Formation of Complex Compounds Between Uranyl Nitrate and Nitrate of the Second Group Elements

The System: $Hg_2(NO_3)_2-UO_2(NO_3)_2-H_2O$ (Conductivity, refractive Index, Spectrophotometry and pH)

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With 3 Figures

Summary

A study of the physicochemical properties like refractive index, spectrophotometry, conductivity and pH measurements of a series of mixed solutions of uranyl nitrate and mercurous nitrate have shown the existence of two complexes in solution in the (1:1) and (1:2) molecular ratios respectively viz.

$$UO_2(NO_3)_2 \cdot Hg_2(NO_3)_2, \quad \text{(i)}$$

$$UO_2(NO_3)_2 \cdot 2Hg_2(NO_3)_2. \quad \text{(ii)}$$

Both the above mentioned compounds have been detected only in the solution by the breaks in the usual curves when various properties like conductivity, refractive index, spectrophotometry and pH were plotted against the m.l. of mercuric nitrate (M/10) added to a fixed volume of uranyl nitrate (M/10).

Introduction

The results based on our studies in the formation of complex compounds between uranyl nitrate and rubidium nitrate have been reported in the previous issue of this series.[1])

It has been observed that the uranyl ion $(UO_2)^{++}$ has a strong tendency towards the formation of complexes. A vast majority of cases are known in which it has increased its covalency by complex formation. This fact initiated early chemists like RIGGS[2]), MALQUOSI[3]), LAYBOURN and MAD-

[1]) S. S. GUPTA and B. N. SHARGA, Z. anorg. allg. Chem. **331**, 216 (1964).

[2]) S. GLASSTONE and E. J. RIGGS, J. chem. Soc. (London) **2**, 2846 (1925).

[3]) G. MALQUOSI, hazz. chim. ital. **58**, 203 (1928); **59**, 355 (1929); Atti Reale Accad. Lincii, naz.-(vi) **9**, 231–233 (1929).

GIN[4]), HILL and KAPLAN[5]), PAUSETHIN and RADIOICIE[6]), NAYAR and PANDE[7]), to study the alkali nitrate complexes with a complex forming nitrate of either a transition metal or that of other rare elements and their efforts proved fruitful in this direction.

The complexes of uranyl nitrate with that of copper and cesium have also been reported by the authors recently[8])[9]). The complexes of uranyl nitrate with that of cobalt nitrate have been reported by GUPTA and MARWAH[10]). But since no systematic work has been done on the formation of complexes between uranyl nitrate and mercurous nitrate so it was thought to be desirable to explore and investigate such system thoroughly.

The present work deals with the studies on the complex formation between uranyl nitrate and mercurous nitrate. The nature of the complexes refractive index, spectrophotometry and pH studies which indicated clearly the existence of two complexes in the (1:1) and (1:2) molecular ratios respectively. The sensitivity of the spectrophotometry helped us to detect all possible complexes in solution.

Experimental

Uranyl nitrate and mercurous nitrate of A.R./B.D.H. quality were employed for the preparation of the standard solutions. The purity of each salt was estimated before use by the usual standard methods. The stock solutions were prepared in conductivity water and were stored in thoroughly cleaned and steamed glass stoppered Jena glass bottles. 5 c.c. of uranylnitrate (M/10) were taken into 50 c.c. standard flask to which a requisite volume of mercuric nitrate solution (M/10) was mixed and the mixture was made up to the mark i.e. 50 c.c. by the addition of conductivity water. In this way a series of 27 mixed solutions were prepared following monovariation method[11]) in which the concentration of uranyl ion was kept constant while that of mercurous nitrate was varied systematically. The solutions were stored in thoroughly cleaned stoppered glass bottles. The composition of the solutions were on the same lines as reported in the previous communication.

Conductivity

Instead of usual KOHLRAUSCH's meter-bridge method a latest and more sensitive electronic magic eye apparatus (type: G.M. 4249 phillips) was employed to determine the conductivity of the solutions. A pyrex glass

[4]) K. LAYBOURN and W. M. MADGIN, J. chem. Soc. (London) **874**, 1360 and 2582 (1932).

[5]) A. E. HILL and N. KAPLAN, J. Amer. chem. Soc. **58**, 1644 (1936).

[6]) M. A. PUSCHIN and M. RADIOICIE, Z. anorg. allg. Chem. **233**, 41 (1937).

[7]) M. R. NAYAR and C. S. PANDE, Proc. Indian Acad. Sci. **27**, 284 (1948); **27**, 343 (1948) Cunent Sci. **27**, 187 (1948).

[8]) S. S. GUPTA and B. N. SHARGA, J. prakt. Chem. **22**, 101 (1963).

[9]) S. S. GUPTA and B. N. SHARGA, J. prakt. Chem. **25**, 318 (1964).

[10]) S. S. GUPTA and S. D. MARWAH (Miss), J. prakt. Chem. **24**, 83 (1964).

[11]) M. R. NAYAR and C. S. PANDE, Proc. Indian Acad. Sci. **27**, 284 (1948); **27**, 343 (1948); Cunent Sci. **17**, 187 (1948).

conductivity cell with electrodes of platinum was used. The cell was well washed and the electrodes were platinized by following all the details given in FINDLAY's practical physical chemistry. The cell was rinsed well with the solutions used. All the measurements were made at a constant temperature by keeping the cell in an electrically maintained thermostat at 35 °C. Atleast three readings were taken for each solution. The solutions were placed for half an hour before observations. The values of conductances are recorded in Fig. 1.

Refractive Index

Measurements of refractive indices were carried out with the help of a direct reading refractometer (Bellingham and Stanley Ltd. Model No. 344223). Before recording any observation the temperature was regulated and it was always tried to maintain a high standard of accuracy. The values of refractive indices are recorded in Fig. 3.

Spectrophotometry

The percentage transmittance and optical density were made by using a unicam 500 cycles spectrophotometer. The solutions were maintained at 35 °C by placing them in a thermostat at that temperature. Before recording the observations the adjustment was made with the blank solvent used in the preparation of solutions. The spectrophotometric observations are recorded in Fig. 2.

pH Measurements

The pH observations for the solutions were made by employing a Beckman pH meter (Model H 2 Serial 119943). Having glass electrode. Before taking any reading it was adjusted with an standard buffer solution and only then the observations were recorded. Fig. 3 indicates the values taken.

Discussion

An examination of the curves in Fig. 1, 2 and 3 which represent the results of conductivity refractive index, percentage transmittance optical density

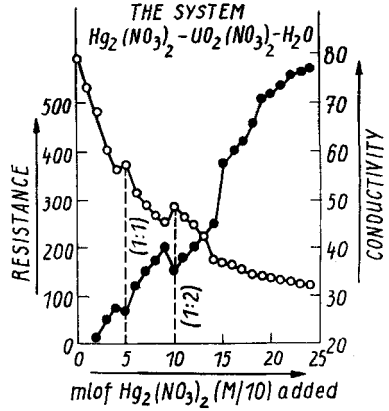

Fig. 1

and pH shows that there are two definite breaks in each case, in the regular curves at intervals corresponding to 5 c.c. and 10 c.c. of mercurous nitrate solution since both the solutions, mercurous nitrate as well as uranyl nitrate

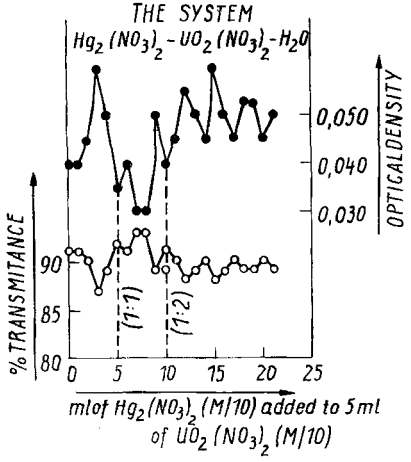

Fig. 2

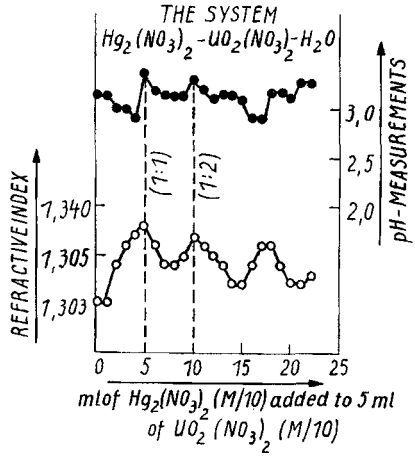

Fig. 3

were of same strength i.e. (M/10) the ratios of uranyl nitrate to mercurous nitrate at these points are (1:1) and (1:2) respectively corresponding to the formation of two compounds in solution having the formulae.

1. $UO_2(NO_3)_2 \cdot Hg_2(NO_3)_2$ or $Hg_2[UO_2(NO_3)_4]$,
2. $UO_2(NO_3)_2 \; 2Hg_2(NO_3)_2$ or $Hg_4[UO_2(NO_3)_6]$.

There is excellent similarity in the curves with respect to all physico chemical properties investigated and therefore there is the least doubt about the genuineness of the phenomenon. The breaks occur at exact stoichiometric ratios of concentrations corresponding to the compounds stated above. Thus the existence of these compounds, become unequivoval when such dissimilar properties like conductance, refractive index, spectrophotometry and pH measurements yield similar results.

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