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

THE EFFECT OF DISSOLVED SUBSTANCES ON THE VELOCITY OF CRYSTALLIZATION OF WATER. II. THE EXISTENCE OF HYDRATES IN SOLUTION AS AN EXPLANATION OF THE RETARDING EFFECT OF THE SOLUTE ON THE VELOCITY OF CRYSTALLIZATION OF WATER.

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Received March 14, 1916.

In a recent paper by the authors[1] it was shown that in the retardation of the velocity of formation of ice crystals from an undercooled solution there is a relation between the number of atoms in a molecule of the solute and its retarding effect. More recent experiments show that this relation does not always hold and in the instances cited is probably largely accidental.

The object of the present paper is to point out that *those substances that undergo hydration in solution to the greatest extent are also the substances that show the greatest retarding effect upon the V. C. (velocity of crystallization) of ice from undercooled solutions.* The experimental data that show this relationship were obtained in the manner described in the previous paper. The results are incorporated in the accompanying tables.

The investigation of the existence of compounds of solute and solvent in solution has been the subject of much investigation.[2] By means of conductivity, lowering of the freezing point and other measurements, Jones[3] and his students have obtained data that show the relative amounts of hydration that many salts undergo in solution. Beginning with those salts that are least hydrated, the following list shows the relative hydration of some of the more common chlorides: ($NaCl$, NH_4Cl, KCl) $LiCl.2H_2O$, $BaCl_2.2H_2O$, $SrCl_2.6H_2O$, $CaCl_2.6H_2O$, $MgCl_2.6H_2O$, $FeCl_3.6H_2O$, $AlCl_3.6H_2O$. The compounds in this group that have been used by the authors are given in Table I. They retard the crystallization of water in exactly the same order, *viz.*, those most hydrated according to Jones, show here the greatest retarding effects.

In this connection the experiments of Smirnoff[4] are of interest. This investigator determined the amount of different salts required to cause the separation of butyric acid from a 16.64% aqueous solution of the acid at

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[1] THIS JOURNAL, **38,** 317 (1916).

[2] For a review of this subject see: "Hydrates in Solution. A Review of Recent Experimental and Theoretical Contributions," E. W. Washburn, *Tech. Quart.*, **21,** No. 4, Dec., 1908.

[3] *Publ. Carnegie Inst.*, No. **60.**

[4] *Z. physik. Chem.*, **58,** 667 (1907).

TABLE I.

The Velocity of Crystallization of 0.1 *M* Undercooled Aqueous Solutions of Chlorides.
Temp. —9.1°.

Compound.	Time per meter in seconds.	Velocity cm. per min.	Compound.	Time per meter in seconds.	Velocity cm. per min.
HCl	24.0	250	$CuCl_2.2H_2O$	40.0	150.0
NaCl	24.3	247	$CeCl_3.7H_2O$	50.0	120.0
$HgCl_2$	27.7	217	$MgCl_2.6H_2O$	50.4	119.0
$LiCl.2H_2O$	35.5	170	$ThCl_4.8H_2O$	60.0	100.5
$CdCl_2.2H_2O$	37.1	162	$FeCl_3.6H_2O$	84.8	70.8
$CaCl_2.6H_2O$	38.6	155	$AlCl_3.6H_2O$	153.2	39.2

different temperatures. It is assumed that, owing to the fixing of part of the water by the salt, the free solvent is no longer able to retain the acid in complete solution. It is believed that this lowering of the solubility is due to hydration of the dissolved salt. The relative amounts of some of the chlorides that were necessary to precipitate the butyric acid are:[1] 0.213 NaCl, 0.191 LiCl, 0.079 $CaCl_2$, 0.076 $MgCl_2$, 0.048 $AlCl_3$. There is a decided parallelism between the action of these salts in precipitating the butyric acid, and their action in retarding the V. C. of water.

TABLE II.

The Velocity of Crystallization of 0.5 *M* Undercooled Aqueous Solutions of Nitrates.
Temp. —9.1°.

Compound.	Time per meter in seconds.	Velocity cm. per min.
KNO_3	43.9	137.0
$AgNO_3$	47.6	129.0
$Pb(NO_3)_2$	102.0	58.9
$Cu(NO_3)_2.6H_2O$	500.0	12.0
$Al(NO_3)_3.8H_2O$	1054.0	5.8

Of the compounds in Table II in which the effects of several nitrates are shown, the nitrates of aluminium and potassium have been investigated by Jones. These two salts occupy the same relative positions in his experiments as they do in ours. The experiments in Table II were carried out with 0.5 *M* solutions instead of 0.1 *M* because it was found that when the less concentrated solutions were used the differences in the effects of two salts are at times not great enough; they might be accounted for by experimental error.

The sulfates (Table III) show an abnormal behavior. Sodium sulfate, for example, in spite of its large content of crystal water has a comparatively slight retarding effect. Aluminium sulfate retards the V. C. more than any other substance used in these experiments. The behavior of the sulfates of zinc and magnesium is very interesting. A tube of the freshly prepared solution of each of these substances was undercooled and allowed to crystallize. The contents of the tube were warmed until

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[1] See Senter, *Trans. Faraday Soc.*, 3, 149 (1907).

TABLE III.

The Velocity of Crystallization of 0.5 *M* Undercooled Aqueous Solutions of Sulfates. Temp. —9.1°.

Compound.	Time per meter in seconds.	Velocity cm. per min.	Compound.	Time per meter in seconds.	Velocity cm. per min.
K_2SO_4	71	84.5	$ZnSO_4.7H_2O$[1]	202	..
$(NH_4)_2SO_4$	83.7	73.4		170	..
$Na_2SO_4.10H_2O$	137	44.0		170	..
$CuSO_4.5H_2O$	177	33.9		150	..
$MgSO_4.7H_2O$[1]	218	..	$FeSO_4.7H_2O$	200	30
	194	..	$Al_2(SO_4)_3.18H_2O$	3000	2
	184	..			
	177	..			
	174	..			

everything was dissolved and the cooling and crystallizing were repeated. With the successive experiments, using the same solution, the retarding effect of the solute became less. Jones found that the sulfates in general gave abnormal results in his experiments. This he believes to be due to association of molecules of the solute. The behavior of the two salts just mentioned can be explained by this hypothesis, providing that the association of the molecules takes place with measurable velocity. The association would mean a lowering of the molecular concentration and a diminishing of the retarding effect of the solute.

Sodium bromide crystallizes with two molecules of water of crystallization while potassium bromide is anhydrous. These two salts should show different degrees of hydration in solution, and measurements of freezing point lowerings show this to be the case. To find out whether or not equivalent solutions of these salts have the same retarding effect on the V. C. of water, measurements were made with solutions of potassium bromide and sodium bromide in which the concentrations varied from one-eighth to one gram molecule per liter. The results are given in Table IV and are shown graphically in the figure. At all concentrations measured the retarding effect of the sodium bromide was much greater than that of an equivalent solution of the potassium bromide. This is again in agreement with the work of Jones, who found that the sodium bromide is more hydrated in solution than the potassium bromide.

TABLE IV.

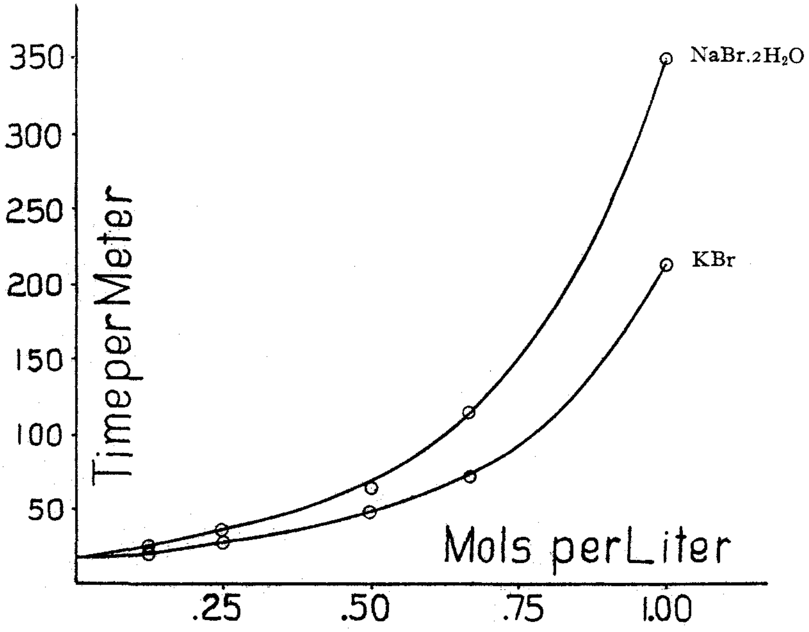
The Velocity of Crystallization of Undercooled Aqueous Solutions of Potassium and Sodium Bromides. Temp. —9.1°.

KBr Mols per liter.	Time per meter in seconds.	NaBr Mols per liter.	Time per meter in seconds.
1.00	212.0	1.00	350.0
0.67	78.2	0.67	114.0
0.50	49.5	0.50	63.8
0.25	29.6	0.25	37.0
0.125	23.1	0.125	27.0

[1] V. C. not constant. Values represent repeated trials with the same solutions.

In the light of the following statement[1] the influence of glucose upon the V. C. is interesting:

> "In connection with the results obtained by Roth (*Z. physik. Chem.*, **43,** 560 (1903)) for glucose one point is worthy of mention. Roth found that freshly prepared solutions of glucose gave smaller values for the molecular lowering than did the same solutions after standing for a few days. The increase in the molecular lowering with the time corresponded to the decrease in the birotation. Hydration has been suggested as a possible explanation of this result, and this is probably true."



Two 0.5 *M* solutions of glucose (*a*) and (*b*) were prepared, the former from anhydrous and the latter from the crystallized substance, which has one molecule of water of crystallization. The V. C. of the two freshly prepared solutions was measured, they were then allowed to stand for ten days and measurements were again made. The time necessary for the crystals to fill a tube one meter in length was as follows:

Glucose (*a*)	Feb. 10, 271 sec.	Feb. 19, 303 sec.
Glucose (*b*)	Feb. 10, 320 sec.	Feb. 19, 320 sec.

This experiment indicates that the more the glucose is hydrated the more it retards the V. C. of water.

By measuring the V. C. of 0.5 *M* solutions of various potassium salts, it has been possible to learn the effects of the different negative radicals. The results are given in Table V. Relative hydration values for these salts have been determined by Jones, Smirnoff, Biltz.[2] Their results do

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[1] Washburn, p. 374.

[2] *Z. physik. Chem.*, 40, 185 (1902).

not entirely agree as to order with the data in Table V but there is a general agreement, however.

TABLE V.

The Velocity of Crystallization of 0.5 *M* Undercooled Aqueous Solutions of Potassium Salts. Temp. —9.1°.

Compound.	Time per meter in seconds.	Velocity cm. per min.	Compound.	Time per meter in seconds.	Velocity cm. per min.
KNO_3..........	43.9	137	KCl........	57.8	104.0
KSCN..........	46.8	128	K_2SO_4.......	71.0	84.5
KBr............	49.5	121	KCN.......	99.3	60.4
KI.............	51.1	117	$KF.2H_2O$....	184.0	32.6

In addition to the foregoing experiments there are a number of others that are also explained by the hydration theory. Urea and glycocoll are not hydrated to any extent; the retarding effects of these substances on the V. C. of water is inconsiderable. Cane sugar is hydrated to a great extent; its retarding effect is marked.

In the first paper the effect of certain of the alkaloids was shown to be great, even when they are present in as low a concentration as 0.02 *M*. The substances used were: cocaine hydrochloride, quinine bisulfate and brucine sulfate. The last three of these compounds have two, seven, seven molecules of water of crystallization, respectively, indicating the formation of hydrates in the solution.

Conclusion.

The experimental data in this paper and in the first communication on this subject are best explained by the hydrate theory. The formation of ice crystals may be represented by an equation similar to the following:

$$3(H_2O)_2 \rightleftarrows 2(H_2O)_3$$

The existence of a part of the solvent in combination with the solute would mean that this combination would have to be broken before crystals could form, consequently the formation of ice crystals in a solution containing a solute that is hydrated would be much slower than their formation from the pure solvent.

The authors do not for one moment believe, however, that the retardation is entirely due to the presence of hydrates in the solution. The heat evolved when ice crystals separate is different for different solutions; the lowering of the freezing point varies to a certain extent with the solute, consequently at the same temperature equimolecular solutions of different compounds may not be equally undercooled; the viscosity, the heat of ionization and the thermal conductivity of the solutions are also factors that must be taken into consideration. In concentrated solutions these factors are doubtless of considerable importance; in dilute solutions the authors believe that the retardation is almost entirely due to the existence of hydrates.

It is of interest to note that in solutions as dilute as 0.1 M there is a marked difference between the behavior of those substances that are hydrated, and those that form hydrates to an inconsiderable extent only.

This investigation is being continued.

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SUPERSATURATED SOLUTIONS OF LIQUIDS IN LIQUIDS.

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Received February 10, 1916.

It is comparatively easy to form supersaturated solutions of solids or gases in liquids, but, up to the present, attempts to form similar supersaturated solutions of liquids in liquids have met with little success.

Rothmund[1] has considered the possibility of the existence of such supersaturated solutions. His criterion for such a condition is based on the following considerations: A small drop of liquid is more soluble than a larger one and a solution can be supersaturated until it is in equilibrium with the smallest drops which are already formed in the liquid. When this concentration is exceeded, these drops rapidly grow, becoming less soluble as they do so and soon reduce the concentration of the supersaturated solution to that of a saturated one. In a case where the solubility increases with the temperature, the cooling of the solution causes drops to appear somewhat below the temperature of saturation for that particular concentration; but when the solution is heated, the larger drops will persist until slightly above the temperature of saturation. That is, there will be a difference between the temperatures at which the cloudiness appears and disappears and the greater the degree of supersaturation, the greater will be the difference in temperature.

In the case of all the liquids he investigated, this difference of temperature was very small; hence Rothmund concluded that there was no evidence of supersaturation.

Füchtbauer[2] carried out some experiments which seemed to give strong evidence of the existence of supersaturated solutions of liquids in liquids. He came to the conclusion that the difficulty in forming supersaturated solutions of liquids in liquids is due to the presence of dust particles or foreign nuclei of some sort, perhaps colloids.

A careful examination of the effect of dust particles on preventing the formation of supersaturated solutions of liquids in liquids was made by Fawcett.[3]

[1] *Z. physik. Chem.*, **26**, 443 (1898).

[2] *Ibid.*, **48**, 566 (1904).

[3] Thesis, University of Toronto, **1912**. For summary see E. Fawcett, *Proc. Roy. Soc. Canada*, **1913**. (I am indebted to Prof. F. B. Kenrick for a copy of this thesis.)