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Article

Formation of Nickel Vanadates as a Function of pH

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A natureza precisa da reação entre ácido clorídrico e *orto*-vanadato de sódio foi estudada por técnicas eletrométricas envolvendo titulações potenciométricas e condutométricas. As inflexões e degraus bem definidas nas curvas de titulações confirmaram a existência de ânions, *pyro*-$V_2O_7^{4-}$, *meta*-VO_3^- e *poly*-$H_2V_{10}O_{28}^{4-}$ correspondendo às razões de VO_4^{3-}:H^+ como 1:1, 1:2 e 1:2,6 na vizinhança do pH 10,5; 7,4 e 3,6, respectivamente. A interação entre soluções de cloreto de níquel e vanadato de sódio a específicos níveis de pH 12,4; 10.5; 7,4 e 3,6 também foi estudada por titulações potenciométricas e condutométricas entre os reagentes. Os pontos finais obtidos a partir de inflexões nítidas nas curvas de titulações forneceram evidências incontestáveis sobre a formação de vanadatos *ortho*-3NiO.V_2O_5, *pyro*-2NiO.V_2O_5 e *meta*-NiO.V_2O_5 de níquel nas proximidades dos valores de pH 8,9; 8,0 e 6,8; respectivamente. Investigações analíticas sobre os precipitados formados confirmam os resultados do estudo eletrométrico.

The precise nature of the reaction between hydrochloric acid and sodium *ortho*-vanadate solution has been studied by means of electrometric techniques involving potentiometric and conductometric titrations. The well defined inflections and breaks in the titration curves confirm the existence of the anions, *pyro*-$V_2O_7^{4-}$, *meta*-VO_3^- and *poly*-$H_2V_{10}O_{28}^{4-}$ corresponding to the ratios of VO_4^{3-}:H^+ as 1:1, 1:2 and 1:2.6 in the neighborhood of pH 10.5, 7.4 and 3.6, respectively. The interaction of nickel chloride with sodium vanadate solutions, at specific pH levels 12.4, 10.5, 7.4 and 3.6 was also studied by potentiometric and conductometric titrations between the reactants. The end-points obtained from the sharp inflections in the titration curves provide definite evidence for the formation of *ortho*-3NiO.V_2O_5, *pyro*-2NiO.V_2O_5 and *meta*-NiO.V_2O_5 vanadates of nickel in the vicinity of pH 8.9, 8.0 and 6.8, respectively. Analytical investigations on the precipitates formed confirm the results of the electrometric study.

Keywords: vanadates, polyvanadates, nickel vanadates, electrometry

Introduction

The chemistry of vanadium is very prominent in both biological and industrial systems.[1] Besides this, a new interest in the chemistry of vanadium has developed during the last decade.[1,2] This has arisen in part from antiviral, including anti-AIDS activity of vanadates and their interaction with biological molecules like proteins.[3,4] Vanadium also exhibits catalytic properties in an extensive variety of chemical reactions. These include the use of vanadium oxide as catalyst in the following reactions: sulfur dioxide to the trioxide, the sulfonation of aromatic hydrocarbons and of pyridine, the reduction of olefines; the oxidation of hydroiodic acid by hydrogen peroxide, of sugar by nitric acid, of alcohol by air, of stannous salts by nitric acid, of cyclic organic compounds by hydrogen peroxide, of naphthalene by air, and the reduction of aromatic hydrocarbons by hydrogen.[5] A number of recent studies have shown that vanadium oxide catalyst is very promising in oxidative dehydrogenation of alkanes but its activity and selectivity depend on the manner in which the catalyst is pretreated.[6-10] The structure of the vanadia is a very important factor.[9,10] Khodakov *et al*.[11] have recently determined that the oxidative dehydrogenation rates of propane increase as the size of *poly*-vanadate domain increases. Efforts aimed at relating the structures of the

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vanadium species to its catalytic activity and selectivity suggest that the catalytic performance depends on the type of structure, bond length and distance between active and selective sites.[6-15]

In highly alkaline solution, pH >14, vanadium(V) exists as a tetrahedral VO_4^{3-} anion.[16] On acidification the aqueous solutions turn from colorless to orange-yellow polymeric species. A survey of the literature suggests the occurrence of a series of alkali metal vanadates having the ratios of Na_2O:V_2O_5 as 3:1, 2:1, 1:1, 1:2, 1:2.5, 1:3, 2:3 *etc* in solution under different conditions. The existence of so many polymeric species seems to be doubtful; moreover, there is a great variance in the results published by earlier workers, which allows no satisfactory interpretation of the mechanism of the condensation process. A further verification of the vanadate system seems very desirable with a view to rationalizing the conflicting details of the previous workers by employing electrometric techniques, which have provided more conclusive evidences on such systems.[17-19] The knowledge on the formation of different species under different conditions may help in the explanation of the catalytic performance of vanadium and may be a key to understanding the catalytic mechanism. In an earlier publication the results of pH change by HNO_3 on solution of Na_3VO_4, and composition of lead vanadates have been reported.[20] The results obtained on pH change of Na_3VO_4 by HCl, and on formation of different vanadates of nickel are presented here.

Experimental

V_2O_5, NaOH, $NiCl_2.6H_2O$, HNO_3, ethanol and hydrochloric acid of extra-pure grade were used and their solutions were prepared with deionized distilled water. The solution of sodium *ortho*-vanadate Na_3VO_4 was prepared by digesting one mol of V_2O_5 in boiling solution of NaOH containing six mol of it.

Potentiometric measurements were carried out on Metrohm Herisau pH-meter using Scott Gerate glass combination electrode. Conductance values were recorded by employing a Metrohm conductometer. A series of potentiometric and conductometric titrations was carried out between sodium *ortho*-vanadate in concentrations $\geq 10^{-4}$ mol L^{-1} and hydrochloric acid using same strength of the reactants in each technique. All observations were taken at the state of chemical equilibrium. For attaining the equilibrium state the titrations were performed by heating the solution after each addition of titrant and cooling to 25 °C before taking observations. The achievement of constant values of pH and conductance required about 40 s boiling after each addition of the titrant for the formation of *pyro*-vanadate, whereas the time needed for attaining the state of chemical equilibrium for the formation of *meta*- and *poly*-vanadate was 1 min and 2.5 min, respectively. The curves were plotted between pH and corrected conductance *versus* volume of acid used. As the inflections of pH curves were not strongly defined, pronounced maxima in dpH/dV were used to locate the end-points.

The formation of nickel vanadates was investigated by the action of nickel chloride with different vanadate anions at specific pH levels 12.4, 10.5, 7.4 and 3.6 using different concentrations of the reactants. For this purpose, the variations of pH of Na_3VO_4 solutions were obtained by progressive additions of determined quantities of hydrochloric acid. A series of potentiometric and conductometric titrations was performed by direct and reverse methods, *i.e.* when nickel chloride solution from the microburette was added to sodium vanadate solution and vice-versa. 25 mL of ethanolic solution (20%) was taken in the cell, which was thermostated at 25.0± 0.1 °C.

The precipitates obtained at the end-points of titrations between nickel chloride and different sodium vanadates were also analyzed to substantiate the electrometric results. The different nickel vanadates were prepared by mixing stoichiometric amounts of nickel chloride solution with the respective sodium vanadate solutions. The precipitates obtained were washed several times with 20% ethanolic solution and dried in a vacuum desiccator for 40 h. A known amount (*ca.* 2 g) of each of the above precipitates was dissolved in a minimum quantity of nitric acid and then analyzed quantitatively for nickel by dimethylglyoxime[21] and vanadium as silver vanadate.[21] From the proportions of nickel and vanadium in the compounds thus obtained their composition was established.

Results and Discussion

In an earlier publication[20] Prasad *et al.* have shown that the addition of HNO_3 to Na_3VO_4 solutions at room temperature causes the formation of various *poly*-anions of uncertain compositions, but when the solutions were heated after each addition of titrant the three different vanadates *viz. Pyro* ($Na_4V_2O_7$), *meta* ($NaVO_3$) and *poly* ($Na_4H_2V_{10}O_{28}$) are formed in the pH ranges 10.1-10.7, 7.0-7.5 and 3.4-3.8, respectively. In the present study related to the formation of different nickel vanadates as a function of pH, by the interaction of nickel chloride with alkali vanadates at specific pH levels, the use of HCl for pH variation was considered more appropriate. Hence it was considered of interest to ascertain whether similar alkali vanadate species are formed by the action of HCl with

Na_3VO_4 solutions. A series of glass electrode and conductometric titrations of Na_3VO_4 solution with HCl were therefore performed. A typical titration curve between pH observed and volume of the acid added is demonstrated in Figure 1 (curve 1). The three inflections in the titration curve at the molar ratios of H^+:VO_4^{3-} as 1, 2 and 2.6 corresponding to the stoichiometry for the formation of *pyro*-V_2O_7, *meta*-VO_3^- and *poly*-$H_2V_{10}O_{28}^{4-}$ anions confirm the formation of the same three vanadate species as obtained by the previous study with HNO_3.[20] The position of these inflections is further checked by dpH/dV graphs (curve 2). The conductometric titrations between the acid and Na_3VO_4 also confirm the formation of the same species (Figure 1, curve 3). The existence of $V_6O_{16}^{2-}$ as reported by Sen Gupta[22] and Russel and Salmon,[23] and of $V_3O_8^-$, $V_5O_{14}^{3-}$, $V_{10}O_{28}^{6-}$ and $HV_{10}O_{28}^{5-}$ as reported by Bystrom and Evans[24] and Naumann and Hallada[25] could not be confirmed by this study.

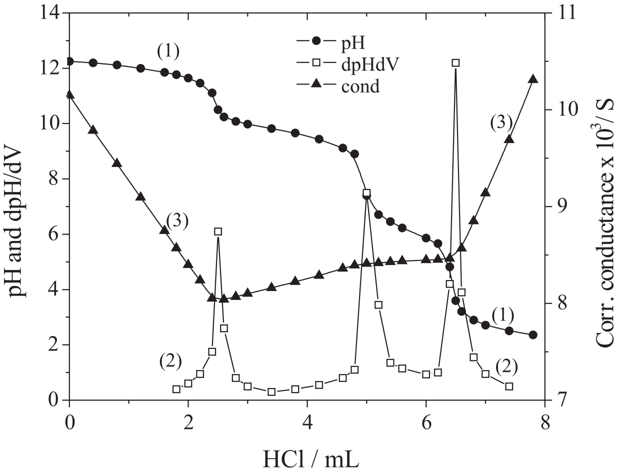

Figure 1. Potentiometric (1, 2) and conductometric (3) titrations of 25 mL of 1.00 x 10^{-2} mol L^{-1} Na_3VO_4 with 1.00 x 10^{-1} HCl.

The stepwise condensation of *ortho*-vanadate to *poly*-vanadate can be represented by the following set of equations:

$$2VO_4^{3-} + 2H^+ = V_2O_7^{4-} + H_2O \qquad (1)$$
$$V_2O_7^{4-} + 2H^+ = 2VO_3^- + H_2O \qquad (2)$$
$$10VO_3^- + 6H^+ = H_2V_{10}O_{28}^{4-} + 2H_2O \qquad (3)$$

The above studies show that the addition of hydrochloric acid to sodium *ortho*-vanadate under suitable conditions causes the formation of three different sodium vanadates containing the anions *Pyro*-$V_2O_7^{4-}$, *meta*-VO_3^- and *poly*-$H_2V_{10}O_{28}^{4-}$. Therefore it was considered suitable to use hydrochloric acid for pH variation of the alkali vanadate for the study on formation of different nickel vanadates as a function of pH. To carry out this study, a solution of sodium *ortho*-vanadate was prepared by digesting one mol of V_2O_5 in boiling solution of NaOH containing six mol of it. The solutions of sodium *pyro*-, *meta*- and *poly*-vanadates were prepared by adding 1, 2 and 2.6 mol of HCl to 1mol of Na_3VO_4 at 100 °C.

$$6NaOH + V_2O_5 = 2Na_3VO_4 + 3H_2O \qquad (4)$$
$$2HNO_3 + 2Na_3VO_4 = Na_4V_2O_7 + 2NaNO_3 + H_2O \qquad (5)$$
$$2HNO_3 + Na_3VO_4 = NaVO_3 + 2NaNO_3 + H_2O \qquad (6)$$
$$26HNO_3 + 10Na_3VO_4 = Na_4H_2V_{10}O_{28} + 26NaNO_3 + 12H_2O \qquad (7)$$

Formation of nickel vanadates

A series of direct and reverse electrometric titrations between the solutions of nickel chloride (pH 6.0) and different sodium vanadates at specific pH levels 12.4, 10.5, 7.4 and 3.6 were realized and the results obtained from the stoichiometric end-points are summarized in Table 1. Only three figures illustrating the formation of nickel *ortho*-vanadate (Figure 2), *pyro*-vanadate (Figure 3) and *meta*-vanadate (Figure 4) by direct titrations have been given for the sake of brevity. The precipitates obtained at the end-points of the electrometric titrations between nickel chloride and sodium vanadates were also analyzed to substantiate the electrometric results. The analytical results are presented in Table 2.

Nickel ortho-vanadate. Using different concentrations of nickel chloride (pH 6.0) and Na_3VO_4 (pH 12.4) a series of potentiometric titrations was carried out. Figure 2 (curve 1) shows the changes occurring in H^+ ion concentration when the solution of Na_3VO_4 was titrated with nickel chloride solution. It may be noted that the first addition of nickel chloride solution to the alkaline vanadate results

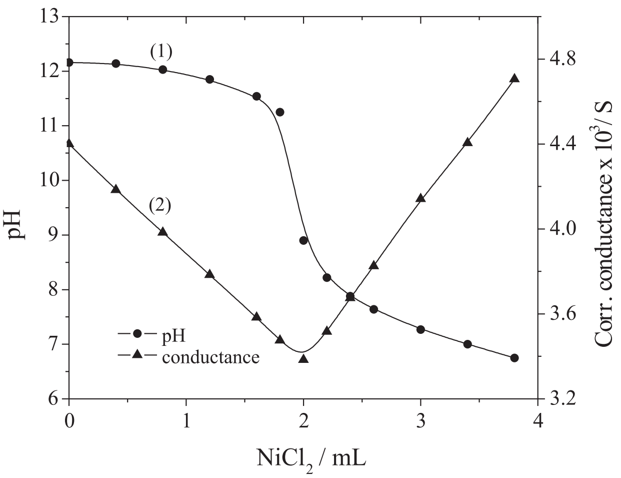

Figure 2. Nickel *ortho*-vanadate titrations. 25 mL of 2.67 x 10^{-3} mol L^{-1} Na_3VO_4 titrated with 5.00 x 10^{-2} mol L^{-1} $NiCl_2$.

Table 1. Summary of the results of electrometric study on the formation of nickel vanadates.Volume of titrated solution taken in the cell = 25 mL

Concentration (mol L^{-1}) of solutions (x 10^3)		Equivalence points (mL)			Formula supported
		Calculated	Observed from		
			pH	Conductance	
$NiCl_2$	Na_3VO_4				
Direct *ortho*-vanadate titrations (Figure 2)					$3NiO.V_2O_5$
200.00	13.33	2.50	2.50	2.50	
50.00	2.67	2.00	2.00	2.00	
10.00	0.57	2.14	2.12	2.15	
Reverse *ortho*-vanadate titrations					$3NiO.V_2O_5$
12.50	100.00	2.08	2.10	2.10	
3.64	25.00	2.42	2.42	2.45	
1.33	10.00	2.22	2.22	2.24	
$NiCl_2$	$Na_4V_2O_7$				
Direct *pyro*-vanadate titrations (Figure 3)					$2NiO.V_2O_5$
200.00	10.00	2.50	2.50	2.48	
50.00	2.00	2.00	2.00	2.00	
10.00	0.44	2.22	2.20	2.20	
Reverse *pyro*-vanadate titrations					$2NiO.V_2O_5$
8.00	50.00	2.00	2.00	2.00	
2.50	12.50	2.50	2.50	2.52	
0.63	3.33	2.34	2.35	2.35	
$NiCl_2$	$NaVO_3$				
Direct *meta*-vanadate titrations (Figure 4)					$NiO.V_2O_5$
200.00	33.33	2.08	2.08	2.06	
50.00	8.00	2.00	2.00	2.00	
10.00	1.82	2.27	2.25	2.25	
Reverse *meta*-vanadate titrations					$NiO.V_2O_5$
4.00	100.00	2.00	2.00	2.00	
1.25	25.00	2.50	2.52	2.52	
0.44	10.00	2.22	2.20	2.25	

Table 2. Summary of analytical results of the precipitates of nickel vanadates

Proposed formula of the compound	Mode of analysis	Analysis % : Found (Calculated)	
		Ni	V
Analysis of nickel *ortho*-vanadate precipitates			
$3NiO.V_2O_5$	Direct[a]	43.34(43.38)	25.12(25.09)
	Reverse[b]	43.41	25.07
Analysis of nickel *pyro*-vanadate precipitates			
$2NiO.V_2O_5$	Direct	35.41(35.44)	30.79(30.75)
	Reverse	35.48	30.72
Analysis of nickel *meta*-vanadate precipitates			
$NiO.V_2O_5$	Direct	22.86(22.88)	39.75(39.71)
	Reverse	22.91	39.68

[a] Nickel chloride solution added to sodium *ortho*-vanadate solution; [b] Sodiun *ortho*-vanadate solution added to nickel chloride solution.

in gradual decrease in pH to about 11.0. Further addition of the titrant brings about steep fall in pH value at a point where the molar ratio of $Ni^{2+}:VO_4^{3-}$ is 3:2 (see Table 1), corresponding to the stoichiometry for the precipitation of nickel *ortho*-vanadate $3NiO.V_2O_5$ in the vicinity of pH 8.9. The reaction can be represented as follows:

$$3NiCl_2 + 2Na_3VO_4 = (3NiO.V_2O_5) + 6NaCl \quad (8)$$

In the case of conductometric titrations of the solution of Na_3VO_4 with nickel chloride (Figure 2, curve 2) the conductance value decreases gradually in the beginning of the titration (due to removal of the VO_4^{3-} ions in the form of a precipitate), but after completion of the reaction, conductance starts rising with the increase in ionic concentration at the ratio $Ni^{2+}:VO_4^{3-}$ as 3:2, which coincides with the stoichiometry for the formation of nickel *ortho*-vanadate as indicated by the potentiometric study.

Nickel pyro-vanadate. Figure 3 (curve 1) illustrates the changes occurring in pH when nickel chloride solution (pH 6.0) was added from the microburette to the solution of sodium *pyro*-vanadate (pH 10.5). The titration curve shows a well-defined inflection at the equivalence point, where the molar ratio $Ni^{2+}:V_2O_7^{4-}$ is 2:1, corresponding to the stoichiometry for the formation of nickel *pyro*-vanadate $2NiO.V_2O_5$ in the neighborhood of pH 8.0. The reaction can be represented by the following equation:

$$2NiCl_2 + Na_4V_2O_7 = (2NiO.V_2O_5) + 4NaCl \quad (9)$$

Employing similar concentrations of the reactants a series of conductometric titrations between the solution of nickel chloride and sodium *pyro*-vanadate was carried out. Well-defined breaks in the titration curves (Figure 3, curve 2) were obtained at 2:1 molar ratio of $Ni^{2+}:V_2O_7^{4-}$, which confirm the formation of the identical compound, nickel *pyro*-vanadate $2NiO.V_2O_5$.

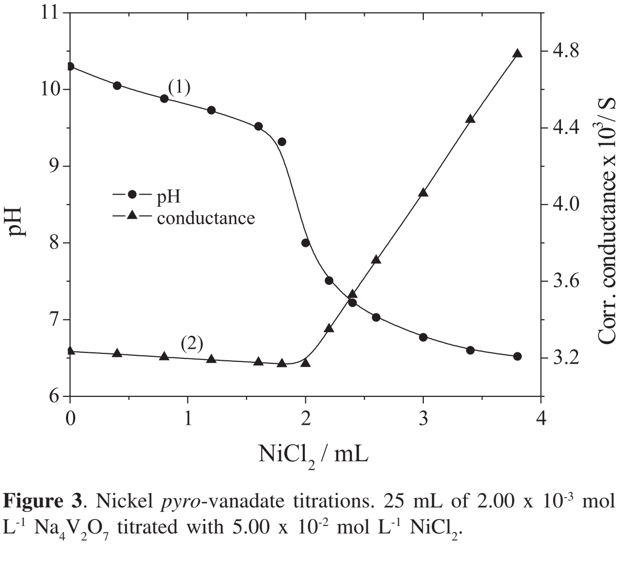

Figure 3. Nickel *pyro*-vanadate titrations. 25 mL of 2.00 x 10^{-3} mol L^{-1} $Na_4V_2O_7$ titrated with 5.00 x 10^{-2} mol L^{-1} $NiCl_2$.

Nickel meta-vanadate. Using different concentrations of nickel chloride (pH 6.0) and sodium *meta*-vanadate (pH 7.4) a series of potentiometric and conductometric titrations (Figure 4) was carried out. The breaks and inflections in the titration curves at the stoichiometric end-point corresponding to the molar ratio $Ni^{2+}:VO_3^-$ as 1:2, suggest the formation of nickel *meta*-vanadate $NiO.V_2O_5$ around pH 6.8, according to the equation:

$$NiCl_2 + 2NaVO_3 = NiO.V_2O_5 + 2NaCl \quad (10)$$

The feeble breaks obtained in the conductometric titration curves (Figure 4, curve 2) may be ascribed to the presence of sodium chloride in appreciable amount in *meta*-vanadate solutions.

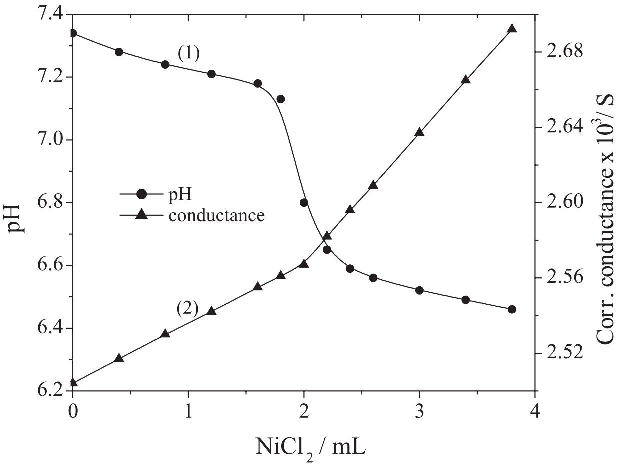

Figure 4. Nickel *meta*-vanadate titrations. 25 mL of 8.00 x 10^{-3} mol L^{-1} $NaVO_3$ titrated with 5.00 x 10^{-2} mol L^{-1} $NiCl_2$.

Similar studies using the different sodium vanadate solutions as titrant (reverse titrations) were also realized (Table 1). The breaks and inflections in titration curves confirmed the results obtained by the direct titrations. As the curves were normal in shape and nature the figures of these titrations are not presented for the sake of brevity.

The reaction between nickel chloride and sodium *poly*-vanadate $Na_4H_2V_{10}O_{28}$ (pH 3.6) was also studied, but the curves did not provide conclusive evidence for the formation of nickel *poly*-vanadate.

The precipitates obtained at the end-points of the titrations of nickel chloride with different sodium vanadates were analyzed by classical methods. Nickel was determined by dimethylglyoxime and vanadium as silver vanadate, and oxygen was calculated from the difference in the percentage. From the proportions of nickel, vanadium and oxygen in the compounds thus obtained, their composition was established. The results obtained (Table 2) confirm those obtained by the electrometric study.

It was noted that the presence of ethanol in nickel vanadate titrations slightly improves the end-points and gives better results as it decreases solubility of the precipitates formed and minimizes hydrolysis and adsorption. 20% ethanolic medium was therefore employed for the entire course of the study. A thorough stirring in the vicinity of the end-point had a favorable effect.

As the structure of these compounds is not known these are represented as double oxides, the manner, which is usually adopted for such compounds.[26,27]

Conclusions

The results of the electrometric investigations on the system hydrochloric acid and sodium *ortho*-vanadate, at the specific concentration level of $\geq 10^{-4}$mol L^{-1}, suggest the formation of *pyro*-V_2O_7, *meta*-VO_3^- and *poly*-$H_2V_{10}O_{28}^{4-}$ vanadate anions in the neighborhood of pH 10.5, 7.4 and 3.6, respectively. The electrometric and analytical investigations on the interaction of nickel chloride with sodium vanadate at specific pH levels 12.4, 10.5 and 7.4 provide cogent evidence for the formation and precipitation of *ortho*-$3NiO.V_2O_5$, *pyro*-$2NiO.V_2O_5$ and *meta*-$NiO.V_2O_5$ vanadates of nickel around pH 8.9, 8.0 and 6.8, respectively. The composition of nickel vanadates can thus be represented by the general formula $nNiO.V_2O_5$, where the proportion of nickel oxide in the vanadate obtained decreases with the pH of the medium.

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