonstrate at any time the presence or absence of water in methyl alcohol which has been previously dried and set aside for future use.

Accordingly, the authors have investigated the effect of small quantities of water upon methyl alcohol dissolved in a solvent chosen to fit the necessities of the case. Crismer,[2] Alexejew,[3] Rothmund[4] and Timmermans[5] have worked extensively upon the mutual solubility of two liquids, and the effect of a third component upon such a system. Crismer studied the behavior of alcohols in ligroin, and the effect of the addition of traces of water to such mixtures, and was the first to make use of the consequent change in physical properties of the mixtures as a test for the purity of alcohols.

Methyl alcohol may be completely dissolved in a chosen solvent, say, at room temperature. When the temperature of the clear solution is lowered beyond the point of complete miscibility a second phase appears. When the mixture is warmed again, at a definite temperature, which may be designated as the solution temperature, the second phase disappears and all parts of the solution are again identical in composition. The solution temperature depends upon the relative concentrations of the two components. Further, the solution temperature is changed by the introduction of a third component, water, and the amount of change is fixed for a definite amount of water. That is, there is a fixed solution temperature for definite concentrations of the three components of the mixture alcohol, solvent and water.

We therefore undertook to determine solution temperatures for methyl

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[1] This paper describes work done by Joseph S. Hicks in partial fulfilment of the requirement for the degrees of Master of Science and Doctor of Philosophy at the University of Chicago, **1925**.

[2] Crismer, *Bull. acad. roy. Belg.*, [3] **30**, 97 (1895); *Bull. soc. chim. Belg.*, **18**, 18 (1904); **20**, 294 (1906).

[3] Alexejew, *Wied. Ann.*, **28**, 305 (1886).

[4] Rothmund, *Z. physik. Chem.*, **26**, 433, 455 (1898). "Löslichkeit und Löslichkeitbeeinflussung," Barth, Leipzig, **1907**, p. 158.

[5] Timmermans, *Z. Elektrochem.*, **12**, 644 (1906); *Z. physik. Chem.*, **58**, 129 (1907).

alcohol-solvent-water mixtures.[6] Anhydrous methyl alcohol was prepared from pure methyl alcohol of commerce by the usual treatment with lime. Samples of alcohol containing various amounts of water were made up from this anhydrous alcohol, the exact amount of water present being determined by specific-gravity measurements. These samples were sealed and set aside for solution-temperature readings.

Careful study was given to the selection of a suitable solvent. Such a solvent must be miscible with alcohol to a degree, but not completely miscible at all temperatures. It may have a boiling point higher than that of methyl alcohol, but not much lower. Since methyl alcohol boils at 66° the solution temperatures of the alcohol-solvent-water mixture should range from 60°, to, for convenience, 0°. A number of solvents were tried by us, including chloroform, kerosene, carbon disulfide, benzene, nitrobenzene, a mixture of benzene and ligroin and ligroin. Low-boiling ligroin was found to show the best range of solution temperatures. Ligroin tends to change in composition if kept for frequent use over a long period of time, due to unequal rates of evaporation of the various ingredients. This difficulty was largely obviated by a distillation of the low-boiling ligroin into several fractions, each of which was collected over a range of five degrees. Of these fractions the one boiling at 50–55° was chosen.[7]

Several liters of the low-boiling ligroin were thoroughly dried over fresh sodium wire and then distilled from the sodium, the fraction boiling at 50–55° being collected in small dry containers which were sealed as soon as filled. Such a distillate can be kept for some time without important change in composition due to evaporation.

The solution-temperature observations were made according to the following procedure: two parts by volume of ligroin of 50–55° boiling point to one part by volume of the methyl alcohol to be tested are brought into a test-tube, each reagent being measured from a dry pipet. The homogeneous mixture is cooled until the appearance of a cloudiness. A thermometer is placed in the solution, which is allowed to grow warm rather gradually to the temperature at which the second phase disappears. The temperature at which the solution again becomes homogeneous is recorded as the solution temperature. It is noteworthy that the temperature at which the second liquid phase appears when the homogeneous mixture is slowly cooled is identical with that at which it disappears when the cloudy solution is slowly warmed.

Cols. 2, 3 and 4 of Table I contain the results of the work so far discussed. The contents of Col. 5 will be explained later.

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[6] See Bur. Standards *Bull.*, **9**, 345 (1913), for a discussion of somewhat similar work with ethyl alcohol.

[7] Crismer also used ligroin as the solvent for methyl alcohol in his work but of a higher boiling point than that selected by us.

TABLE I

WATER CONTENT AND SOLUTION TEMPERATURES OF METHYL ALCOHOL (1 VOL.) WITH LIGROIN (2 VOL., B. P. 50–55°C.) AND WITH HEXANE (2 VOL.)

1 Sample of CH_3OH	2 d_4^{15}[a]	3 Purity[b]	4 Soln. temp., °C. ligroin, b. p. 50–55° as solv.	5 Soln. temp., °C. hexane, b. p. 68.6–69.0° as solv.
1	0.79578	100.00	8.65	36.55
2	.79634	99.80	10.70	37.90
3	.79676	99.65	12.05	38.95
4	.79718	99.50	13.90	40.05
5	.79760	99.35	15.35	41.00
6	.79810	99.18	17.00	42.05
7	.79845	99.05	18.25	43.00
8	.79947	98.69	21.55	45.00
9	.80016	98.56	22.80	45.55
10	.80026	98.41	23.65	46.25
11	.80058	98.30	24.95	46.90
12	.80140	98.01	27.15	48.05
13	.80165	97.92	27.90	48.50
14	.80292	97.48	30.90	50.15
15	.80390	97.13	33.20	51.10
16	.80407	97.07	33.75	...
17	.80488	96.79	35.60	...
18	.80590	96.43	37.50	...
19	.80673	96.13	39.10	...
20	.80698	96.05	39.55	...

[a] Determinations were made with an Ostwald pycnometer upon air-saturated alcohol.

[b] Expressed in parts in one hundred of alcohol. Water regarded as the impurity.

The data in Cols. 3 and 4 are conveniently recorded in the accompanying graph, which shows the variation in water content of the alcohol with change in solution temperature. By reference to Curve I the water content of any sample of alcohol containing not more than 4% of water may be determined, providing the solution temperature of the sample with ligroin of 50–55° boiling point is known.

Curve I has been used for this purpose in this Laboratory. It is obvious that the curve will reach a limit of usefulness, however, when the supply of ligroin used in accumulating data for the curve is exhausted. Since the ingredients of ligroin from different sources vary considerably, it will become necessary to obtain a new set of solution-temperature data when a new batch of solvent has been prepared.

The method under discussion was standardized and its usefulness enhanced by the use as solvent of pure synthetic normal hexane of boiling point 68.6–69.0° (uncorr.) at atmospheric pressure. Hexane is the chief ingredient of low-boiling ligroin. The use of a pure solvent afforded a standard and permanent set of solution-temperature data. Solution-temperature determinations were made upon mixtures of hexane (two volumes) with samples of methyl alcohol (one volume) containing measured amounts of water by exactly the same procedure as with ligroin. The solution temperatures of the alcohol-water-hexane system are recorded in Col. 5 of the table. The relation of variation of water content of the alcohol to change in solution temperature is shown in Curve II. By consulting Curve II, the water content of any sample of alcohol containing not more than 3% of water may be determined, providing the solution temperature of that sample with hexane is known.

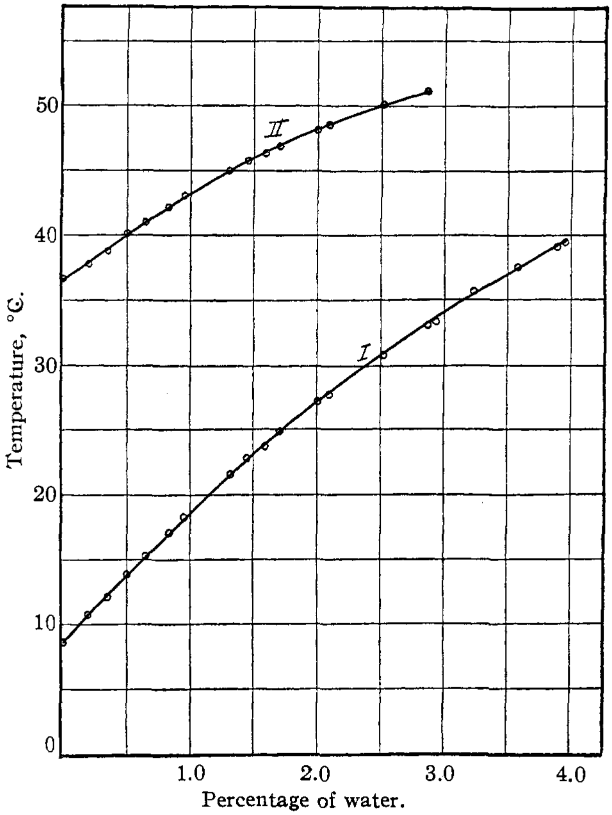

Fig. 1.—Curve I. Water content and solution temperatures of methyl alcohol (1 vol.) with ligroin (2 vol., b. p. 50–55°). Curve II. Water content and solution temperatures of methyl alcohol (1 vol.) with hexane (2 vol.).

It will be observed that the range of solution temperatures with ligroin is 31° for 4% of water, and with hexane over 15° for 3% of water. These are sufficiently wide ranges to make the method a delicate one, and this feature is therefore worthy of particular emphasis.

Summary

1. This paper describes an application of Crismer's method for measuring quantitatively the amount of water in methyl alcohol.

2. The method is based upon the determination of solution temperatures of the three component systems methyl alcohol-water-ligroin, and methyl alcohol-water-hexane; the exact amount of water present in a given case is determined, once for all, by specific-gravity measurements.

3. The wide range of solution temperatures observed with the two solvents used makes the method accurate and sensitive.

4. The use of pure hexane as solvent is recommended, since by its use a set of permanent data can be obtained.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE DIVISION OF BIOCHEMISTRY AND PHARMACOLOGY, UNIVERSITY OF CALIFORNIA MEDICAL SCHOOL]

OBSERVATIONS UPON THE SYNTHESIS OF PYRROLE- AND PYRROLIDONE-CARBOXYLIC ACIDS, AND UPON THE SYNTHESIS OF ALPHA-THIONIC ACID OF PYRROLE[1]

BY C. M. MCCAY AND CARL L. A. SCHMIDT

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Introduction

One of the problems which continually confront biochemists is the lack of a satisfactory supply of the constituents of the protein molecule. With the exception of glutamic acid[2] which is used in Japan as a condiment the production of the amino acids is extremely limited. In certain instances the known methods of preparation are such as to yield products of doubtful purity. This is particularly true of the amino acids which contain the pyrrole ring. While our attempts to synthesize proline have been unsatisfactory some additional information regarding the behavior of certain of the pyrrole compounds has been gained.

The two methods for the synthesis of proline which are best known are those of Sörensen[3] and of Fischer and Zemplén.[4] The former carried out his synthesis by permitting the diethyl ester of sodium phthalimidomalonic acid to react with trimethylene-bromide with the formation of α-bromopropyl-phthalimidomalonic ester. When this substance is boiled with potassium hydroxide, proline, glycine and a number of other products

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[2] Ikeda, Eighth Intern. Cong. Appl. Chem., **18**, 147 (1912). Ikeda and Suzuki, U. S. pat. 1,015,891, 1,035,591 (1912). Schmidt and Foster, *Proc. Soc. Exptl. Biol. Med.*, **18**, 205 (1921).

[3] Sörensen, *Compt. rend. trav. lab. Carlsberg*, **6**, 137 (1905).

[4] Fischer and Zemplén, *Ber.*, **42**, 1022, 2989 (1909).