STUDIES ON NESSLER'S REAGENT AND NESSLER'S PRECIPITATE PART II

by

PULIN BIHARI SARKAR AND NRIPENDRA NATH GHOSH

Inorganic Chemistry Laboratory, University College of Science, Calcutta (India)

For the detection of ammonia, NESSLER¹ first introduced a reagent, the preparation of which has subsequently been modified by different workers² — the presence of $[HgI_4]^{-2}$ ions being varied from 0.08M to 0.1M and the concentration of caustic alkalies from 0.5M to 3M. The existence of an intermediate compound has been shown in our previous communication³.

The composition of the characteristic brown precipitate, formed when the Nessler's reagent is treated with ammonia, has been described in the literature as $NHg_2I_1H_2O$ by some workers⁴ and as $NH_2Hg_2I_3$ by others⁵. In our present communication attempts have been made to arrive at a definite conclusion regarding its composition from potentiometric study, assuming that the formation of the precipitate takes place in the following manner:

$$[HgI_4]^{-2} + 2 OH^- \rightleftharpoons [Hg \frac{(OH)_2}{I_2}]^{-2} + 2I^-$$
 (1)

$$2[Hg \frac{(OH)_2}{I_2}]^{-2} + NH_3 \gtrsim NH_{n-1}Hg_2I_n, aq. + (4-n)I^- + nOH^-$$
(2)

Now if the initial molar concentration of $[HgI_4]^{-2}$ ions used be A, then,

$$A - A_1 + A_2 + 2A_3 \tag{3}$$

where A_1 and A_2 are the ultimate concentrations of $[HgI_{41}^{-2}]^{-2}$ and $[Hg] \frac{(OH)_2}{I_2}]^{-2}$ ions respectively and A_3 the number of moles of $NH_{n-1}Hg_2I_n$, aq. precipitated from a litre of the Nessler's solution, due to addition of a known amount of ammonia, the concentration of which is denoted by a. Throughout the series of an experiment, the concentration (B) of potassium hydroxide has been assumed to remain constant as it was present in large excess. So the apparent equilibrium constant K' from (I)

$$K' = \frac{A_2 I^2}{A_1} \tag{4}$$

where I is the concentration of total iodide ion liberated. And from (r) and (2), we have,

$$I = 2A_2 + (8-n)A_3 \tag{5}$$

References p. 212

is given by,

As $NH_{n-1}Hg_2I_n$ aq. is practically insoluble and ammonia remaining unreacted is infinitely small, it can be deduced from (2),

$$-1_3$$
 α . (6)

From (3), (4), (5) and (6) by solving, the expression for n is given by,

$$n = 8 - \frac{r}{a} \left\{ \frac{I - \frac{2(A - 2a)}{I^2}}{r + \frac{K'}{K'}} \right\}$$
(7)

EXPERIMENTAL

The values of I, with or without addition of ammonia to the Nessler's reagent, were calculated from the observed e.m.f. of the concentration cells containing iodide-hypoiodite system, following similar procedure and using the reagents of the same grade as described in detail in our previous communication. The concentration of iodide ion in the reference cell was 0.02M. It was observed that when caustic alkalies of high concentration were present in the Nessler's reagent, there was a deposition of yellow HgO at the liquid junction of the KCI bridge during e.m.f. measurements. This difficulty had been avoided by replacing KCI in the bridge with KOH, the concentration of which was the same as that of the alkali present in the concentration cells, and the observed e m.f. values were corrected as usual. In each case, knowing the value of I before adding ammonia, K' was calculated from the relation (4) and from the corresponding value of I, after adding a known amount of ammonia, n in (7) was evaluated. The results are stated in Table I. The amount of ammonia was added in such a proportion as to precipitate 160°_{0} of mercury initially present in the solution.

TABLE I

CONCENTRATION OF TODIDE TON IN THE REFERENCE CELL = 0.02M

Conen. of [11g14]-2 A	Conen of alkalı 11	F (corrected) in Volts Wethout With		Concn. of	h	
		ansmonte	ammonta	ci	1,1-2011	,,
0.05	3 03	0 0140	0 0105	0 00.4	2 2()	0.8
0 10	3 03	0.0105	0 0225	0.008	1.96	1.0
0,20	3 03	0 0245	0.0285	0.010	1.66	1.1
0.05	2.02	0.0130	0.0155	0.001	1.01	1.0
0 10	2 0 2	0 0175	0.0210	0.008	1.61	1 1
0.20	2.02	0.0230	0 0275	0.010	1 31	1.3
0.05	1,00	0 0100	0.0130	0 004	1.30	13
0 10	1,00	0.0150	0.0100	0.008	1.00	1.5
0,20	1.00	0.0220	0.0265	0.016	0.70	1.8
0.05	0 10	0 0070	0.0105	0.00.1	0.68	1.8
0.10	0.49	0.0120	0.0165	0.008	0.38	2.3
0.20	0.49	0.0205	0.02.15	0.016	0.08	29

From the experimental data, it has been observed that n is a function of both A and B. In order to find out any empirical relation between n, A and B, a curve (Fig. 1) has been obtained by plotting n against the corresponding values of $(p_A - 2p_B)$ and the following empirical relation has been derived.

$$n (\log_{10} \frac{B^2}{.1} + r) = 3.$$

Another set of experiments was carried out by adding the different amounts of annonia to the same solution of Nessler's reagent and the results are stated graphically in Fig. 2, by plotting n against logarithm of the percentage of mercury precipitated as annoniated product. It has been found that the value of n increases with the increase in concentration of ammonia. The colour of the precipitate also deepens

210

References p 212



from brown to chocolate with the increase in iodine content and the chance of the formation of a precipitate containing no iodine is very remote.

Hence it may be concluded that the composition of the precipitate depends on the concentrations of $\{\Pi g I_4\}^{-2}$ and OH^{-1} ions as well as on the amount of ammonia added. The possible compositions are as stated below:

$$\begin{split} & \mathrm{NHg}_{2}\mathrm{I}_{1}\mathrm{H}_{2}\mathrm{O}_{-}(\mathrm{O}_{-}\frac{\mathrm{Hg}}{\mathrm{Hg}}\mathrm{>}\mathrm{NH}_{2}\mathrm{I}) \quad \text{brown} \\ & \mathrm{NHHg}_{2}\mathrm{I}_{2}\mathrm{,}\mathrm{H}_{2}\mathrm{O}_{-}(\frac{\mathrm{HO}_{-}\mathrm{Hg}}{\mathrm{I}_{-}\mathrm{Hg}}\mathrm{>}\mathrm{NH}_{2}\mathrm{I}) \quad \mathrm{deep}_{-}\mathrm{brown} \\ & \mathrm{NH}_{2}\mathrm{Hg}_{2}\mathrm{I}_{3}_{-}(\frac{\mathrm{I}_{-}\mathrm{-}\mathrm{Hg}}{\mathrm{I}_{-}\mathrm{Hg}}\mathrm{>}\mathrm{NH}_{2}\mathrm{I}) \quad \mathrm{chocolate}. \end{split}$$

It may be of interest to recall the properties of Millon's Base⁶:

 $\frac{\text{HO}_{--}\text{Hg}}{\text{HO}_{--}\text{Hg}} \text{NH}_{2}\text{OH} \text{ or } O^{\times} \frac{\text{Hg}}{\text{Hg}} \text{NH}_{2}\text{OH}_{1}\text{H}_{2}\text{O}.$

Ordinary salt solutions + Millon's Base \rightarrow Salts of Millon's Base (very difficultly soluble) + hydroxide of metal, e.g.

(i) Dilute KI solution + Millon's Base \rightarrow Iodide of Millon's base + KOII, the filtrate being free from iodide ion.

(ii) $CuSO_4$ or $FeCl_3$ solution shaken with Millon's Base gives rise to a filtrate free from all salts.

Therefore the suggested overall reactions are:

$$1) \quad 2[Hgl_4]^{-2} + NH_3 + 3OH^{-} \rightleftharpoons O < \frac{Hg}{Hg} NH_2 I + 7I^{-} + 2H_2 O$$

2)
$$2[HgI_4]^{-2} + NH_3 + 2OH^- \Rightarrow \frac{HO-Hg}{I-Hg}NH_2I + 0I^- + H_2O$$

3)
$$2[HgI_4]^{-2} + NH_3 + OH^- \Rightarrow \frac{1 - Hg}{1 - Hg} NH_2I + 5I^- + H_2O$$

References p. 212

From the experimental data it may be observed that as the concentration of ammonia or iodomercurate ion increases, alkali remaining constant, the precipitate tends towards the formula $NH_2Hg_2I_3$; while when alkali concentration increases and the other reactants are constant, the formula of the precipitate approaches to NHg₂I, H.,O.

As the Nessler's reagent is mainly used for the detection or estimation of traces of ammonia, so it may be stated that the characteristic brown coloration or precipitation is due to the formation of NHg_aI,H₂O,

SUMMARY

The composition of the precipitate formed when the Nessler's reagent is treated with ammonia, is assumed as $NH_{n-1}Hg_{2}I_{n}$, aq. and has been studied potentiometrically from iodide-hypoioditesystem. It has been observed that the value of n depends on the concentrations of $[HgI_{1}]^{-2}$ and OH⁻ ions as well as on the amount of ammonia added and it may vary from 1 to 3. The colour of the precipitate deepens from brown to chocolate as the value of n increases

RÉSUMÉ

Les auteurs attribuent au précipité, formé lorsque le réactif de Nessler est traité par l'ammoniaque, la formule suivante $NH_{n-1}Hg_2I_n$, aq. La formation de ce composé a été étudiée potentiométriquement à partir du système iodure-hypoiodite. On a constaté que la valeur de n dépend des concentrations des ions [Hgl4]² et OH², ainsi que de la quantité d'ammoniaque ajoutée; elle peut varier de 1 à 3. La coloration du précipité fonce du brun au chocolat lorsque la valeur de n croit.

ZUSAMMENFASSUNG

Die Autoren geben dem Niederschlag, welcher sich bildet wenn man das Nesslersche Reagenz mit Ammoniak behandelt, folgende Formel: $NH_{n-1}Hg_2J_{n}aq$. Die Bildung dieser Verbindung wurde potentiometrisch vom System Jodid-Hypojodit ausgehend untersucht. Man stellte fest, dass der Wert *u* von den Konzentrationen der Ionen $[Hg]_1]^2$ und OH, sowie auch von der Quantität des hinzugefügten Ammoniaks abhängt; er kann zwischen 1 und 3 varueren. Die Farbe des Niederschlages vertieft sich mit wachsendem Wert von n von braun zu Schokoladebraun.

REFERENCES

- J. NESSLER, Chem. Zentr., 27 (1856) 529
 J. NESSLER, Z. anal. Chem., 7 (1868) 415; L. W. WINKLER, Chem. Ztg., 23 (1899) 454; G. FRE-RICHS AND E. MANNHEIM, A poth Ztg., 29 (1914) 972; O. FOLIN AND W. DENIS, J. Biol. Chem., 26 (1916) 473; C. O. WILLITS, Unpublished Master's Thesis, 1926.
- ^a P. B. SARKAR AND N. N. GHOSH, Anal. Chim. Acta, 13 (1955) 195.
- D. BARRAR AND R. N. GHOSH, FRAN. COMM. 1916, 15 (1953) 195.
 K. F. RAMMELSBERG, J. prakt. Chem., [2] 38 (1888) 558; K. A. HOFMANN AND E. C. MARBURG, Ann., 305 (1899) 194; E. C. FRANKLIN, Am. Chem. J., 47 (1912) 361.
 N. L. NICHOLS AND C. O. WILLITS, J. Am. Chem. Soc., 56 (1934) 769
- ⁶ H. BILTZ AND W. BILTZ, Laboratory method of Inorganic Chemistry, 1st Edition, John Wiley & Sons, New York, 1909, p. 162.

Received May 13th, 1955

212