

INVESTIGATION ON NICKEL AMMINES. PART IV. THE INFLUENCE OF THE PRESENCE OF NEUTRAL AND AMMONIUM SALTS OF VARIOUS ANIONS ON THE SOLUBILITY OF NICKELOUS HYDROXIDE IN AQUEOUS AMMONIA SOLUTIONS

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Observations on the effect of sodium, potassium and ammonium salts of various anions, on the solubility of nickelous hydroxide in ammonia solutions have been recorded and the results explained in the light of the amphoteric nature of the hydrated nickel oxide.

The presence of ammonium salts affecting the solubility of the hydrated nickel oxide has been reported, only generally, by workers like Rogers (*Phil. Mag.*, 1834, 3) and Kato (*J. Chem. Soc. Japan*, 1937, 48, 1146). Recently Archipov and Pakschur (*J. Appl. Chem. Russ.*, 1943, 16, 356) have shown a definite increase in the solubility of cupric hydroxide in ammonia in the presence of ammonium carbonate, chromate, sulphocyanide and sulphide. Our results on the solubility of hydrated nickel oxide in ammonia in presence of various ammonium salts as well as neutral salts of sodium and potassium have been recorded in this communication.

EXPERIMENTAL

A suspension of hydrated nickelous oxide (22 c.c.) obtained by the interaction of equivalent amount of nickel sulphate and caustic soda at 80° and containing 67.32 mg. atoms per litre of nickel, was taken in glass stoppered Jena bottles and 3 c.c. of *M/2* sodium, potassium or ammonium sulphate, nitrate, acetate, or sulphocyanide were added to each of the suspensions separately so that the ratio of nickel to ammonium, sodium or potassium was 1:2. To these mixtures 50 c.c. of ammonia solutions of various concentrations were added and the solubility of the hydroxide determined as described in part II of this series (this *Journal*, 1950, 27, 679). The associated sulphate with the hydrated oxide was also estimated and the following table gives some of the typical results.

TABLE I

Solubility in ammonia solutions.

Nickel in suspension = 67.32 mg. atoms/litre. Sulphate associated with the precipitate = 7.91 mg. ions/litre. Temperature = 30°.

Solubility of the nickelous hydroxide sample in 0.5 *M* ammonia soln. = 0.32250 mg. atom/litre of Ni.
Amount of nickel dissolved in mg. atoms/litre

Solubility in presence of	Sulphate.	Chloride.	Nitrate.	Acetate	Sulphocyanide.
Ammonium salts	5.732	5.730	5.728	5.725	5.720
Sodium salts	0.3220	0.3220	0.3220	0.3198	0.3195
Potassium salts	0.3220	0.3199	0.3199	0.3198	0.3195

TABLE I (contd.)

Solubility in presence of	Sulphate.	Chloride.	Nitrate	Acetate.	Sulphocyanide.
Solubility of the nickelous hydroxide sample in 1.0 M ammonia soln. = 1.9507 mg. atoms/litre of Ni.					
Amount of nickel dissolved in mg. atoms/litre					
Ammonium salts	11.380	11.280	1.1990	10.850	9.998
Sodium salts	1.9512	1.9510	1.9508	1.9500	1.9499
Potassium salts	1.9505	1.9510	1.9508	1.9500	1.9500
Solubility of the nickelous hydroxide sample in 1.5 M ammonia soln. = 3.366 mg. atoms/litre of Ni.					
Ammonium salts	12.01	11.91	11.51	11.89	11.88
Sodium salts	3.375	3.369	3.365	3.362	3.363*
Potassium salts	3.368	3.379	3.365	3.362	3.363

From the data presented the presence of various neutral salts, viz., the sulphate, chloride, nitrate, acetate and sulphocyanide of sodium and potassium, appears to have no appreciable effect on the solubility of nickelous hydroxide in aqueous ammonia; but the solubility increases in the presence of ammonium salts. Thus for instance, even in such a low concentration of ammonia as 0.5 M, the amount of nickel dissolved from a sample of nickelous hydroxide precipitated by an equivalent alkali in the hot, is only 0.3125 mg. atom/litre, whereas the solubility increases to 5.732, 5.730, 5.728, 5.725 and 5.720 mg. atoms/litre of Ni in presence of ammonium salts of various anions. Our results also indicate that the anions have only a slight effect on the solubility. It is, however, to be noted that the presence of sulphate increases the solubility slightly more than the other salts of ammonium.

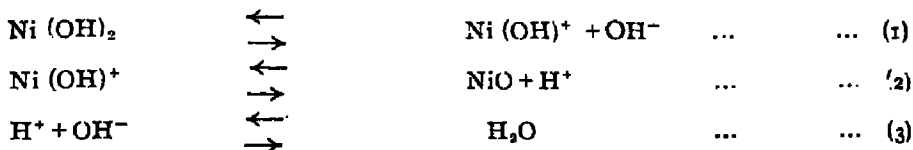
Our observations with nickelous hydroxide thus differ from those of the other workers referred to (*loc. cit.*); because these workers have given no consideration to the character of the hydroxides used and to the method of precipitation, which is important, as has been shown by our work (*loc. cit.*).

This enhanced solubility of nickelous hydroxide in aqueous ammonia in presence of ammonium salts have been explained by Kato (*loc. cit.*) to be due to the buffer action of ammonium salt-ammonia mixtures. Considering the following equilibrium which exists in a solution of ammonia (cf. Everett and Wynne-Jones, *Proc. Roy. Soc.*, 1938, 169A, 190)



it is evident that the addition of ammonium salts will necessarily increase the concentration of NH_3 in solution which in its turn will favour the formation of ammine with nickel ion. This factor is, however, not prominent as we have noted that the partition coefficient or the distribution ratio of ammonia to chloroform or amyl alcohol is hardly affected by the presence of ammonium salts (cf. Hantzsch and Sebaldt, *Z. physikal. Chem.*, 1899, 30, 258). We therefore suggest that the acid character of the ammonium ion is also of importance. On the basis of the Lowry Bronsted concept, ammonium ion behaves as a proton donator; thus $\text{NH}_4^+ = \text{NH}_3 + \text{H}^+$

Now considering the amphoteric behaviour of nickelous hydroxide as suggested by us (*loc. cit.*) and as shown by the following equations:



We find that in equation (1), the liberation of OH^- will mean a tendency in the hydroxide to seek protons, which could be furnished by the NH_4^+ ion if present in solution. Consequently a large proportion of Ni (OH)^+ will be formed, because of the basic character of the hydroxide, and this will have a greater affinity for electrons. Thus the formation of a co-ordinated ammine and the solubility of the hydrated oxide will increase in the presence of ammonium salts. This also explains the negligible effect of the sodium and potassium salts.

From the experimental results recorded in the last three parts of the series, we have concluded that the character of the hydrated oxide is the sole guiding factor for its dissolution in aqueous ammonia solutions. We therefore emphasise that the wide variation and anomalies in the results of the various earlier workers are due to their failure to recognise the importance of the conditions of precipitation and character of nickelous hydroxide. We are therefore of the opinion that favourable conditions for dissolution of hydroxides in ammonia consists in the precipitation of the hydroxide in the cold with deficient alkali or by carrying out the dissolution in presence of ammonium salts, as under all these conditions, the basic character of the hydroxide, which is necessary for co-ordinations, is prominent.

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