CCLV.—*The Constitution of Magnesium Acetate Solutions. Part II. Evidence from Vapour Pressures.*

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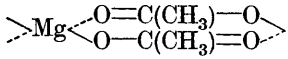
IN order to explain qualitatively the relations between concentrations and viscosities, freezing points, and conductivities of solutions of magnesium acetate in water, it has been suggested (J., 1926, 1063) that at high concentrations there is considerable polymerisation of the salt molecules. This association may reasonably be attributed to chelate ring formation where the magnesium atom exercises a co-ordination number of four, and chains (straight or branched) of indefinite extent are built of the unit



$$>\mathrm{Mg}<\begin{matrix}\mathrm{O{=}C(CH_3){-}O}\\ \mathrm{O{-}C(CH_3){=}O}\end{matrix}>$$

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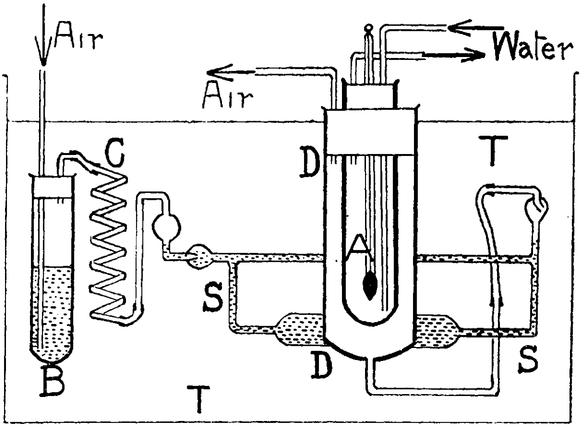
Evidence bearing on this point has now been obtained from a consideration of the lowering of the vapour pressure of water brought about by solution of the salt. For this purpose it was necessary to work at a fairly low temperature (25° was chosen), though this greatly increased the difficulty of accurate measurement. At higher temperatures the tendency to association is decreased, and magnesium acetate falls more nearly into line with most other salts.

EXPERIMENTAL.

The dew-point method of Cumming (J., 1909, **95**, 1772), as modified by McBain and Salmon (*Proc. Roy. Soc.*, 1920, *A*, **97**, 44), was adopted, its obvious advantages being the rapidity with which measurements can be made and the unimportance of dissolved or entangled air in the solution. With the more viscous solutions, other methods would have been as inapplicable as McBain found them to be for soap solutions. The silver tube A (Fig. 1), on which the dew deposited, was highly polished, the final polishing being done with chamois leather and levigated rouge. McBain's device of dipping part of the tube in boiling water was used. The dew then deposits only on the part which has not been dipped and can be sharply detected at the boundary. It would seem that dipping removes nuclei, such as traces of dust or polishing material, which are necessary if condensation is to occur. On a very highly polished, undipped tube, it is often difficult to obtain condensation at all, but if the tube be held for an instant in hydrogen chloride fumes, the necessary nuclei are produced at once. Water was circulated through the silver tube from a reservoir heated or cooled as required. Temperatures in the tube and in the surrounding bath (T, Fig. 1) were read to 0·01°.

McBain's procedure, which is suitable for solutions at or near the boiling point and having a vapour pressure of the order of 600 mm., was not satisfactory with such low vapour pressures as those examined at 25°, the complete range of which was from 19 to 25 mm.

Fig. 1.



Thus there was an uncertainty of several tenths of a degree in the dew point as determined for pure water and for some test solutions of potassium chloride : nor was the accuracy improved by exhausting the apparatus. Probably with so little vapour round the tube the rate of diffusion was insufficient. If, however, a current of saturated air was circulated through the system, the accuracy was greatly increased, and differences in successive determinations of dew point were reduced to a few hundredths of a degree. The mean of five measurements of each solution was taken.

Fig. 1 indicates the arrangement adopted. Three saturators, of the type S, contained the solution on which the determination was required. They were separated from one another by a bubbler, B, and a metal coil, C, all immersed in the thermostat, T, and connected as shown with the deposition vessel, D, into which dips the silver tube, A, with its circulating system. It was found inadvisable to place any solution in D, as the slight splashing on to A tended to obscure the observation.

With a current of laboratory air it was impossible to get satisfactory evidence of condensation. This was no doubt due to the fact that it carried with it impurities like sulphuretted hydrogen which acted upon the dipped silver surface and formed condensation nuclei, thus destroying the contrast between dipped and undipped areas. The trouble was eliminated by passing the air first through a sulphuric acid bubbler and then through a soda–lime tower. We acknowledge our indebtedness to Professor E. J. Hartung for much help in making this apparatus effective.

The success of the method depends upon attainment of complete saturation of the air stream with respect to the solution. Great care must be taken to prevent ingress to the apparatus of traces of water or water vapour.

In making observations, the temperature of appearance of the vapour could be determined much more accurately than that of disappearance. Test measurements with pure water and potassium chloride solutions showed that if the temperature of appearance was taken as the dew point, the error in the vapour-pressure determination was of the order of 0·03 mm. : hence this, and not the mean of the temperatures of appearance and disappearance, was recorded throughout.

Concentrations of solutions were determined after dew-point measurements by evaporating with sulphuric acid a known weight of solution from the last saturator, and weighing the anhydrous magnesium sulphate obtained. They are expressed as g.-mols. per 1000 g. of water (M_w).

Table I gives the results. In the first column is M_w; in the second the temperature of the bath and solution (T_B); and in the fourth that of the dew point (T_D); whilst in the third and fifth are the vapour pressures of pure water (P_B and P_D) at these temperatures, taken from the tables of the International Bureau of Weights and Measures.

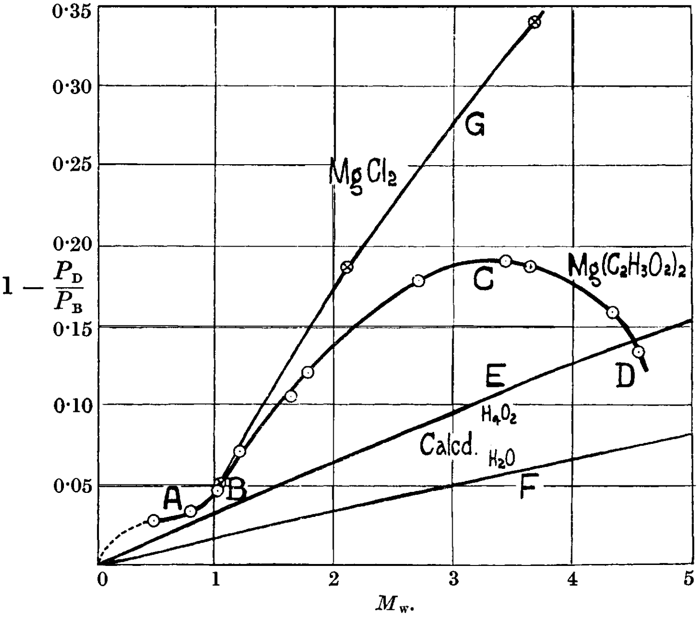
TABLE I.

M_w.	T_B.	P_B.	T_D.	P_D.	$1 - P_D/P_B$.
0·4185	25·03°	23·57	24·55°	22·90	0·028
0·800	25·00	23·52	24·42	22·73	0·034
1·026	24·98	23·50	24·18	22·40	0·047
1·205	25·00	23·52	23·78	21·86	0·071
1·650	24·99	23·51	23·13	21·03	0·106
1·784	25·01	23·54	22·88	20·71	0·120
2·703	25·01	23·54	21·73	19·33	0·179
3·430	25·05	23·60	21·51	19·05	0·192
3·645	25·00	23·52	21·58	19·11	0·187
4·331	25·01	23·54	22·16	19·83	0·158
4·55	24·99	23·51	22·60	20·36	0·134

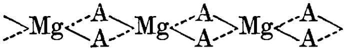
Discussion of Results.

In discussing results such as these, it is not justifiable to use the vapour-pressure lowerings as a basis for calculating molecular weights of the solute, since, apart from all question of applicability of the gas laws, to do so ignores the fact that the second component, water, is by no means a simple substance, and its behaviour, no less than that of the solute, will affect the vapour pressures. It is best to look at the figures from the point of view of Raoult's law. If this holds, $1 - P_D/P_B$ gives the mean molar fraction of the solute at each concentration. The values obtained experimentally are quoted in the sixth column of the table and they are plotted against M_w in curve ABCD of Fig. 2. For comparison, curves E and F give the molar fractions calculated on the assumptions that the solute particles are simply $Mg(C_2H_3O_2)_2$ and the solvent H_4O_2 (E) or H_2O (F). Lastly, the curve G shows $1 - P_D/P_B$ for magnesium chloride calculated from values obtained by extrapolation to 25° of Tammann's figures for vapour-pressure lowerings (Landolt–Börnstein Tabellen, 5th edition, p. 1386). The contrast with the acetate is very marked, just as it has been found to be in other physical properties.

Fig. 2.



The "molar fraction" $1 - P_D/P_B$ represents the ratio between the number of entities of magnesium acetate or its derived products (hydrates, polymerides, or ions) in a given solution and the sum of this number plus that of the free solvent entities. What the latter are, we do not know, but to assume that the molecule is H_4O_2 is probably less incorrect than to take it as H_2O. In any case the qualitative argument is not greatly affected. In dilute solution (A, Fig. 2) the relatively high value of the molar fraction given by the vapour-pressure measurements is undoubtedly due mainly to ionisation of the salt and consequent increase of the numerator in relation to its value calculated on an assumption of the presence of molecules only. The degree of ionic dissociation decreases as concentration increases, so the gradient is not maintained; but after about $M_w = 1$ (B) there is a steady rise which one may assume to be due to a continuous decrease in the denominator of the molar fraction consequent upon the removal of solvent molecules to form hydrates. No doubt such hydration occurs from the beginning, but in dilute solutions the effect on the denominator will be relatively small. In any case it will be in the same direction as the ionisation effect. Presumably the water (whether as single or double molecules or as chains) attaches itself to the Mg radical through the oxygen atom (acting as donor of electrons) to the extent required by the co-ordination number of the ion, which may or may not be also attached to acetate radicals. With magnesium chloride, this continues steadily to high concentrations, but with the acetate a counter-influence of some kind overcomes this hydration effect at C (M_w about 3·25), the curve passing through a maximum. After this point it falls off rapidly, and at D ($M_w = 4{\cdot}5$) it has even come below the molar fraction calculated on an assumption of the presence of undissociated molecules of anhydrous salt and H_4O_2 only. Evidently some cause has reduced the numerator, or increased the denominator, of the molar fraction, or both.

A simple explanation is that at these higher concentrations of magnesium acetate, polymerisation begins to dominate the situation; added molecules link up with others to form complexes of the indeterminate type  $>\mathrm{Mg}<^{\mathrm{A}}_{\mathrm{A}}>\mathrm{Mg}<^{\mathrm{A}}_{\mathrm{A}}>\mathrm{Mg}<^{\mathrm{A}}_{\mathrm{A}}>$, in which the magnesium co-ordination number of four is satisfied by two ordinary attachments to hydroxylic oxygen (the respective atoms contributing an electron apiece) and two to the doubly bound oxygen atoms of other acetate radicals (oxygen here contributing both electrons to the covalent bond). When this occurs, any water previously bound will be set free, and so we should get diminution of the numerator as the result of polymerisation, and increase of the denominator as the result of this freeing of previously bound water. Magnesium chloride cannot form similar rings and chains, so that with it the hydration effect continues unchecked as concentration increases.

The vapour-pressure evidence for magnesium acetate thus supports the view deduced from viscosity and other properties (*loc. cit.*). Lithium acetate, but not potassium, is similar to magnesium acetate, as will be shown later. The property of polymerisation in the way suggested would be expected to appear in the initial rather than the later members of periodic groups.

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