7. Sugars are hydrated to an unusual degree in their dilute solutions.

8. Colloids particularly substantiate the assumption that the retardation of the V. C. is a hydration effect.

9. The V. C. of water has been shown to vary as the size of the bore of the tube. The thickness of wall of the tube apparently has no effect on the V. C.

10. No mathematical statement has been derived by which the absolute degree of hydration of substances can be calculated. The effects on the V. C. are believed to be specific in nature.

The author desires to express his sincere appreciation of the kind help and suggestions given by Professor James H. Walton, under whose direction the work was outlined and carried to completion.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN.]

THE EFFECT OF DISSOLVED SUBSTANCES ON THE VELOCITY OF CRYSTALLIZATION OF FORMAMIDE.[1]

BY ALBERT BRANN.

Received May 7, 1918.

Introduction.

In the foregoing paper it has been shown that the chief influence of dissolved substances in retarding the V. C. of water is probably due to the combination of the solvent and solute to form solvates. It was therefore of interest to find out if analogous phenomena occur in solvents other than water. To determine this point experimentally, formamide was chosen as the best solvent, because it, of all organic liquids, is most closely allied to water in its physical properties.

Historical.

Walden[2] first pointed out the similarities between formamide and water. Formamide dissolves many of the more common inorganic salts. Bruni and Mannuelli[3] have shown that just as water hydrolyzes the salts of weak bases, such as those of bismuth and copper, forming unstable basic salts, so formamide, by a process of aminolysis, forms basic salts of these same metals. Rohler[4] has isolated basic salts of copper, cobalt, nickel and zinc. He has also obtained amidates similar to hydrates, such as $PbCl_2.HCONH_2$. Davis and Putnam[5] have determined the tempera-

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[1] Part of a thesis submitted to the graduate school of the University of Wisconsin as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Walden, *Z. phys. Chem.*, **46**, 145 (1903); **55**, 230 (1906); **75**, 575 (1910); *Bull. Imp. Acad. Sci.*, St. Petersburg, 1911.

[3] *Z. Elektrochem.*, **11**, 554 (1905).

[4] *Ibid.*, **16**, 418 (1910).

[5] Jones, "Conductivities and Viscosities in Solvents," *Carnegie Inst. Publication* **230**.

ture coefficients of the electrical conductance of a number of formamide solutions. From these measurements they argue that the same substances which are hydrated most in aqueous solutions are the ones that are solvated most in formamide solutions. Gertrud Kornfeld[1] has pointed out that experiments on the freezing points of solutions of cupric sulfate, ferric chloride, sodium sulfate and calcium chloride in formamide furnished evidence of the existence of solvates in solution.

Experimental.

The experiments with formamide were carried out in the same manner as those with water and with the same tubes. The solvent was prepared in this laboratory and its preparation is described in a previous communication.[2]

Work was confined to the use of selected salts of the alkali metals. All compounds containing water of crystallization were carefully dehydrated at as low a temperature as permitted. Lithium chloride, $LiCl.2H_2O$, was dehydrated by heating the salt to 90° in a vacuum desiccator containing $CaCl_2$. The vacuum was released from time to time and the desiccator swept out by a current of dry air. All flasks and the crystallization tubes were thoroughly dried before solutions were poured into them.

Discussion of Results.

The V. C. of Pure Formamide.—Pure formamide proved to be very unstable when undercooled, and spontaneous crystallization set in even at small degrees of undercooling. The freezing point of formamide is 2.25° and when undercooled to —2.5° was stable enough to give good results in this work. This was not as low a temperature at which to make the experiments as was really desired, for the liquid was undercooled only 4.75°. However, relative effects of different substances on the V. C. could be studied and all of the experiments were run at —2.5°.

Once only was it possible to obtain a reading with pure formamide at as low a temperature as —4.65°. Its V. C. at this temperature is 25.4 cm. per minute. This value is about one-seventh that of the V. C. of water at the same degree of undercooling. That the V. C. of formamide is much less that that of water can be explained in part on the basis that the former is a more highly associated liquid than the latter. The association factors of the two liquids are water 3.81 at 10° (Ramsay and Shields),[3] formamide 6.18 at 20–30° (Turner and Merry).[4] In both cases, the molecular aggregates must undergo rearrangement before crystallization can take place. Formamide being more highly associated than water,

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[1] *Monatsh.*, **36,** 865–897 (1915).

[2] Brann, THIS JOURNAL, **40,** 793 (1918).

[3] *J. Chem. Soc.*, **63,** 1106 (1893).

[4] *Ibid.*, **97,** 2076 (1910).

the resistance to crystallization due to intermolecular attraction would be greater, and the V. C. less.

The V. C. of benzene was also determined. Benzene was stable and easily undercooled 10°. When undercooled 7°, its V. C. is 476, nearly 3 times that of water. Benzene is not an associated liquid and consequently the inter-attraction of its molecules is very slight compared to that of the associated liquids, water and formamide. Hence, in benzene, the molecular resistance to crystallization is small and the V. C. large.

The above discussion is offered as an explanation of the crystallization phenomena encountered with these 3 liquids, and the limited amount of experimental data presented here seem to substantiate the assumptions made. However, further work with other liquids is necessary before a generalization of real worth can be made. There are probably important factors other than the disrupting of large molecular aggregates in these crystallization phenomena, both in regard to the pure liquids and their solutions.

The Effect of Alkaline Halides on the V. C. of Formamide.—In Table I are incorporated the results obtained with 0.1 *M* solutions of alkaline halides. The retardation of the V. C. is in exactly the same order as it is with the same substances in water. Salts of lithium retard the most, those of sodium less than the lithium, and those of potassium least of all. A series of experiments was run using sodium and potassium bromides in equimolecular proportions at different concentrations (see Table II). Sodium bromide retards the V. C. more than potassium bromide in all concentrations. These results are exactly analogous to the effects produced in a like series of experiments[1] by the same two substances on the V. C. of water.

In order to be sure that the difference in freezing points of the solutions was not an important factor as regards the relative values of the V. C., the freezing points of the 0.1 *M* solutions of sodium bromide and potassium bromide in formamide were determined. They were found to be identical. Both substances lowered the freezing point of the pure solvent 0.7°.

TABLE I.

The Effects of Alkaline Halides on the V. C. of Formamide. Temperature —2.5°.

Substance.	Concentration. Gram mols per liter.	Time per meter in seconds.
Pure formamide	...	351.0
LiBr	0.1	862.0
NaBr	0.1	819.0
KBr	0.1	718.0
LiCl	0.1	860.0
KCl	0.1	743.0
NaI	0.1	824.0
KI	0.1	723.0

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[1] Walton and Brann, THIS JOURNAL, **38**, 1161 (1916).

TABLE II.

The Effects of Sodium and Potassium Bromides on the V. C. of Formamide.

Temperature —2.5°.

NaBr mols per liter.	Time per meter in seconds.	KBr mols per liter.	Time per meter in seconds.
0.15	996.0	0.15	852.0
0.10	819.0	0.10	718.0
0.05	550.0	0.05	481.0
0.025	441.0	0.025	436.0

From these experiments it is probable that the relative effect produced by dissolved substances on the V. C. of formamide is chiefly due to solvation in solution. Further, those substances which are solvated to the greatest extent in water are also solvated to the greatest extent in formamide.

Summary.

1. The velocity of crystallization of formamide has been determined at several temperatures.

2. Formamide is very susceptible to spontaneous crystallization even when but slightly undercooled.

3. The values for the V. C. of the pure liquids, water, formamide and benzene are numerically wide apart. An explanation why this should be so is offered.

4. The effect of dissolved substances on the V. C. of formamide is probably a solvation effect.

5. Substances which are hydrated most in aqueous solutions are also solvated most in solutions of formamide.

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EXPERIMENTS IN RHYTHMIC BANDING.

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Received May 10, 1918.

Rhythmic banding of precipitates was first observed and recorded by Liesegang, hence the name "Liesegang's rings." His original experiment dealt with the rhythmic precipitation of silver chromate in gelatin. A solution of silver nitrate was poured on a solid gel containing dilute potassium chromate. The precipitate of silver chromate formed was not continuous but marked by gaps or empty spaces at regular intervals.

Ostwald[1] held that the silver chromate of Liesegang's original experiment formed a supersaturated solution. When crystallization started at any given point the excess beyond that required for saturation migrated to the points where crystals were forming. By repetition of this process gaps and bands were produced.

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[1] *Z. phys. Chem.*, **23**, 365 (1897).