

CXXXVI.—*The Constitution of Magnesium Acetate Solutions.*

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THE constitution of basic beryllium acetate (Urbain and Lacombe, *Compt. rend.*, 1901, **133**, 874; Bragg, *Nature*, 1923, **111**, 532; Sidgwick, *ibid.*, 808; Bragg and Morgan, *Proc. Roy. Soc.*, 1923, *A*, **104**, 437) is explicable in terms of a marked tendency on the part of the beryllium atom to exercise a co-ordination number of 4 in its linkings with oxygen. The readiness with which this occurs may be connected with the fact that the outer electrons in the atoms of beryllium and oxygen are at similar energy levels: there may thus be a decreasing tendency towards such linkings with oxygen as one passes down Group II of the Periodic Classification through magnesium, calcium, strontium, and barium. In magnesium acetate one might expect to find, at any rate, an appreciable tendency for the formation of a compound analogous to the basic beryllium salt.

In preparing hydrated magnesium acetate from magnesium oxide, acetic acid, and water, with a view to seek such a basic acetate in the ternary system oxide-acetate-water, one was struck by the ease with which supersaturated solutions could be formed, by the slow rate of their crystallisation after seeding, and by the very high viscosity possessed by solutions above a certain range of concentration. Measurements of some of the properties of these solutions have therefore been made, and from them it seems that some guidance may be obtained as to the probable condition of magnesium acetate in solutions of varying concentrations.

E X P E R I M E N T A L.

The solid salt used was prepared from magnesium oxide (B. D. H.), free from sulphur, and excess of acetic acid (A. R.) diluted about fourfold with water. The crystals formed were separated on a silver gauze basket in a centrifuge of 6-inch radius at 1800 r.p.m., and kept for some weeks in a vacuum desiccator over concentrated caustic soda to remove excess acetic acid. Analysis showed them to be $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$.

All solutions were analysed by conversion of dissolved salt into anhydrous magnesium sulphate and weighing as such. Compositions of solutions are given throughout the sequel in percentages of anhydrous salt by weight; but, in the discussion, concentrations are usually quoted in g.-mols. per 1000 g. of water (M_w) or g.-mols. per litre at 25° (M_v).

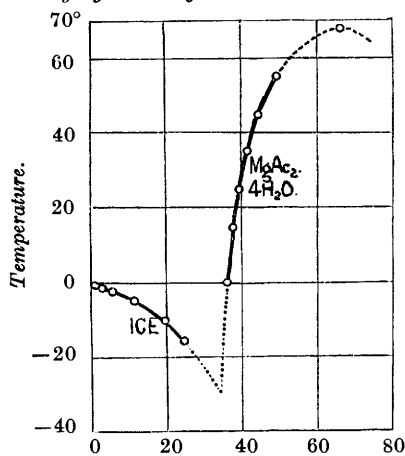
TABLE I.
Binary System Magnesium Acetate-Water.

t .	% anhyd. salt.	M_w .	Δ/M_w .	Solid phase.
-0.364°	1.068	0.0758	4.80	Ice.
-0.531	1.804	0.1290	(4.12)	"
-1.083	3.08	0.2232	4.85	"
-2.179	5.92	0.442	4.93	"
-4.687	11.45	0.908	5.16	"
-9.99	19.81	1.735	5.76	"
-15.28	25.0	2.345	6.52	"
-29 (extrap.)	34.5	3.70	7.8	Ice and MgAc ₂ .4H ₂ O.
+ 0.1°	36.2	3.986		MgAc ₂ .4H ₂ O.
+14.9	37.97	4.300		"
24.9	39.61	4.607		"
35.0	41.78	5.041		"
45.0	44.76	5.691		"
55.0	49.46	6.874		"
68±	66.4	—		(Approx. m. p. of hydrate.)

Table I gives the binary system acetate-water (plotted in Fig. 1) so far as it has been possible to determine it. On the ice curve,

FIG. 1.

Binary system magnesium acetate-water.



Percentage of magnesium acetate by weight.

solutions in the region of 30% by weight are so viscous that the phase-reaction between ice and solution proceeds too slowly for accurate measurements. On the salt-solution curve, hydrolysis sets an upper limit. The solid hydrate begins to melt at about 68°, so that this curve reaches a maximum somewhere near that temperature, as indicated by the dotted extension in Fig. 1. An extrapolation of ice and salt curves downwards points to a eutectic temperature (hydrate-ice-solution) of about -29°: but a figure so obtained is very uncertain.

Table II gives the viscosities of solutions of magnesium acetate (and a few, for comparison, at high concentrations of magnesium chloride and sodium acetate) at 25° relatively to water taken as unity. They have been measured in viscosimeters of the Ostwald pattern with time of water-flow of about 3 minutes. Pyknometers of 5 c.c. were used for determinations of density.

TABLE II.

Relative Viscosities at 25° (water = unity).

% Anhyd. salt.	M_w .	M_v .	D .	Relative viscosity.
$Mg(C_2H_3O_2)_2$				
6.19	0.463	0.450	1.0345	1.466
13.27	1.075	1.002	1.0754	2.421
20.14	1.772	1.579	1.1160	4.325
24.51	2.280	1.966	1.1422	6.593
28.80	2.841	2.365	1.1692	10.83
32.65	3.405	2.742	1.1954	18.69
36.01	3.953	3.075	1.216	31.78
36.58	4.051	3.137	1.221	35.02
38.72	4.438	3.355	1.234	53.83
40.20	4.721	3.514	1.245	72.7
41.14	4.909	3.609	1.249	84.2
41.91	5.067	3.694	1.255	104.35
42.67	5.228	3.777	1.261	125.3
43.63	5.436	3.877	1.265	155.2
$MgCl_2$				
17.90	2.289	2.172	1.1558	2.379
25.02	3.503	3.217	1.2247	3.952
31.79	4.893	4.322	1.2962	7.737
$[Na(C_2H_3O_2)]_2$				
21.05	1.625	1.427	1.1119	2.628
31.71	2.831	2.264	1.1716	5.195

Table III includes measurements for certain solutions at temperatures from 25° to 55°, to give indications of the temperature coefficients of viscosity.

TABLE III.

Relative Viscosities at Different Temperatures.

Solution A 18.44%, M_w 1.588; B 41.38%, M_w 4.958; C 45.95%, M_w 5.970.

Temperature.	D .			Relative viscosity.		
	A.	B.	C.	A.	B.	C.
25.0°	1.1057	1.2515	—	3.73	92.9	Soln. crysd.
35.1	1.1050	1.249	1.2780	3.395	62.3	187.6
45.0	1.1048	1.247	1.2757	3.15	45.0	115.6
55.0	1.105	1.246	1.2744	2.93	34.1	78.05

In Table IV are the specific conductivities ($\text{ohm}^{-1} \text{cm.}^{-1}$) at 18° and 25° measured in a cell of the form shown in Fig. 4. The total volume of the cell is 400 c.c., that of the lower tube, a , being 15 c.c. This is a useful shape when a series of dilutions is to be examined, since, provided that the lower tube be filled, the resistance of a solution is independent of the volume taken. Successive dilutions were effected by additions of water from a weight burette.

Table V shows the way in which the conductivity of a highly concentrated solution ($M_w = 5.5$) varies with temperature.

TABLE IV.

Specific Conductivities ($\text{ohm}^{-1} \text{ cm.}^{-1}$) of Magnesium Acetate Solutions at 25° and 18° .

% Anhyd. salt.	M_w .	M_v .	$\kappa \times 10^3$.		$\frac{100(\kappa_{25} - \kappa_{18})}{7 \times \kappa_{18}}$
			25° .	18° .	
3.55	0.259	0.255	19.97	17.06	2.44
5.64	0.420	0.409	26.28	22.38	2.49
7.45	0.565	0.546	30.10	25.55	2.54
9.31	0.721	0.688	32.67	27.67	2.58
11.63	0.924	0.871	34.36	28.94	2.67
14.04	1.147	1.065	34.67	29.02	2.78
18.70	1.616	1.389	32.12	26.44	3.07
23.41	2.147	1.868	26.69	21.53	3.42
28.21	2.760	2.309	19.84	15.50	4.00
33.08	3.472	2.782	12.89	9.68	4.74
37.95	4.295	3.276	7.11	5.05	5.83
43.93	5.503	3.872	2.58	1.69	7.53

TABLE V.

Specific Conductivity of a 43.9% ($M_w = 5.50$)-Solution of Magnesium Acetate at Various Temperatures.

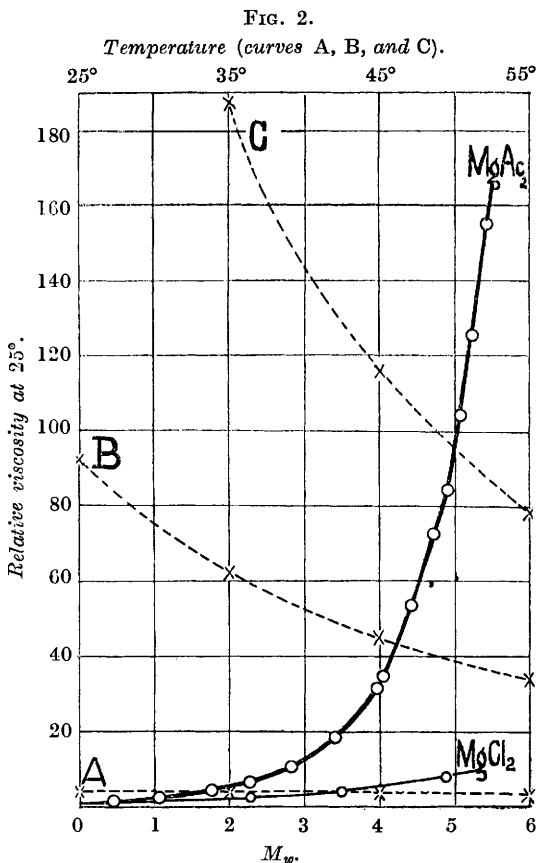
$t^\circ (\pm 0.05^\circ)$	55.1	49.7	44.95	40.0	35.8	29.8	25.0	18.0	12.7
$\kappa \times 10^3$	10.02	8.26	6.28	5.58	4.60	3.38	2.58	1.69	1.16

Discussion.

Fig. 2 shows the remarkable rapidity with which viscosity at 25° increases with concentration. No simple equation has been found to cover the relation between the two. Rapid rise begins at about $2.5M_w$, the value relative to water as unity increasing from approximately 7 at that concentration to 155 at $M_w = 5.4$ ($M_v = 3.9$), a supersaturated solution. One might suppose this great change to be due to hydration of the salt, the amount of free solvent water becoming steadily less. The evidence is, however, rather contrary to any such supposition. Thus, ease of hydration is doubtless, to some extent, a characteristic of both radicals of the salt, yet neither magnesium chloride nor sodium acetate shows anything approaching the behaviour of magnesium acetate. At $4.5M_v$ the former has a relative viscosity of only about 9: the latter, at $2.5M_v$ (calculated on a doubled formula), the maximum concentration attainable, has the value 5.5. There is no indication in either case that a rapid rise is likely.

Further, if the production of heavily hydrated molecules were the cause of the high viscosity of magnesium acetate solutions compared with those of magnesium chloride, one would expect the curve of the molecular lowering of freezing point of the former to lie well above that of the latter. Fig. 3 shows how very far

this is from being the case. The figures for magnesium chloride at the dilute end are by the author (*Z. physikal. Chem.*, 1912, **80**, 546), while those for concentrated solutions are taken from the Landolt-Börnstein "Tabellen." In infinitely dilute solution a lowering of $3 \times 1.85^\circ$ is to be expected for a ternary electrolyte fully dissociated. As concentration increases, the lowering diminishes with decreasing dissociation and then, as is usual, passes



through a minimum and begins to rise. This rise is commonly attributed, in part at least, to removal of solvent by hydration of solute. With magnesium chloride it becomes very great, exceeding 12° at $2.7M_w$; with the acetate it is only 6.5° at $2.35M_w$. If the extrapolation in Fig. 1 to a eutectic at -29° and 34.5% anhydrous salt ($M_w = 3.7$) is correct, the molecular lowering at that temperature is only 7.8° ; but one cannot be sure of this figure. Thus

the relation to magnesium chloride is incompatible with an assumption that the acetate is the more highly hydrated, and it appears that the increase in viscosity in concentrated solutions of the latter is due to some other property of the magnesium and acetate radicals in conjunction.

A plausible suggestion is that as one passes from relatively dilute solutions, where ionic dissociation is considerable, there is an increasing tendency for association of molecules to occur, such association being the result of chelate ring-formation by means of the magnesium atom exercising a co-ordination number of 4 towards oxygen atoms. In a single molecule, such a structure as $H_3C \cdot C \begin{matrix} \diagup O \\ \diagdown O \end{matrix} \cdots Mg \begin{matrix} \diagdown O \\ \diagup O \end{matrix} \cdots C \cdot CH_3$, with four-atom rings, is not likely to

FIG. 3.

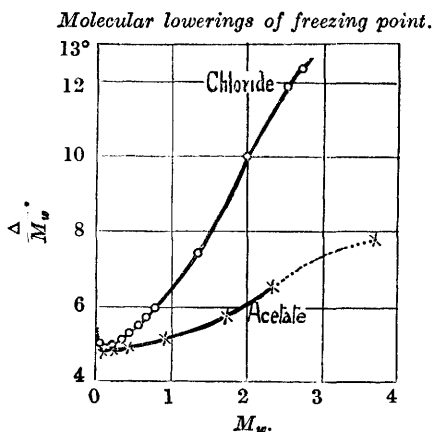
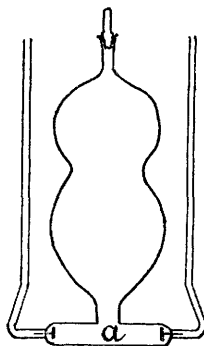
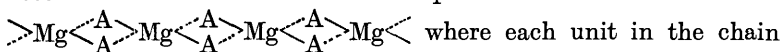


FIG. 4.



be stable, particularly in dilute solution where ionisation is considerable; but, with increase of concentration, polymerisation may occur to an indefinite extent with production of such chains as



(straight or branched) is $\cdots Mg \begin{matrix} \diagup O=C(CH_3)-O \\ \diagdown O-C(CH_3)=O \end{matrix} \cdots$, a magnesium atom being linked by a co-valence to a doubly-linked oxygen atom of an acetate radical other than that originally attached to itself. It is a simple matter to draw possible spatial structures for di-, tri-, and higher molecular aggregates. Such polymerisation is of a type similar to that which apparently is shown by basic beryllium acetate.

Chains of this kind will no doubt contribute very greatly to the viscosity of a solution and might well account for the values recorded

at high concentrations. If now there is such a progressive alteration in the constitution of solute, from simple ionised salt to more or less highly polymerised molecules, there should be marked differences in the effects of temperature upon differing concentrations. At higher concentrations, increase of temperature, by promoting dissociation, should have a much greater effect upon viscosity, for instance, than it will have at lower concentrations where there is little or no polymerisation. The measurements of Table III, shown in the broken lines of Fig. 2, prove quite definitely that this is the case. Three solutions have been measured at several temperatures and each viscosity has again been expressed relatively to water at the same temperature. For an 18.4% ($1.805M_w$) solution the curve (A, Fig. 2) is almost horizontal; for 46% ($5.97M_w$) it (C) is very steep, and the lower the temperature the steeper is the gradient.

The measurements of specific conductivity (Table IV) show the usual maximum as concentration increases, but whereas this occurs at $2.5M_w$ with magnesium chloride, it is at under $1M_w$ with magnesium acetate, the conductivity being only one-fifth of the corresponding value for the former. It is idle, on the basis of conductivity work, to attempt comparisons of dissociation and ionic concentrations in cases like these, where one cannot be certain that the ions are the same in concentrated as in dilute solutions, and where any allowance for viscosity can be nothing more than conjecture. Some interest, however, attaches to the temperature coefficient of the conductivity. Values at both 18° and 25° are included in Table IV, so that for each solution one can obtain the mean percentage increase in conductivity per degree between these two temperatures. The values of $100(\kappa_{25} - \kappa_{18})/7 \times \kappa_{18}$ are given in the sixth column of the table. Up to about $1M_w$ the increase is close to 2.5% per degree—quite a normal figure for salts—but the coefficient continues to grow at an increasing rate as concentration rises, reaching 7%, and rising rapidly, at $5.5M_w$. Here again magnesium acetate furnishes an unusual case and an assumption of polymerisation leads to a qualitative explanation. Dissociation of polymerides with rising temperature will increase the number of simple molecules, which presumably are much more capable of ionisation, and so give increased conductivity: here also, however, it is unfortunate that one cannot deduct the effect, if any, due to change of viscosity between 18° and 25° .

Keeping to one and the same highly concentrated solution, containing 43.9% of anhydrous acetate ($M_w = 5.50$; $M_v = 3.87$) the figures of Table V show how conductivity varies over a wider range of temperature (12.7° to 55.1°). This solution is saturated

at 45°, but may be kept indefinitely at room temperature. Between the temperatures mentioned, the conductivity changes by more than 850% of its initial value—a very high figure for a salt. The rate of increase of conductivity with temperature is greater at higher temperatures, but the relative increase in value per degree is greater at the lower temperatures.

While this high temperature coefficient may simply reflect altered mobility consequent upon altered viscosity, it is more probable that both viscosity and conductivity changes are due to a common cause, polymerisation, which is highly sensitive to temperature change.

Some approximate measurements of surface tension have been made by the capillary tube method at 25°. There would seem to be little difference between the surface tensions of water and magnesium acetate solutions. Multiplying each rise by the density of the solution and dividing by the rise of pure water in the same tube, the following relative figures were obtained :

% anhyd. $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$	6.01	14.0	23.5	23.6	31.4	39.3
S	1.013	1.006	1.002	1.001	0.980	0.968

No great accuracy is claimed for the figures and the third decimal place may be incorrect by several units, but it appears fairly certain that there is an initial rise, as is usual with salts, which is followed by a decrease to less than the value for water : at none of the concentrations examined does the change in surface tension due to the presence of the salt exceed a few parts per cent.

There are other physical properties of these solutions which will be investigated later and a comparison will be made with the acetates of calcium, strontium, and barium, the higher positivity of the atoms of which will presumably involve less tendency towards formation of polymers by non-polar linkages of the type so markedly shown by beryllium, and apparently still characteristic in magnesium.