STUDIES ON THE BASIC CARBONATES OF NICKEL

Part II. Hydrated Basic Nickel Carbonates

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ABSTRACT

The precipitates obtained during the addition of an alkali carbonate to an aqueous nickel salt solution under reproducible conditions of precipitation were analysed in the wet state. The influence of variation in the molar ratio of reactants on the compositions of the wet precipitates obtained at 25°C from the various systems of nickel salts and alkali carbonates was studied in detail. The formation of three basic carbonates $NiCO_3 . Ni(OH)_2 x H_2O$, $NiCO_3 . 2Ni(OH)_2 . x H_2O$ and $NiCO_3 . 3Ni(OH)_2 . x H_2O$ has been observed. Even when the composition of the wet precipitate $NiCO_3 . 3Ni(OH)_2 . x H_2O$ did not undergo any appreciable change, it was found that the surface area increased with time as the precipitate aged. The surface area measurements were made by means of dye adsorption.

INTRODUCTION

It has been shown by the present authors that the amount of nickel precipitated from a nickel salt solution by the addition of an alkali carbonate depends on several factors such as temperature, mode of addition and agitation.[1] In addition to the fact that different amounts of nickel are thrown out from the solution by alkali carbonate it has also been observed that the compositions of the basic salts precipitated vary with the conditions of precipitation.[2-4] Such variations in the chemical compositions of these basic precipitates have resulted in ambiguity regarding their nature as non-stoichiometric or stoichiometric basic compounds. Such precipitates have also been considered as mixtures of the normal salts and the hydroxides.[5] In the case of some basic metal compounds such a confusion is partly due to the very low solubility of the normal salt as

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well as the hydroxide of the metal. In such a case the simultaneous precipitation of both salts from various mixtures of the reactants is a distinct possibility.[5] A detailed investigation was therefore undertaken to study this phenomenon.

EXPERIMENTAL

Reagents Employed :—Aqueous 0.05 molar solutions of nickel sulphate, chloride and nitrate and exactly decinormal solutions of sodium and potassium carbonates were prepared and standardised as described already.[1]

Procedure :—The precipitation of nickel carbonates was conducted at 25°C in the reproducible manner described earlier.[1] To an aliquot of 0.05 M nickel salt solution taken in a 250 *ml.* pyrex beaker, maintained at $25.0 \pm 0.1°C$ in a thermostat, a known amount of 0.1 N alkali carbonate solution corresponding to a definite molar ratio of reactants, was added dropwise. The solution was stirred mechanically during the addition of the precipitant. The contents of the beaker were centrifuged immediately after the addition of the precipitant was over. The supernatant clear liquid was removed and the precipitate was dispersed into fresh distilled water by agitation and the liquid centrifuged again. The washing process was repeated six to eight times till the precipitate had been washed free of all salts and alkali. (This was determined by taking 10 *ml.* of the clear supernatant liquid and adding a drop of methyl orange indicator to it. When titrated against standard decinormal hydrochloric acid it should not require more acid than an equal volume of distilled water treated similarly, to attain the orange-red colour). The precipitate, in the wet condition, was analysed for its carbon dioxide and nickel contents.

Analysis for carbondioxide and nickel oxide: The precipitate was completely transferred to a flask and the carbonate content of the precipitate was determined by decomposing the wet nickel carbonate by the addition of slight excess of 4N sulphuric acid. The liberated carbondioxide was displaced by drawing a current of carbondioxide-free air, into a series of four successive gas wash bottles, each containing an aliquot of standard barium hydroxide solution. The current of carbondioxide-free air was drawn continuously and till half an hour had elapsed after the reaction was complete. The amount of unreacted barium hydroxide in each of the gas wash bottles was determined by titration against standard decinormal hydrochloric acid using thymolphthalein indicator.[6, 7] A blank experiment was run under identical conditions but without the presence of a carbonate and the necessary correction was made. It was found that this correction was small when compared with the titre value. By employing a known amount of analar anhydrous sodium carbonate, it was found experimentally, that under identical conditions, all the carbondioxide liberated could be absorbed in four successive gas wash bottles containing barium hydroxide since absorption of carbon dioxide gas in the liquid phase was sluggish.[7]

After determining the carbon dioxide content of the basic nickel carbonate, the solution in the flask was analysed for its nickel content gravimetrically by the dimethyl glyoxime method. From the analytical results, the composition of the basic carbonate was expressed in terms of nickel oxide, NiO and carbon dioxide.

RESULTS AND DISCUSSION

The values for the carbon dioxide and nickel oxide contents of the precipitates formed at 25°C from solutions of nickel nitrate and sodium carbonate,

TABLT I

Composition of the wet precipitates obtained at 25°C from the system $Ni(NO_3)_2 - Na_2CO_3$

Amount of $Ni(NO_3)_2$ taken $= 12.50 \times 10^{-4} g$. moles

Molar Ratio $\dfrac{Na_2CO_3}{Ni(NO_3)_2}$	Composition of the Precipitate			
	$NiO \times 10^4 g$ moles	$CO_2 \times 10^4 g$ moles	NiO/CO_2	Mean values of NiO/CO_2
0.25	6.94	3.46	2.01	1.99
	5.89	3.01	1.96	
0.50	6.09	3.08	1.98	2.00
	4.97	2.47	2.01	
0.75	7.54	3.79	1.99	2.00
	7.93	3.95	2.01	
1.00	8.24	4.09	2.02	2.02
	8.55	4.24	2.02	
1.25	7.94	3.46	2.30	2.29
	7.52	3.31	2.27	
1.50	8.42	3.37	2.50	2.62
	7.95	2.98	2.73	
2.00	8.23	2.38	3.46	3.44
	8.51	2.49	3.42	
3.00	9.96	2.16	4.15	4.08
	8.74	2.18	4.01	
4.00	9.21	2.30	4.01	3.96
	9.06	2.32	3.91	

mixed in various molar ratios, are presented in Table I. The results obtained with other systems of nickel salts and alkali carbonates are similar as is evident from Figure I.
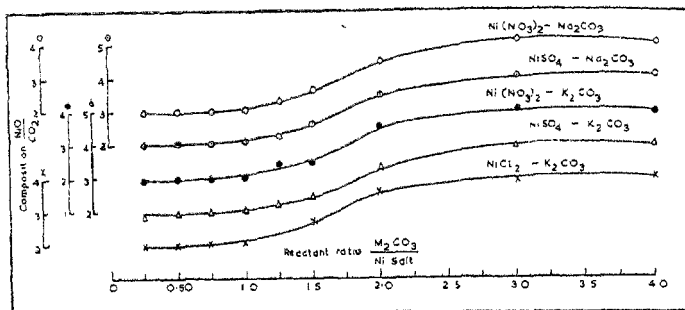
FIG. I

Composition of basic nickel carbonates precipitated at 25°C

The results show that up to a molar ratio of 1.0, the composition of the precipitate does not change and is given by $NiO/CO_2 = 2.0$. At molar ratios of reactants, (alkali carbonate/nickel salt), ranging from 1.0 to 3.0, the composition ratio NiO/CO_2, of the precipitate varies continuously from 2.0 to 4.0. Thereafter, in the molar ratio region 3.0 to 4.0, the composition of precipitate does not alter, but is maintained constant at $4NiO : CO_2$.

It has to be pointed out that all the nickel present in solution is not precipitated unless the amount of alkali carbonate added is about three times the molar concentration of nickel taken[1]. When less than this amount of alkali carbonate was added different amounts of nickel were retained in solution depending on the amount of alkali carbonate added. However, in the present work, it was observed that in two regions composition of the precipitate remained the same even when the reagents were added in different amounts. One such region was when the reactants ratio (alkali carbonate/nickel salt) was between 0.25 and 1.0 and the next when the ratio was between 3.0 and 4.0. This indicates that in each of these regions the solid consits of only one phase and implies the formation of a definite compound.[8] In the first region, the composition of the precipitate may be computed as $NiCO_3 \cdot Ni(OH)_2$ and in the second it is $NiCO_3 \cdot 3Ni(OH)_2$. It has to be mentioned that these precipates are very gelatinous and are known to retain large quantities of water in the wet states.

It was of interest to find out whether the basic nickel carbonate $NiCO_3 \cdot Ni(OH)_2$ precipitated from equimolar mixtures of the reactants undergoes change to the more basic composition $NiCO_3 \cdot 3Ni(OH)_2$ on the addition of two more moles of alkali carbonate per mole of nickel salt taken. The other possibility is that the further addition of a quantity of alkali carbonate might cause the precipitation of more nickel as hydroxide or highly basic carbonate. The following experiment was therefore conducted. The precipitate obtained

at 25°C from an equimolar mixture of nickel salt and alkali carbonate was filtered immediately after the addition was complete and to the filtrate two more moles of alkali carbonate were added dropwise in the same manner as before and with mechanical stirring. The precipitate now obtained was separated from the mother liquor by centrifuging and washed free of adherent ions as described earlier. It was then analysed for its carbon dioxide and nickel oxide contents. For the system nickel sulphate—sodium carbonate, the composition of the precipitate obtained in this manner and expressed in the ratio nickel oxide to carbon dioxide was $(NiO/CO_2) = 3.81$, 3.98 and 4.07 in three different experiments. This composition is the same as that of the precipitate obtained directly at a molar ratio 3.0. It may therefore be concluded that the precipitate is not a mixture of the hydroxide and the normal salt. The above also indicates that the precipitate $NiCO_3 \cdot Ni(OH)_2$ obtained from an equimolar mixture of nickel salt and alkali carbonate, undergoes transformation to the more basic composition $NiCO_3 \cdot 3Ni(OH)_2$ on addition of two more moles of alkali carbonate to the precipitate and mother liquor. It may therefore be observed that the basic character of such precipitates may be increased by carring out the precipitation with higher amounts of alkali carbonate.

Similar results have been obtained with the other systems of nickel salts and alkali carbonates used in the present work.

Influence of ageing on the composition of precipitated basic nickel carbonates :—The influence of time on the amounts of nickel precipitated has been presented in an earlier communication.[1] The effect of ageing on the compositions of precipitated basic nickel carbonates at molar ratios 1.0, 1.5 and 3.0 at 25°C are presented in Table II for a few systems of nickel salt and alkali carbonate.

The results show that in about 20 hours the composition of the precipitate, $NiCO_3 \cdot Ni(OH)_2$ obtained at a molar ratio $Na_2CO_3/NiSO_4 = 1.0$, changes to nearly $NiCO_3 \cdot 2Ni(OH)_2$. After this period, keeping for a longer interval of time has little effect on the composition of the precipitate. It is also seen that mechanical stirring during the period of ageing brings about this change within about two hours. The precipitate obtained at molar ratio 1.5 has ordinarily the approximate composition corresponding to $NiO/CO_2 = 2.5$ and this composition changes on ageing for eight hours, (or for one hour with mechanical stirring) to the composition $NiO/CO_2 = 3.0$. When prepared rapidly (within five minutes mixing of the reagents) the initial composition of this precipitate is nearly $NiO/CO_2 = 2.0$. The precipitates obtained at molar ratios 0.5 and 3.0 do not change their compositions on ageing even for such a long period as 150 hours. These observations are explained in the final papers of this series[9].

Adsorption of methylene blue on the wet basic nickel carbonate $NiCO_3 \cdot 3Ni(OH)_2 \cdot xH_2O$:—It was of interest to find out whether ageing causes any alterations in the physical nature of the precipitated basic nickel carbonates.

TABLE II

Influence of ageing on the composition of Basic Nickel Carbonate

Precipitated from	Initial Compn. NiO/CO₃	Compn. NiO/CO₂ after ageing for the interval					Compn. NiO/CO₂ after agitation for	
		2 hrs.	8 hrs.	24 hrs.	72 hrs.	100 hrs.	2 hrs.	4 hrs.
1. Na₂CO₃/NiSO₄ = 1.0	2.04	2.20	2.49	2.86	.....	2.98	.....	2.82
	1.93	2.18	2.52	2.74	.....	3.11	.....	2.96
2. Na₂CO₃/Ni(NO₃)₂ = 1.0	1.95	2.12	2.52	2.80	3.01	.....	2.93	.....
	1.84	2.24	2.39	2.91	2.96	.....	3.02	.....

By rapid pptn

Precipitated from	Initial Compn. NiO/CO₃	0 hrs.	4 hrs.	8 hrs.	1 hour	2 hrs.
1. Na₂CO₃/NiSO₄ = 1.5	2.51	2.02	2.79	2.91	2.87	2.98
	2.47	2.08	2.84	3.04	2.91	3.02
2. K₂CO₃/NiCl₂ = 1.5	2.46	2.10	2.81	2.98	2.83	3.04
	2.48	2.03	2.89	3.01	2.88	2.98

Precipitated from	Initial Compn. NiO/CO₃	60 hrs.	150 hrs.
1. Na₂CO₃/NiSO₄ = 3.0	3.88	4.06	.....
2. K₂CO₃/Ni(NO₃)₂ = 3.0	3.98	4.03	.....
3. K₂CO₃/NiSO₄ = 3.0	3.98	.....	4.09

The changes in surface properties during the ageing of precipitates are usually followed by employing tracer techniques or also the dye adsorption method.[7] In the previous section it has been shown that the precipitate of composition $NiCO_3 \cdot 3Ni(OH)_2 \cdot xH_2O$ obtained at a molar ratio of reactants (alkali carbonate/nickel salt) = 3.0, does not undergo change in composition on ageing. Preliminary experiments showed that the surface characteristics of this precipitate were altered during ageing as was indicated by the different extents of dye adsorbed on the precipitate. Among the several dyes tried for this purpose. methylene blue was found to be the most suitable.

Reagent employed:—The methylene blue solution was prepared by dissolving 200 mg. of methylene blue crystals (B. D. H.) in distilled water and the solution was made up to a litre to get 0.02 per cent solution. This solution was suitably diluted to get solutions of desired concentrations.

Estimation of methylene blue:—The concentration of methylene blue in the solution was determined spectrophotometrically using a Coleman Universal Spectrophotometer. Distilled water was used as the reference solution. It was found that at a wave-length of $680\,m\mu$ there was maximum absorption of incident radiation by methylene blue solution. This wave-length of light was therefore used for the estimation of methylene blue in all subsequent experiments.
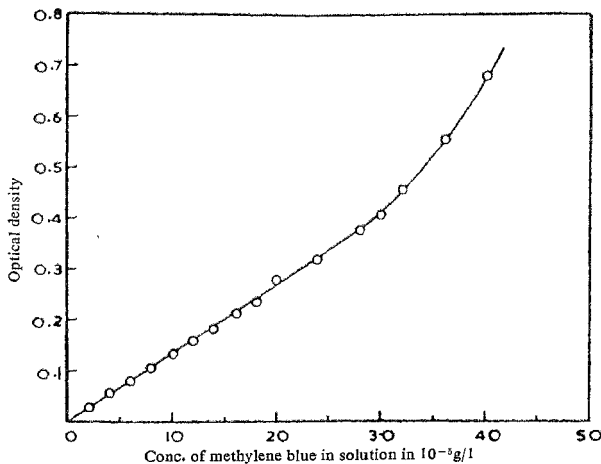

Fig. II
Calibration graph for spectrophotometric estimation of methylene blue

The concentration limits within which Beer's law was applicable to methylene blue solutions was determined by employing solutions of concentration ranging from $2 \times 10^{-5} g/l$ to $50 \times 10^{-5} g/l$. It was found that the optical density was a linear function of concentration up to a concentration of $30 \times 10^{-5} g/l$ as shown in Fig. II. All the measurements of the dye concentrations were adjusted suitably so as to be in this region.

The time required for equilibration of the dye between the adsorbed phase and the solution was found experimentally to be one hour with mechanical agitation as there was no further increase in the amount of dye adsorbed on shaking for a longer period up to 24 hours.

Determination of adsorption isotherm:—The adsorption for methylene blue on the wet nickel carbonate $NiCO_3 \cdot 3Ni(OH)_2 \cdot xH_2O$ was determined by employing methylene blue solutions of concentration ranging from $10 \times 10^{-4} g/l$ to $100 \times 10^{-4} g/l$. The experimental procedure was exactly the same as described earlier for reproducible manner of precipitation[1] and the methylene
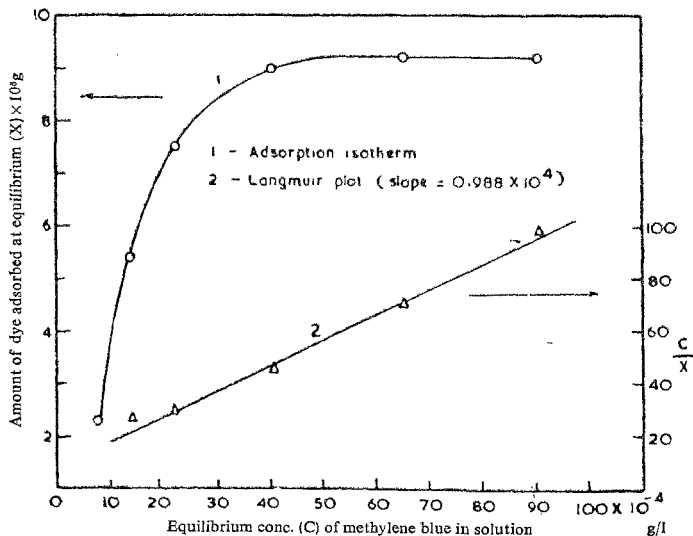

FIG. III
Adsorption of methylene blue on unaged basic nickel carbonate
$NiCO_3 \cdot 3Ni(OH)_2 \cdot xH_2O$

blue solution was agitated with the precipitate for one hour for equilibrium to be attained. The mixture was then centrifuged and the decreased dye concentration in the clear supernatant liquid was determined spectrophotometrically. The results are presented in Figure III, curve 1. The results show that above a concentration of 50×10^{-4} g/l there was no increase in the amount of dye adsorbed beyond the saturation limit, which is 9.0×10^{-5} g. This amount of dye may be regarded as nearly that required to form a monolayer on the substrate.

The surface area of the basic nickel carbonate may be approximately calculated from a knowledge of the cross-sectional area of the methylene blue molecule and the amount of dye required to form a monomolecular layer on the precipitate. It is assumed that the adsorbed molecules lie flat on the surface of the basic nickel carbonate. No data on the cross-sectional area of the methylene blue molecule is available from literature. However, from the following structure of methylene blue :
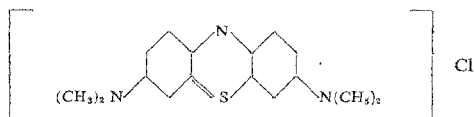
it is apparent that the cross-sectional area of this molecule is nearly three times that of a benzene ring which is nearly 33 Å^2 units. Hence the cross-sectional area of methylene blue may be taken as 100 Å^2 units.

The Langmuir plot for the adsorption of methylene blue on the basic nickel carbonate is shown in plot 2, Fig. III and the calculated slope is 0.988×10^4. Hence the value of x_m the amount of methylene blue required to form a monolayer on the surface of the unaged basic nickel carbonate $NiCO_3.3Ni(OH)_2$ is 1.013×10^{-4} g per 0.07336 g of Nickel (which is the nickel content of the precipitate taken for adsorption).

So the number of molecules of methylene blue adsorbed per gram of nickel in the basic carbonate $= 1.013 \times 10^{-4} \times 6.023 \times 10^{23}/(0.07336 \times 322.7)$ $= n_1 = 2.577 \times 10^{18}$ since the molecular weight of methylene blue is 322.7. This corresponds to an area of $2.577 \times 100 \times 10^{18}/10^{20} = 2.58 m^2/g$. of Ni.

Effect of ageing on the amount of dye adsorbed :—The manner in which the surface area of the basic precipitate alters on ageing in contact with the mother liquor was followed by determining the amounts of dye adsorbed on the same quantity of the precipitate aged for different intervals of time. The same quantity of the basic nickel carbonate $NiCO_3 \cdot 3Ni(OH)_2 \cdot xH_2O$ as in the previous set of experiment was precipitated and the amount of dye adsorbed at equilibrium from a methylene blue solution of concentration $100 \times 10^{-4} g/l$, was determined in each case. The results are presented in Table III. Each value

TABLE III

Effect of ageing on the amount of dye adsorbed by methylene blue

Period of Ageing hrs.	0	2	12	24	48	72	96	120	240
Amount of Dye Adsd. $\times 10^5$ g.	9.0	10.6	15.0	18.1	23.7	26.5	27.1	27.0	26.8

in the Table represents the average of three experimental values which do not differ by more than $0\cdot3 \times 10^{-5}$ g.

It is seen from the experiments that the amounts of dye adsorbed by the precipitate increases on ageing to a maximum value within four days. This value shows that the adsorption of methylene blue by the nickel carbonate aged for four days is thrice that of the unaged sample. Thereafter, ageing even up to ten days time causes little change in the amounts of dye adsorbed.

Similar behaviour was observed when the basic carbonate was prepared from other systems of nickel salts and alkali carbonates.

It is general behaviour of precipitates that when aged they tend to aggregate to longer crystallites causing a decrease in their surface areas. In the present work, the precipitate does not consist of small particles uniformly distributed in the medium, but it is a heavy gelatinous precipitate which settles down occupying nearly a quarter of the bulk of the medium. The increase in the amount of dye adsorbed on ageing for four days during which period there is no change in chemical composition can be attributed to the break up of the gelatinous precipitate causing the extrusion of water molecules. This probably leads to the formation of larger crevices and pores than were already present thus exposing a larger surface of the precipitate to the methylene blue molecules. It is likely that the freshly-formed precipitate has really a more extensive surface, than determined by the dye adsorption method, but composed of tiny pores and capillaries filled with water molecules and too narrow to permit the entry of the larger dye molecules. Ageing would cause the widening of these capillaries and the consequent availability of more of the surface to the dye molecules. This accounts for the increase in the amount of dye adsorbed on ageing.

REFERENCES

1. Mallya, R. M. and Vasudeva Murthy, A. R.   ..   *J. Indian Inst. Sci.*, 1961, **43**, 44.

2. Weber, R.   ..   *Pogg. Ann.*, 1861, **112**, 619.

3. Setterberg, J.   ..   *Ibid.*, 1830, **19**, 56.

4. Rose, H.   .. *Ibid.*, 1851, **84**, 563.

5. Mellor, J. W.   .. "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", 1936, XV, 484-6 (London: Longman's)

6. Treadwell, F. P. and Hall, W. T.   .. "Analytical Chemistry—Quantitative Analysis", 1951, Vol. II, 9th Revised Edn., 491 (New York: Wiley)

7. Kolthoff, I. M. and Sandell, E. B.   .. "Text Book of Quantitative Inorganic Analysis", 1952, 3rd Edn., 106-137, 429, 526 (New York: Macmillan)

8. Cloutier, L., Pelleteir, P. E. and Gagnon, P. E.   .. *Trans. Roy. Soc.*, Canada, 1936, **30**, Sec. 3, 149-64.
Can. J. Research, 1938, **16 B**, 37.

9. Mallya, R. M. and Vasudeva Murthy, A. R.   .. *J. Indian Inst. Sci.*, 1961, **43**, 76, 87 (Part V: to be published)