# MAGNETIC STUDY OF DOUBLE SALTS IN SOLUTION

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WHEN two salts, each primarily formed by the union of a base and an acid, are dissolved in water and the solution evaporated, it sometimes happens that they combine in a definite molecular proportion to form a compound of greater complexity which is called a molecular compound or a double salt. On solution a double salt yields the same ions as the single salts from which it is derived, but the physical properties of the salt are not necessarily additive. Various physical properties, such as solubility, viscosity, rates of diffusion of the constituents, volume change and others of the binary mixtures of the component salts have been used to investigate the formation of double salts in solution. Schonrock[1] has reported that the rotation of the polarised light is additive for solutions of mixtures of salts which do not form double salts while there is a marked deviation from additivity for the mixtures known to form double salts. The measurements of the heats of solutions of the mixture of the constituents of double salts led Graham,[2] and Berthelot[3] to establish the existence of double salts in solution. The temperature-concentration curves of a number of binary mixtures of salts having the same anion but different cations show that more than one double salt is formed in solution. Thus, ammonium chloride unites with the chlorides of magnesium, zinc, cadmium and mercury to form as many as three salts with each one of them. In some cases these salts have been isolated in the solid state while in others their presence has been inferred from the phase rule study of the systems.

Recently Nair and Pande[4] have carried out measurements of pH, viscosity, transport number and magnetic susceptibility of $Pb(NO_3)_2$—$KNO_3$—$H_2O$ and $Pb(NO_3)_2$—$NH_4NO_3$—$H_2O$ systems. They have reported the formation of three different double salts in each system. In the present communication the authors have investigated some ternary systems by the magnetic method with the idea of examining the formation of double salts in these systems.

## EXPERIMENTAL

All the substances used for studying the ternary systems were of Merck's pure quality. They were crystallised twice from distilled water before use and their purity was ascertained by estimating the amount of cation in them. The following five systems were chosen for investigation: (i) $NH_4NO_3$—$Pb(NO_3)_2$—$H_2O$, (ii) $NH_4NO_3$—$AgNO_3$—$H_2O$, (iii) $NH_4Cl$—$ZnCl_2$—$H_2O$, and (iv) $NH_4Cl$—$CdCl_2$—$H_2O$. The procedure followed for preparing these systems was as follows: Stock solutions of one molar concentration of the components of the systems were prepared by the standard method. In the case of the first two systems 20 c.c. of the stock solution of $NH_4NO_3$ were pipetted out into a standard flask of 50 c.c. capacity, the requisite amount of the other component was added by means of a standard burette and the whole mixture was made upto 50 c.c. with distilled water. 20 such mixtures were prepared in which the amount of the other component varied from 0 c.c. to 30 c.c. In the last three systems varying amounts of the second component were added to 20 c.c. of $NH_4Cl$ solution.

Magnetic susceptibilities of the mixtures were measured on a modified form of Gouy's balance by the method described by Prasad, Dharmatti and Gokhale.[5] The values of the specific susceptibilities ($\chi a$) of the several mixtures are given in columns 2 and 5 of Tables I–IV. In columns 3 and 6 of the same tables are given the changes in the values of specific susceptibilities of the mixtures per addition of 1 c.c. of the second component and are denoted by $\Delta\chi a$. The susceptibility values are expressed in terms of $-1 \times 10^{-6}$ c.g.s. units. The experimental error was found to be within ± 1%.

TABLE I

$NH_4NO_3$—$Pb(NO_3)_2$—$H_2O$

| c.c. of $Pb(NO_3)_2$ solution | $\chi a$ | $\Delta\chi a$ | c.c. of $Pb(NO_3)_2$ solution | $\chi a$ | $\Delta\chi a$ |
|---|---|---|---|---|---|
| 0 | 0·7018 | .. | 12 | 0·6610 | 0·0025 |
| 1 | 0·6987 | 0·0031 | 14 | 0·6560 | 0·0025 |
| 2 | 0·6954 | 0·0033 | 16 | 0·6506 | 0·0027 |
| 3 | 0·6918 | 0·0036 | 18 | 0·6440 | 0·0033 |
| 4 | 0·6878 | 0·0040 | 20 | 0·6366 | 0·0037 |
| 5 | 0·6832 | 0·0046 | 22 | 0·6326 | 0·0020 |
| 6 | 0·6801 | 0·0031 | 24 | 0·6287 | 0·0020 |
| 7 | 0·6771 | 0·0030 | 26 | 0·6251 | 0·0018 |
| 8 | 0·6739 | 0·0032 | 28 | 0·6214 | 0·0019 |
| 9 | 0·6702 | 0·0037 | 30 | 0·6176 | 0·0019 |
| 10 | 0·6660 | 0·0042 | | | |

### TABLE II

$NH_4NO_3$—$AgNO_3$—$H_2O$

| c.c. of $AgNO_3$ solution | $\chi_a$ | $\Delta\chi_a$ | c.c. of $AgNO_3$ solution | $\chi_a$ | $\Delta\chi_a$ |
|---|---|---|---|---|---|
| 0 | 0·7018 | .. | 12 | 0·6767 | 0·0015 |
| 1 | 0·7003 | 0·0015 | 14 | 0·6736 | 0·0016 |
| 2 | 0·6987 | 0·0016 | 16 | 0·6702 | 0·0017 |
| 3 | 0·6969 | 0·0018 | 18 | 0·6664 | 0·0019 |
| 4 | 0·6950 | 0·0019 | 20 | 0·6619 | 0·0023 |
| 5 | 0·6929 | 0·0021 | 22 | 0·6587 | 0·0016 |
| 6 | 0·6906 | 0·0023 | 24 | 0·6554 | 0·0017 |
| 7 | 0·6881 | 0·0025 | 26 | 0·6521 | 0·0017 |
| 8 | 0·6855 | 0·0026 | 28 | 0·6487 | 0·0017 |
| 9 | 0·6827 | 0·0028 | 30 | 0·6456 | 0·0015 |
| 10 | 0·6797 | 0·0030 | | | |

### TABLE III

$NH_4Cl$—$ZnCl_2$—$H_2O$

| c.c. of $ZnCl_2$ solution | $\chi_a$ | $\Delta\chi_a$ | c.c. of $ZnCl_2$ solution | $\chi_a$ | $\Delta\chi_a$ |
|---|---|---|---|---|---|
| 0 | 0·7089 | .. | 12 | 0·6857 | 0·0016 |
| 1 | 0·7079 | 0·0010 | 14 | 0·6825 | 0·0016 |
| 2 | 0·7066 | 0·0013 | 16 | 0·6789 | 0·0018 |
| 3 | 0·7049 | 0·0017 | 18 | 0·6747 | 0·0021 |
| 4 | 0·7027 | 0·0022 | 20 | 0·6693 | 0·0027 |
| 5 | 0·6998 | 0·0029 | 22 | 0·6661 | 0·0016 |
| 6 | 0·6976 | 0·0022 | 24 | 0·6629 | 0·0016 |
| 7 | 0·6953 | 0·0023 | 26 | 0·6599 | 0·0015 |
| 8 | 0·6933 | 0·0020 | 28 | 0·6570 | 0·0015 |
| 9 | 0·6912 | 0·0021 | 30 | 0·6542 | 0·0014 |
| 10 | 0·6888 | 0·0024 | | | |

TABLE IV

$NH_4Cl—CdCl_2:2H_2O—H_2O$

| c.c. of $CdCl_2$ solution | $\chi a$ | $\Delta\chi a$ | c.c. of $CdCl_2$ solution | $\chi a$ | $\Delta\chi a$ |
|---|---|---|---|---|---|
| 0 | 0·7089 | .. | 12 | 0·6922 | 0·0015 |
| 1 | 0·7076 | 0·0013 | 14 | 0·6885 | 0·0019 |
| 2 | 0·7061 | 0·0015 | 16 | 0·6842 | 0·0022 |
| 3 | 0·7044 | 0·0017 | 18 | 0·6792 | 0·0025 |
| 4 | 0·7026 | 0·0018 | 20 | 0·6736 | 0·0028 |
| 5 | 0·7005 | 0·0021 | 22 | 0·6694 | 0·0021 |
| 6 | 0·6996 | 0·0009 | 24 | 0·6654 | 0·0020 |
| 7 | 0·6986 | 0·0010 | 26 | 0·6614 | 0·0020 |
| 8 | 0·6976 | 0·0010 | 28 | 0·6573 | 0·0021 |
| 9 | 0·6965 | 0·0011 | 30 | 0·6533 | 0·0020 |
| 10 | 0·6952 | 0·0013 | | | |

Values of the specific susceptibilities ($\chi a$) of mixtures of different concentrations for each system were plotted against the volume of the second component added to 20 c.c. of the ammonium salt and the curves obtained are shown in full lines in Figs. 1–4. It will be seen that these curves are non-linear and show breaks at some points. In order to bring out the breaks in the curves more clearly, the changes in the susceptibility value per addition of 1 c.c. of the second component ($\Delta\chi a$) were plotted against the number of c.c. of the second component added to the fixed quantity of the ammonium salt and the curves obtained are shown in Figs. 1–4 in dotted lines.

## DISCUSSION OF RESULTS

(*a*) $NH_4NO_3—Pb(NO_3)_2—H_2O$.—The curves (Fig. 1) obtained for this system show breaks at three points, corresponding to the addition of 5 c.c., 10 c.c. and 20 c.c. of $Pb(NO_3)_2$ solution. These breaks indicate the formation of $4NH_4NO_3 \cdot Pb(NO_3)_2$, $2NH_4NO_3 \cdot Pb(NO_3)_2$ and $NH_4NO_3 . Pb(NO_3)_2$, in solution. These observations are in agreement with those of Nair and Pande.[4] None of these compounds has been isolated so far. Bogitch[6] dissolved lead nitrate in molten ammonium nitrate but did not get any evidence for the formation of the double salt with mixtures containing up to 55% lead nitrate.

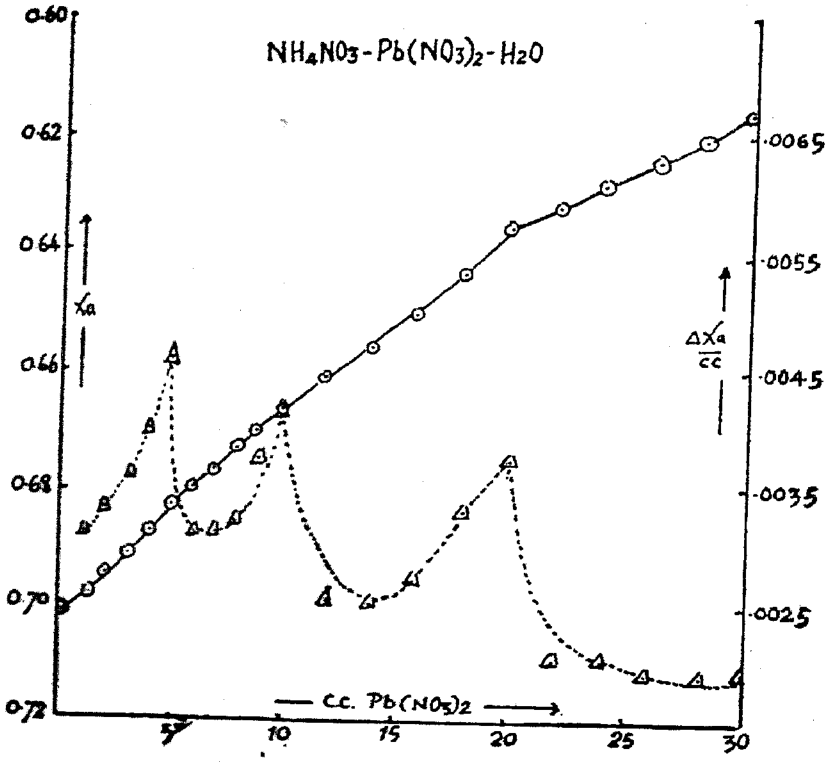
NH₄NO₃-Pb(NO₃)₂-H₂O
0.60
0.62
0.64
0.66
0.68
0.70
0.72
χa
Δχa/cc
·0065
·0055
·0045
·0035
·0025
cc. Pb(NO₃)₂
5
10
15
20
25
30

FIG. 1

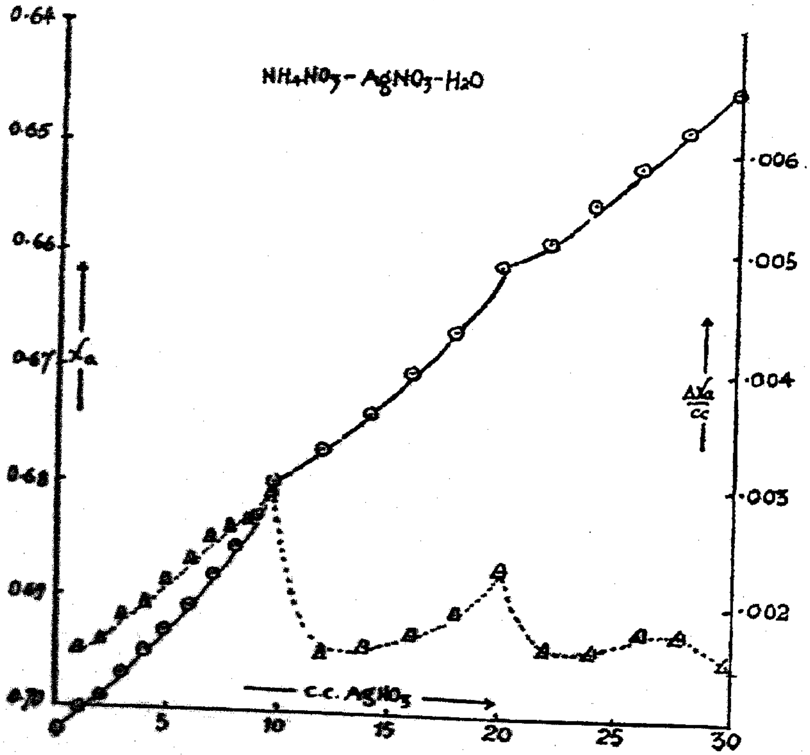
NH₄NO₃-AgNO₃-H₂O
0.64
0.65
0.66
0.67
0.68
0.69
0.70
χa
Δχa/cc
·006
·005
·004
·003
·002
c.c. AgNO₃
5
10
15
20
25
30

FIG. 2

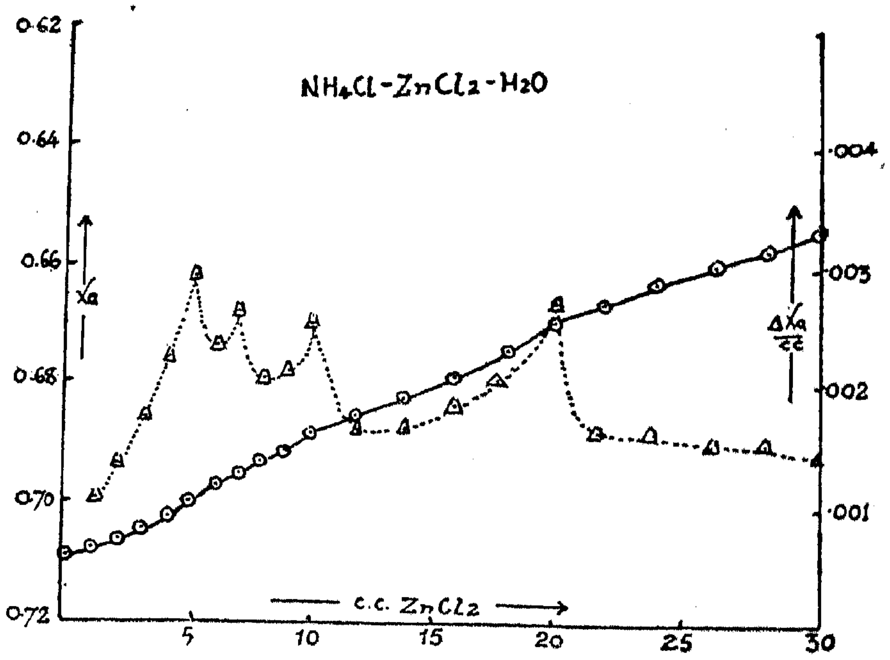
NH₄Cl-ZnCl₂-H₂O
0·62
0·64
0·66
0·68
0·70
0·72
χa
Δχa/cc
·004
·003
·002
·001
c.c. ZnCl₂
5
10
15
20
25
30

FIG. 3

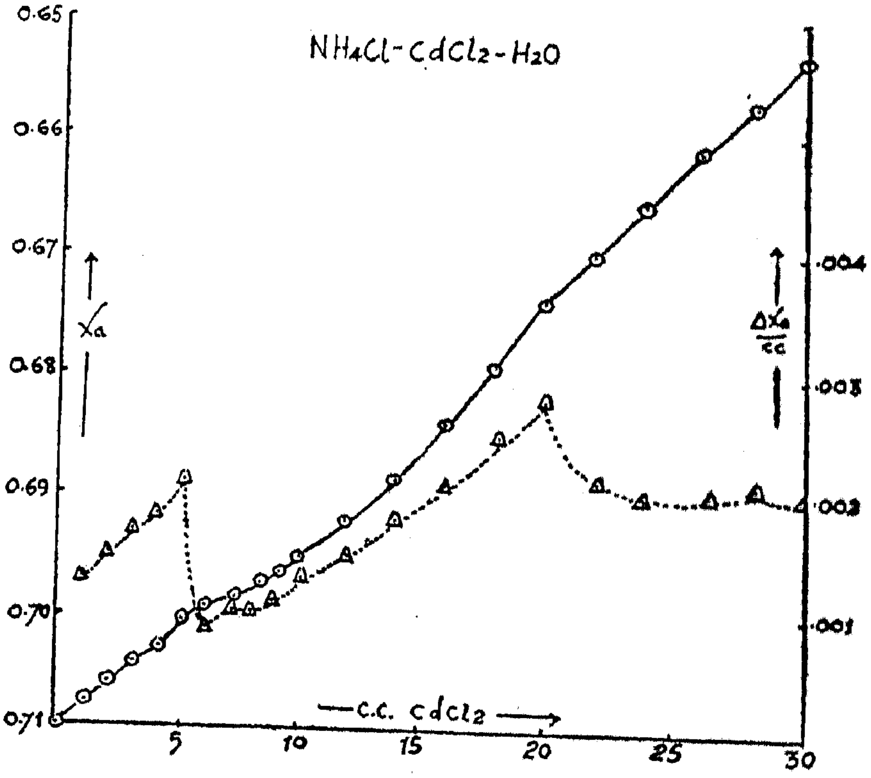
NH₄Cl-CdCl₂-H₂O
0·65
0·66
0·67
0·68
0·69
0·70
0·71
χa
Δχa/cc
·004
·003
·002
·001
c.c. CdCl₂
5
10
15
20
25
30

FIG. 4

(*b*) *$NH_4NO_3 \cdot AgNO_3$—$H_2O$*.—The curves (Fig. 2) obtained for this system show definite breaks at the points corresponding to the addition of 10 c.c. and 20 c.c. of $AgNO_3$ solution, indicating the formation of $2\,NH_4NO_3 \cdot AgNO_3$ and $NH_4NO_3.AgNO_3$. The existence of $NH_4NO_3 \cdot AgNO_3$ has been confirmed by Zawadsky and Flavitzky[7] and Russell and Maskelyne[8] from freezing point curves of the mixtures of $NH_4NO_3$ and $AgNO_3$. The existence of $2\,NH_4NO_3 \cdot AgNO_3$ has not been reported so far.

(*c*) *$NH_4Cl$—$ZnCl_2$—$H_2O$*.—The breaks observed in the curves (Fig. 3) for this system occur for the addition of 5 c.c., 6·67 c.c., 10 c.c. and 20 c.c. of $ZnCl_2$ solution, indicating that as many as four compounds, namely, $4\,NH_4Cl \cdot ZnCl_2$, $3\,NH_4Cl \cdot ZnCl_2$, $2\,NH_4Cl \cdot ZnCl_2$ and $NH_4Cl \cdot ZnCl_2$, exist in solution. Grunauer[9] measured the melting points of nine different mixtures of $ZnCl_2$ and $NH_4Cl$ and obtained a V-shaped curve with eutectics at three different points corresponding to three different double salts. From the study of freezing, melting and boiling points of the binary mixtures of $NH_4Cl$ and $ZnCl_2$, Hachmeister[10] has shown that $NH_4Cl$ and $ZnCl_2$ combine in the ratio 4: 1, 3: 1, 2: 1 and 1: 2. Though Hachmeister has not reported the existence of the salt $NH_4Cl \cdot ZnCl_2$, Mellor[11] states that it is obtained by the fractional crystallisation of a solution containing equimolecular parts of $ZnCl_2$ and $NH_4Cl$. Marignac[12] has reported the isolation of $2\,NH_4ClZn \cdot Cl_2$ and $3\,NH_4Cl \cdot ZnCl_2$.

(*d*) *$NH_4Cl$—$CdCl_2$—$H_2O$*.—The formation of $4\,NH_4Cl \cdot CdCl_2$ and $NH_4Cl \cdot CdCl_2$ in solution is indicated by the breaks in the curves (Fig. 4) occurring for the addition of 5 c.c. and 20 c.c. of $CdCl_2$ solution. These observations support the results obtained by Hachmeister[10] from the study of the freezing, boiling and melting points of the binary mixtures of these two salts. Croft,[13] Crossman[14] and Rimbach[15] have reported the isolation of $CdCl_2 \cdot NH_4Cl$. Von Hauver[16] has prepared the compound $CdCl_2 \cdot 4NH_4Cl$, as a crystalline solid.

## SUMMARY

Magnetic susceptibilities of ternary systems consisting of (i) ammonium nitrate and the nitrates of lead and silver and (ii) of ammonium chloride and the chlorides of zinc and cadmium have been measured in solution on a modified form of Gouy's balance. The results obtained have been utilised to reveal the formation of double salts in solution in each system.

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