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MOLTEN HYDRATED SALTS AS SOLVENTS FOR THE FREEZING POINT METHOD II.

BY J. LIVINGSTON R. MORGAN AND F. T. OWEN.

In a recent paper[1] Morgan and Benson have shown that the molten hydrated salts $CaCl_2.6H_2O$, $LiNO_3.3H_2O$, and $Na_2CrO_4.10H_2O$, when used as solvents for the freezing point method, lead to molecular weights for the dissolved substances which are similar to those obtained when water is the solvent, except that when the substance added has an ion in common with the molten hydrated salt, its ionization is prevented either wholly or in part. And when the ions of the dissolved substance are different from those of the solvent, its ionization is apparently unaffected, the molecular weights calculated, not differing materially from those observed in water solutions. In this investigation three other molten hydrated salts, $Ca(NO_3)_2.4H_2O$, $Zn(NO_3).3H_2O$, and $Mn(NO_3)_2.3H_2O$, have been studied as solvents.

The apparatus employed was the one already described by Morgan and Benson, except that a Beckmann thermometer, reading to 0°.01, and set by aid of a normal thermometer, reading to 0°.02, was used throughout. The depressions recorded are each the average of three determinations, agreeing among themselves to 0°.02. Just as with the other salts the separation of the solid phase was induced by infection with a crystal of the pure solvent; and the overcooling was kept below 1° to avoid the necessity of correcting for the fraction of solvent separating as a solid phase.

Determination of the Constants.

For $Ca(NO_3)_2.4H_2O$ the latent heat of fusion is 33.49 gram-calories per gram, according to Pickering[2], so that the freezing point constant can be calculated directly from the relation $K = \frac{0.02T^2}{w}$, where T is the absolute freezing point of the pure solvent, w its latent heat of fusion for 1 g. at that temperature, and K the depression of the freezing point in degrees, caused by the presence of 1 mol. of dissolved substance in 100 g. of the solvent. Since the freezing point of molten $Ca(NO_3)_2.4H_2O$, as determined by us, is 42°.31, we have

[1] This Journal, **29**, 1168-75, 1907.

[2] See Landolt-Börnstein-Meyerhoffer. Tabellen. Third ed., p. 470.

$$K = \frac{0.02\,(273 + 42.31)^2}{33.49} = 59^\circ.41.$$

For neither $Zn(NO_3)_2.3H_2O$, nor $Mn(NO_3)_2.3H_2O$ could the latent heat of fusion be found in the literature, hence it was necessary to determine the values of K by direct observation of the freezing point depressions. For this purpose ammonium nitrate was used as the solute, for it dissolved readily in both solvents, and the work of Morgan and Benson, with molten $LiNO_3.3H_2O$ as solvent, showed it to possess a normal molecular weight when the solvent contained NO_3 ion, *i. e.*, showed that under these circumstances it dissolved in practically the un-ionized state. The freezing point depressions observed for solution of ammonium nitrate, of known strength, in these two solvents are given in Tables I and II, below, the value of K in each case being the depression which would be caused by the presence of 1 mol. (80 g) of ammonium nitrate in 100 g. of the solvent, as calculated by the proportion 80:K::g. per 100:Δ.

IN $Zn(NO_3)_2.3H_2O$ AS SOLVENT. F. P. = 44°.07.

I. Ammonium Nitrate (*M* = 80).

g. NH_4NO_3 per 100	Δ°	K°
1.470	1.071	58.3
2.528	1.830	57.9
3.794	2.773	58.5
5.249	3.910	59.6
	Average	58°.6

Using this average value of K, 58°.6, in the relation $K = \frac{0.02T^2}{w}$, and solving for w, we find the latent heat of fusion of $Zn(NO_3)_2.3H_2O$ to be 34.3 gram-calories per gram at its freezing point 44°.07.

IN $Mn(NO_3)_2.3H_2O$ AS SOLVENT. F. P. = 34°.81.

I. Ammonium Nitrate (*M* = 80).

g. NH_4NO_3 per 100	Δ°	K°
1.063	0.882	66.4
1.492	1.273	68.3
3.052	2.573	67.4
	Average	67°.4

Using this average value of K, 67°.4, in $K = \frac{0.02T^2}{w}$, and solving for w, we find the latent heat of fusion of 1 g. of $Mn(NO_3)_2.3H_2O$ to be 28.09 gram-calories, at its freezing point, 34.81.

Molecular Weights in Solution.

IN $Ca(NO_3)_2.4H_2O$ AS SOLVENT. K = 59°.4. F. P. = 42°.31.

III. Urea (*M* = 60).

g. per 100	Δ°	M
0.9868	1.038	56.5
1.9030	1.920	58.9
2.9900	3.071	57.9

g. per 100	Δ°	M
IV. Ammonium Nitrate (*M* = *80*).		
2.280	1.702	79.6
4.789	3.577	79.5
5.644	4.311	77.8
V. Glycol (*M* = *62*).		
0.9249	0.884	62.2
1.8660	1.779	62.3
2.8080	2.730	61.1
3.6640	3.588	60.7
VI. Acetic Acid (*M* = *60*).		
1.092	1.078	60.2
2.138	1.995	63.7
3.497	3.006	69.1
IN $Zn(NO_3).3H_2O$ AS SOLVENT. K = 58°.6. F. P. = 44°.07.		
VII. Ethyl Alcohol (*M* = *46*).		
0.8397	1.083	45.5
1.3500	1.728	45.8
VIII. Methyl Alcohol (*M* = *32*).		
0.4776	0.843	33.2
0.8198	1.375	34.9
1.141	1.906	35.1
1.461	2.440	35.1
1.814	3.030	35.1
2.448	4.103	35.0
IX. Acetic Acid (*M* = *60*).		
0.5663	0.550	60.3
1.273	1.188	62.8
2.475	2.236	64.9
3.681	3.197	67.5
X. Acetone (*M* = *58*).		
0.8435	0.828	59.7
1.7344	1.578	64.4
2.626	2.358	65.3
3.536	3.119	66.4
XI. Formamide (*M* = *45*).		
1.357	1.442	55.1
2.514	3.195	46.1
3.026	4.180	42.4
XII. Iso-butyl Alcohol (*M* = *74*).		
1.007	0.757	77.9
2.131	1.611	77.5
IN $Mn(NO_3)_2.3H_2O$ AS SOLVENT. K = 67°4. F. P. = 34°.81.		
XIII. Glycol (*M* = *62*).		
0.8350	0.938	60.0
1.641	1.858	59.5
2.516	2.893	57.3
3.395	3.929	58.2
XIV. Ethyl Alcohol (*M* = *46*).		
0.6322	0.732	58.2
1.149	1.448	53.5
2.179	2.793	52.6
3.200	4.240	50.9

XV. Methyl Alcohol ($M = 32$).

g. per 100	Δ°	M
0.5657	1.149	33.2
1.154	2.225	34.4
1.857	3.575	35.0
2.304	4.320	35.9

XVI. Glycerol ($M = 92$).

0.7927	0.607	88.0
2.062	1.702	81.7
3.394	3.288	69.6

XVII. Acetic Acid ($M = 60$).

0.5902	0.640	62.2
1.247	1.343	62.6
2.593	2.641	66.0

XVIII. Urea ($M = 60$).

1.672	1.676	67.2
2.332	2.356	66.7
3.692	3.574	69.6

It will be observed that the general trend of the molecular weights determined here is similar to that of those determined in $CaCl_2.6H_2O$, $LiNO_3.3H_2O$, and $Na_2CrO_4.10H_2O$, except that in the cases of ethyl alcohol and glycerol in $Mn(NO_3)_2.3H_2O$ (Tables *XIV* and *XVI*), and formamide in $Zn(NO_3)_2.3H_2O$ (Table *XI*) the molecular weights show a decided decrease with increased concentration. As soon as sufficient data of this sort are at hand, a quantitative study of the thermal relations of these solutions will be made, in order, if possible, to test the effect of the heat of dilution upon the molecular weight, as calculated by the freezing point law, the possible effect of which has already been sketched by Morgan and Benson[1].

Summary.

The results of this work may be summarized as follows:

1. The freezing point constants of molten $Ca(NO_3)_2.4H_2O$, $Zn(NO_3)_2.3H_2O$, and $Mn(NO_3)_2.3H_2O$ are respectively: 59°.4(F. P. =42°.31); 58°.6(F. P. = 44°.07), and 67°.4(F. P. = 34°.81).

2. The heats of fusion for 1 g. each of $Zn(NO_3)_2.3H_2O$ and $Mn(NO_3)_2.3H_2O$, as calculated from the experimentally determined values of K, and the relation $w = \frac{0.02T^2}{K}$, are respectively 34.3 gram-calories at freezing point, 44°.07, and 28.09 gram-calories at the freezing point, 34.°81.

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PLATINUM RESISTANCE FURNACE FOR MELTING POINTS AND COMBUSTIONS.

BY SAMUEL A. TUCKER.

Received June 28, 1907.

The small furnace here described was the outcome of some work in

[1] Loc cit.