into the apparatus, determining the boiling point of the solution, and then calculating the amount of solvent present in the vapor phase and in the condenser, with the aid of Equation 9, the values of L_v and of a being known. With a given sized flame and uniform conditions of experimentation it is probable that the amount of solvent which exists outside of the solution at its boiling point will be practically a constant for a given piece of apparatus. Having determined the boiling-point raising for a given solution and having applied the necessary corrections as explained in Section 6, the molecular weight of a solute can then be accurately calculated with the aid of Equation 9, provided of course, that the solute and solvent are sufficiently alike chemically to make the laws of ideal solutions applicable. This assumption can, of course, be tested by making a series of boiling-point determinations and noting whether they all give the same value for the molecular weight.

If there is reason to believe that solvation occurs, the true molecular weight of the unsolvated solute can still be calculated from Equation 9, provided the solution is an ideal solution, that is, provided Equation 9 is really applicable when the influence of solvation is taken account of. In order to do this it is only necessary to substitute the following expression for x in Equation 9:

$$x = \left(\frac{1000}{M} - s\underline{N}_1\right) \div \left(\frac{1000}{M} - s\underline{N}_1 + \underline{N}_1\right)$$

and to make two boiling-point determinations, one giving Δt_B equal to, say, 3°, and another giving Δt_B equal to 6°, and from the two expressions thus obtained the quantity s, which represents the number of solvent molecules combined with each solute molecule, can be eliminated. This procedure will then give an accurate value of the molecular weight of the solute provided of course, that s is constant over the temperature range in question, and provided that the solution is sufficiently near an ideal solution to make Equation 9 applicable.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 319.]

A UNIQUE CASE OF A LIQUID THAT EXHIBITS A MINIMUM SOLUBILITY IN AN UNSTABLE REGION.

BY MARSTON TAYLOR BOGERT AND JACOB EHRLICH.

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Introductory.

When the hydrate of 3,5-dimethoxy-acetophenetide described in another article[1] was first prepared and its approximate solubilities in

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[1] "The Synthesis of Certain Substituted Pyrogallol Ethers, Including a New Acetophenetide Derived from the Ethyl Ether of Syringic Acid," Bogert and Ehrlich, THIS JOURNAL, 41, 798 (1919).

various solvents were being ascertained, the striking observation was made that on slowly cooling a clear solution of the substance in boiling water there appeared first a cloud consisting of minute droplets which disappeared on further cooling with formation again of a clear solution, and on still further lowering of the temperature white crystals separated.

Since an explanation of these unusual phenomena seemed highly desirable, a careful study was made of the solubilities of the hydrate in water, with the interesting results described in the following pages.

3,5-Dimethoxy-acetophenetide monohydrate is difficultly soluble in water at room temperature, the solubility increasing with rise of temperature up to 87.5° (see Fig. 1), when the solid in contact with water melts. At this point two liquid phases are formed and there is a marked discontinuity of the solubility curve. Inspection of the solubility curve of the liquid hydrate also shows an increased concentration of substance in solution as the temperature rises above 87.5°. Below this point, *i. e.*, in the region unstable with respect to liquid hydrate, the solubility of the latter decreases with falling temperature until a point somewhere between 68.5° and 58.1° is reached. If the temperature is now still further lowered, the solubility of the liquid hydrate *increases*, hence the liquid hydrate must possess a minimum of solubility at about 63°.

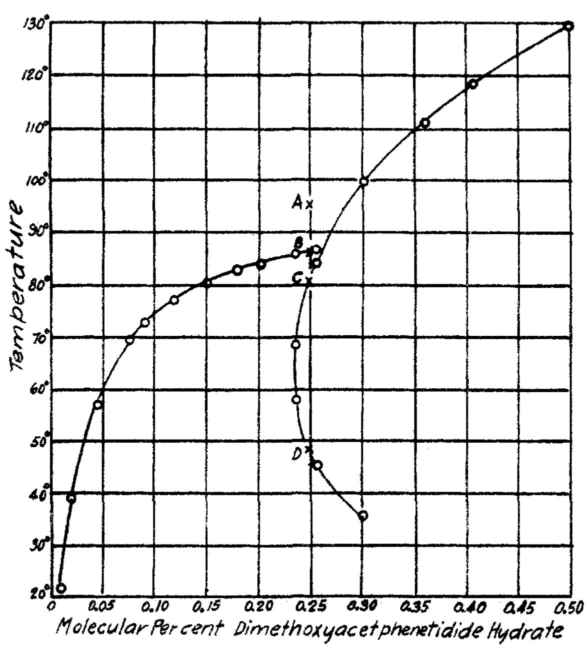

Fig. 1.

If, for example, a 0.250 molecular per cent. solution of the hydrate in water is slowly cooled from the temperature A until the point B is passed, no solid hydrate will precipitate, owing to the readiness with which the solution may be supercooled at this concentration with respect to the solid phase. On further cooling of the solution, it remains clear until the point C is reached, when a cloud forms consisting of minute drops of the liquid hydrate. This cloud persists until D is reached, when a clear solution is once more obtained. The temperature of this solution, still supercooled with respect to solid, must then be appreciably lowered before the solid hydrate suddenly precipitates.

Thus it will be seen that for this concentration the liquid hydrate possesses two saturation temperatures, both of which lie in the unstable region; while for concentrations over 0.251 molecular per cent., the upper point will be in the stable and the lower in the unstable region.

The authors have not found described in the literature any other substance showing this peculiar behavior, and are therefore led to believe that it is the first instance of the kind observed.

Experimental.

Kendall's freezing-point curve method[1] was employed up to 57°, above which point the evaporation of water became too rapid for accurate determination. From this temperature, therefore, up to the melting point of the hydrate under water (87.5°) the solubilities of the solid were carefully determined by the sealed-tube method, essentially as described by Smith and Eastlack.[2] The solubility measurements of the liquid hydrate in water were made according to the sealed-tube process of Rothmund[3] with very satisfactory results.

Up to 100° a standard mercury thermometer was employed, graduated in tenths of a degree; above this point there were used accurately calibrated mercury thermometers of the Anschuetz type graduated in fifths of a degree. The temperature readings were corrected for exposed stem and, as given in the tables, are accurate to within less than ±0.2°, *i. e.*, these were the average deviations from the mean, each reading being the average of several.

The volume of the gas space in the closed tubes was of the order of 4 cc. Nevertheless, no correction was necessary for the weight of water in the vapor phase except from the point 99.8° up, because the molecular percentage of the dimethoxy-acetophenetide hydrate was very low and the actual liquid water present about one g. At 99.8 failure to make this correction causes the calculated molecular percentage of hydrate to be too low by 2 units in the third decimal place. At the last point on the curve, namely 173.6°, the error is 5 units in the second decimal place. Below 99.8°, the third place is not affected.

The volume of gas space above the liquid at the saturation temperature was measured by marking the tubes at the level of the inclosed liquid, and then opening and filling to the mark with water from a buret. The correction involved being small for the region investigated, this method was sufficiently accurate.

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[1] THIS JOURNAL, 36, 1222 (1914).

[2] *Ibid.*, 38, 1261 (1916).

[3] *Z. phys. Chem.*, 26, 444 (1898).

The experimental data for the solid and liquid hydrates are given in Tables I and II, respectively.

TABLE I.

The Solid Hydrate in Water.

Wt. $C_{12}H_{17}O_4NH_2O$. G.	Wt. H_2O. G.	Vol. of gas space. Cc.	Wt. of H_2O vapor (calc.). G.	Molecular per cent. $C_{12}H_{17}O_4NH_2O$.	Temp. of satn. ° C.
0.0361	25.00	......	......	0.010	21.8
0.0722	25.00	......	......	0.020	39.4
0.1623	25.00	.....	......	0.046	57.0
0.0110	1.0118	......	......	0.076	69.5
0.0131	1.0104	......	......	0.091	72.8
0.0176	1.0257	......	......	0.120	77.1
0.0213	0.9900	......	......	0.151	80.2
0.0262	1.0148	......	......	0.180	82.6
0.0288	0.9940	......	......	0.203	84.2
0.0340	1.0027	......	......	0.237	86.0[1]
0.0369	1.0023	......	......	0.257	86.9[2]

[1] Same tube. [2] Same tube.

TABLE II.

The Liquid Hydrate in Water.

0.0340	1.0027	...	..	0.237	68.5[1]
0.0340	1.0027	...	..	0.237	58.1[1]
0.0369	1.0023	...	..	0.257	84.3[2]
0.0369	1.0023	...	..	0.257	45.6[2]
0.0421	0.9733	4.3	0.0025	0.303	99.8[3]
0.0421	0.9733	...	..	0.301	35.6[3]
0.0512	0.9943	3.2	0.0027	0.361	111.1
0.0579	0.9980	3.8	0.0040	0.407	118.4
0.0709	0.9961	3.8	0.0054	0.499	129.2
0.1737	0.5985	3.2	0.0135	2.041	173.6

[1] Same tube. [2] Same tube. [3] Same tube.

On plotting molecular percentages against the corresponding saturation temperatures, two smooth curves are obtained, one for the solid and the other for the liquid hydrate. In the accompanying figure, the results are indicated graphically up to 129.2°, corresponding to 0.499 molecular per cent. of the hydrate.

The point corresponding to 173.6° and 2.041 molecular per cent., also lies on the curve, and was the first of a series of points, a few molecular per cent. apart, which it was intended to determine in order to ascertain the critical solution temperature and close the upper portion of the liquid-liquid curve of the two-component system. However, since a mixture of the hydrate and water containing approximately 10 molecular per cent. of the former failed to clear at 200°, the solubilities of the liquid hydrate in water were not determined above 173.6° because of the experimental difficulty involved. Moreover, at 200° it was evident that some decomposition was occurring as the mixture turned blue. This is probably explainable on the assumption of hydrolysis of the acetophenetide at this temperature with formation of free amine which latter acquires a blue coloration very quickly in the presence of air.

The solubilities of the liquid hydrate below the melting point of the solid under water, that is in the unstable region, were determined by first agitating the sealed tubes in a water-bath heated above the saturation temperature of the solid, until the last faint traces of crystals had disappeared, and then cooling. The procedure was then that of Rothmund.[1] Obviously for the 0.301 molecular per cent. concentration, it was only necessary to allow the tube to cool after determining the upper equilibrium point, since the latter was in the stable region. No supersaturation of the liquid hydrate in water was observed.

In concentrations greater than 0.301 molecular per cent., the requisite supercooling of the solution with respect to solid could not be obtained, the solid hydrate forming before all the liquid phase had dissolved. Nevertheless, enough points were determined on the solubility curve of the liquid hydrate in the unstable region to prove clearly that the liquid hydrate possessed a minimum of solubility in water and that this point lay in the unstable region.

Repeated attempts to discover a similar behavior of water dissolved in the fused hydrate were without result, due to inability to obtain sufficient supercooling with respect to the solid hydrate.

Summary.

The solubilities in water of the monohydrate of 3,5-dimethoxy-acetophenetide have been determined from 21.8° to 173.6°. The fused hydrate has been shown to possess a minimum of solubility in the region unstable with respect to liquid hydrate.

NEW YORK, N. Y.

THE STANDARDIZATION OF THE SULFUR BOILING POINT.[2]

BY E. F. MUELLER AND H. A. BURGESS.

Received February 2, 1919.

CONTENTS.—I. Introduction. II. Apparatus Used. III. Description of Experiments; *a*. Comparison of Radiation Shields; *b*. Comparison of Types of Boiling Apparatus; *c*. Purity of Sulfur; *d*. Relation between Vapor Pressure of Sulfur and Temperature. IV. Summary. Appendix. Proposed Standardization of the Sulfur Boiling Point.

I. Introduction.

The sulfur boiling point occupies a position of unusual importance among the thermometric fixed points on account of the care and accuracy with which its temperature has been determined, the precision with which

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[1] *Loc. cit.*

[2] Publication of this paper has been authorized by the Director of the Bureau of Standards.