
Formation of insoluble polynuclear Ni(II)–citrate complexes in alkaline solutions

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When the excess of Ni(II) ions as compared to citrate concentration is used, both Ni(II) ions and citrate can be precipitated in alkaline solutions. The molar ratio of Ni(II) and citrate in the precipitate and the completeness of citrate precipitation depend on the ratio of the Ni(II) and citrate concentrations in the initial solution and its pH. The precipitate formed is composed of the insoluble Ni(II)-citrate compound and Ni(OH)₂.

The data of chemical analysis, potentiometric titration, FT-IR as well as visible spectrophotometric investigations suggest that Ni(II) in the insoluble compound is bound with three –COO[–] groups and –OH group of the citrate. The insoluble compound also contains sulphate and hydroxides.

Key words: nickel ions, citrate, polynuclear complexes

INTRODUCTION

Metal complexes are widely used in metal finishing, dyeing, painting, printed circuit board industries in order to enhance metal solubility or avoid formation of insoluble metal compounds. Citrate is among the complexing agents that possess the ability to form strong metal complexes with a number of heavy metals such as Pb(II), Cu(II), Ni(II), Co(II), Pb(II), Fe(III), etc.

Nickel–citrate complexes are widely used in metal finishing industry for electroless nickel plating. These solutions due to the technological peculiarities become unfit for use and should be decontaminated. The presence of the complexing agents hinders metal recovery by precipitation of insoluble (mostly hydroxide) compounds. The chemical precipitation is the most cost-effective treatment technology. In practice, the metals from the complex solutions are usually removed in the form of insoluble hydroxides after oxidative destruction of the complexing agents [1].

When an excess of metal ions is used, the ability of carboxylic ligands to form soluble metal complexes considerably differs from that of amino ligands. It is possible to remove carboxylic metal complexes by the excess of metal ions in the form of insoluble compounds from both acidic (pH 3–4) and alkaline (pH >12) solutions; meanwhile, the amino comple-

xes totally remain in the solution. The excess of Ni(II) causes precipitation of carboxylic ligands in alkaline solutions. X-ray investigations have shown that the complex formed is amorphous [2].

The citrate as a polydentate ligand forms a number of complexes with Ni(II) both in acidic and alkaline solutions [3, 4]. Polynuclear complexes are formed in alkaline solutions. In alkaline solutions containing transition metal ions, the dissociation not only of three –COOH groups but also of hydroxyl –OH group of citric acid proceeds. Authors of paper [3] indicate the following dissociation constant of citric acid: pK₁ = 3.08, pK₂ = 4.39, pK₃ = 5.49 and pK₄ = 11.6 [4]. The coordination of the citrate ion with transition metal ions substantially lowers the pK of the citrate hydroxyl group. When the molar ratio Ni(II) to citrate makes up 1:1, the ionisation of –OH group proceeds at pH 8.7 [5]. In the case of the 1:1 ferrous and manganous citrate complexes, the tetraionized form of citrate predominate in neutral and alkaline solutions [6].

The current study examines the regularities of formation of insoluble nickel–citrate compounds and their chemical composition in alkaline solution. Results of these investigations may be used for recovery of Ni(II)–citrate from spent solutions and their reuse in practice.

EXPERIMENTAL

The precipitation was carried out at ambient temperature by adding Ni(II) sulphate solution to Na–

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citrate solutions by vigorous mixing. pH was adjusted with 0.01–5 mol/l NaOH or 0.1–1 mol/l H₂SO₄ solutions. The precipitates formed were centrifuged and rinsed with cold (–5 °C) water.

All the experiments were carried out with reagents at least of analytical grade of purity. Additionally, nickel sulphate and trisodium citrate were purified by re-crystallization using bi-distilled water. The chemical composition of the precipitates was determined after their dissolution in diluted H₂SO₄. The citrate concentration was determined after oxidation in the alkaline solutions with KMnO₄, its excess was retitrated in acidic solutions with oxalic acid. Ni(II) in the solutions was determined complexometrically using EDTA as a titrant and murexide as an indicator. Low values of Ni(II) concentrations were determined photometrically at $\lambda = 490$ nm using dimethylglyoxime as an indicator.

The light absorption spectra were recorded with a Perkin–Elmer Lambda 35 UV/VIS spectrometer at 20 °C in 1 cm thick cells. Distilled water was used as reference.

The infrared spectra of the precipitates were recorded in KBr pellets on a Fourier transformation infrared spectrometer (Hartman & Braun, Canada). The spectra were recorded in the region of wave number between 4000 and 500 cm^{–1}.

RESULTS AND DISCUSSION

The interaction of Ni(II) with citrate is thoroughly studied in acidic solutions [7]. The insoluble polynuclear metal complexes with the crystalline structure have been studied as well [8, 9]. However, the alkaline solutions of Ni(II)–citrate complexes and the insoluble amorphous complexes are much less investigated.

The formation of Ni(II)–citrate complexes depends on the molar ratio between Ni(II) and citrate. Figure 1 shows the effect of added Ni(II) amounts on the concentrations of both Ni(II) and citrate in solutions at pH 11. When the Ni(II) concentration is low as compared with the citrate concentration, soluble Ni(II)–citrate complexes are formed. When Ni(II) concentration is 3-fold higher than that of citrate, insoluble compounds begin to form. With a further increase in Ni(II) concentration the residual Ni(II) and citrate concentrations decrease continually. Citrate precipitation is most complete at Ni(II) concentrations 5 to 6-fold higher than citrate concentration.

The proportion of Ni(II) to the citrate precipitated depends on their initial con-

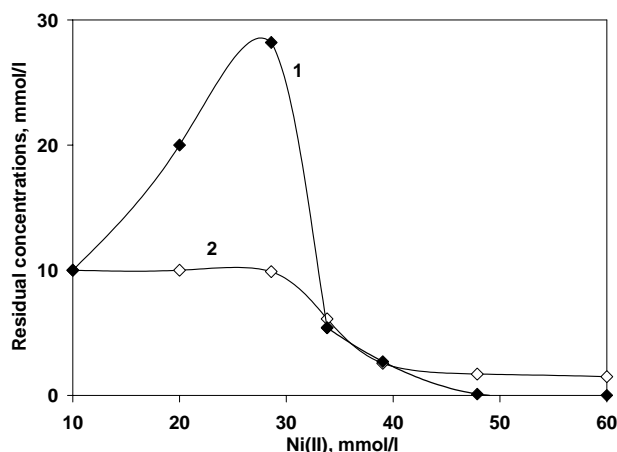


Fig. 1. Effect of Ni(II) concentration on residual Ni(II) (1) and citrate (2) concentrations at pH 11. Initial Ni(II) and citrate concentrations – 10 mmol/l

centrations and the pH (Fig. 2). With increase in the initial Ni(II) concentration the residual concentrations of Ni(II) decrease. The residual Ni(II) and citrate concentrations are higher in the solutions with their higher initial concentrations, though the extent to which citrate is removed increases considerably. The pH value at which the most complete precipitation takes place depends on the initial concentrations of the substances (Table 1). As a rule, the residual concentrations decrease with an increase in pH. It is worth noting that the extent of citrate removal makes up 70 to 80% in the most favourable cases. Only repeated precipitation with excess of Ni(II) makes it possible to remove citrate most efficiently. Ni(II) in these cases is removed completely.

The insoluble compounds are formed when the concentration of Ni(II) is higher than that of the soluble complexes. It means that in alkaline solutions precipitation of Ni(OH)₂ is possible, especially when

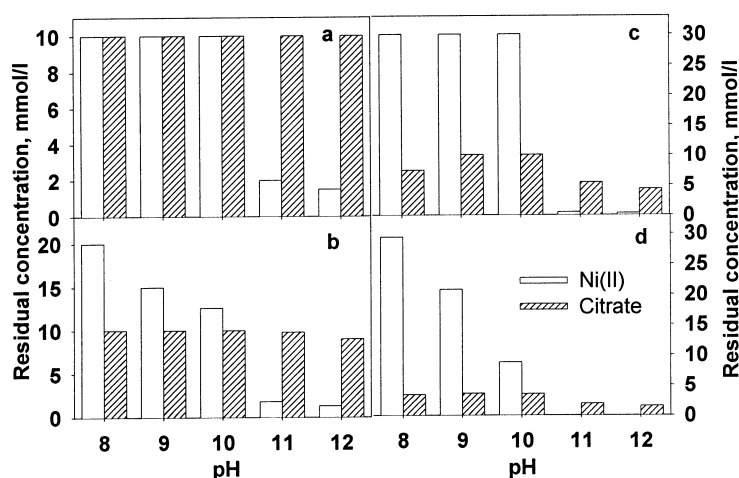


Fig. 2. Influence of pH on precipitation in solutions containing, mmol/l: citrate –10, Ni(II)- a – 10, b – 20, c – 40, d – 60

the initial concentration of Ni(II) is higher than that of citrate. Actually, in these cases the precipitate formed is a mixture of an insoluble Ni(II)-citrate complex and Ni(OH)₂. Such a composition of the precipitate was confirmed by chemical analysis. Investigations have shown that the least Ni(II) : citrate molar ratio is about 4. As in alkaline solutions the dissociation of three -COOH groups and -OH group proceeds, it may be assumed that 4 mol of Ni(II) and 1 mol of citrate form an insoluble complex. The residual Ni(II) in the precipitate exists as Ni(OH)₂.

Theoretically, the precipitation of Ni(OH)₂ in dilute solutions (10 mmol/l) starts at pH 7.7. However, in these solutions, when the dilute NaOH (~0.1 mol/l) is used, the hydroxide formation is slow (5–10 h). The decrease in solution pH indicates the beginning of this process. Therefore, it is possible to prepare solutions without Ni(OH)₂ precipitate at pH 8. The experiments carried out at pH 7 and at pH 8 have indicated essential changes in complex formation (Table 2). The mixing of Ni(II) and citrate solutions of the same pH gives different pH shifts. When the pH of the initial solutions is 7, its value in the resulting solution decreases and at pH 8 its value increases. At pH 2 to 7, Ni(II) forms complexes with H₂Citr⁻, HCitr²⁻ and Citr³⁻ [3]. The complex formation with a decrease in pH indicates liberation of H⁺ ions. In alkaline Ni(II)-citrate solutions dissociation not only of three -COOH groups but also of -OH group is possible [5, 6].

Therefore, the citrate complexing ability increases. The increased pH value after mixing Ni(II) and citrate solutions at pH 8 indicates formation of different complexes. The reason for such a change of pH could be participation of SO₄²⁻ ion in insoluble complex formation. Data of chemical and FT-IR analysis show the presence of sulphate in the precipitate.

The pH-metric titration curves (Fig. 3) are strongly influenced by the Ni(II) concentration. At low Ni(II) concentrations a plateau appears at pH 11, and at a high Ni(II) (0.6 mol/l) concentration it appears at pH 7–9. It probably indicates the dissociation of -OH group in dependence on Ni(II) concentration. In all cases at pH~13 a complete Ni(II) precipitation takes place. With an increase in Ni(II) concentration the formation of the precipitates begins and comple-

tes at lower pH values, but the demand of NaOH for complete Ni(II) precipitation is much higher. Especially high amounts of NaOH are used in the case of high Ni(II) concentrations. Apparently, in this case NaOH is used not only for free Ni(II) precipitation, but also for Ni(II)-citrate complex precipitation, which contains OH⁻ groups. The absence of sharp changes in the titration curves for alkaline solutions at a high Ni(II) concentration indicates a gradual change in complex formation. It should be taken into account that the concentrations of soluble

Table 1. Formation and composition of insoluble Ni(II)-citrate precipitate

pH	Total amount, mmol/l		Residual concentration, mmol/l		Ni(II):citrate ratio in the precipitate, mol:mol
	Ni(II)	Citrate	Ni(II)	Citrate	
12.5	58	8	1.3	4.1	8
	110	15	0.6	4.6	8
	160	22	1.2	7.1	7
	470	64	1.5	19	4.4
8	50	9	0.4	4.4	3.9
10	50	7	0.1	3.5	8.2
11	27	5	-0	2.6	9.3
12	22	4	0.1	2.6	10
11	24	6	0.02	4	8.4
12	10	5	0.1	2.1	10
	20	5	0.1	2	18.8
	6	10.5	0.05	9	11.8
	85	50	1.4	42	6.4
	104	50	0.5	36	6.3
	209	50	0.2	25	7.2
	316	50	0.6	18	8.1
	418	50	0.2	12	12.6
12.5	24	40	5	31	4.1
	48	40	1.7	39	4.5
	94	40	0.6	23	5.8
	182	40	0.2	13	6.2
	262	40	0.2	10	8.9

Table 2. Changes in pH after mixing nickel sulphate and trisodium citrate solutions

Initial concentration, mmol/l		pH value of initial solutions	pH value after mixing
Ni(II)	Citrate		
10	10	7	5.1
20	10		4.95
30	10		4.90
40	10		4.88
10	20	8	6.5
10	30		6.6
10	40		6.8
10	10		9
20	10		8.7
30	10		8.6
40	10		8.3

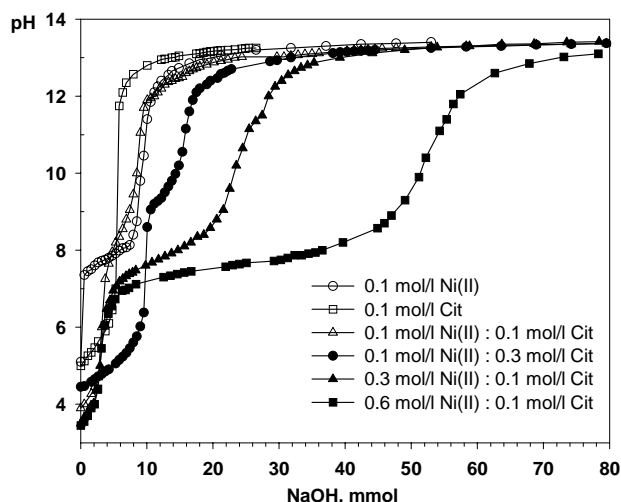


Fig.3 pH-metric titration of 50 ml of Ni(II) and citrate containing solutions

citrate compounds decrease with an increase in Ni(II) concentration, and such a form of the titration curves is partly due to the formation of the different stability complexes and partly due to changes in their concentrations.

The visible (Fig. 4) spectra of the residual solutions after precipitation at different Ni(II) and citrate concentrations and pH are similar and the peak wave length does not depend on the pH. This peculiarity distinguishes them from the spectra of Ni(II)-citrate complexes when the precipitate does not form. When the excess of Ni(II) ions is used, all COO^- groups and probably the OH group of citrate are bound with Ni^{2+} ions, and therefore the alkali OH^- group cannot interact with the complex in the solution. It only influences precipitate formation.

The results obtained for the solutions are not always applicable for the complexes existing in solid state, but the nature of binding is the same in a solid and in a solution, therefore it can be expected that the insoluble Ni(II)-citrate compound has partly the same bindings as the solution.

FT-IR investigation of the precipitates (Table 3) has shown a complex composition of the precipitate. In sodium citrate asymmetric (ν_{as}) and symmetric (ν_{s}) bands emerged at 1609 and 1402 cm^{-1} , respectively. The band between 3550–3300 cm^{-1} corresponds to a characteristic stretching vibration of OH groups (H_2O); a certain contribution of OH from C–OH vibration is also

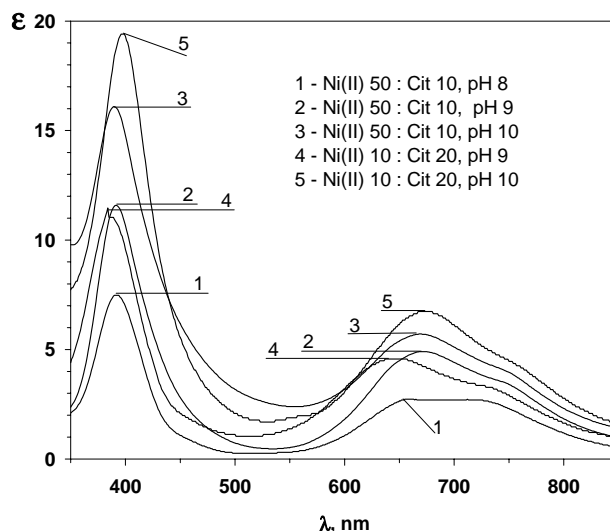


Fig. 4. Visible spectra of Ni(II)-citrate complexes

possible. The bands characteristic of nickel sulphate are observed at 1110 cm^{-1} and 664–612 cm^{-1} . The study compound do not show any IR absorption above 1700 cm^{-1} indicating the absence of free COOH groups. A very strong band at 1590 cm^{-1} (ν_{as} of COO^-) and the feature at 1400 cm^{-1} (ν_{s} of COO^-) are characteristic of complex compounds.

The OH group gives the deformation vibration bands at 1290, 1210, 1136, 1089 and 1080 cm^{-1} , which are also characteristic of the undissociated alcoholic OH group. In the precipitates investigated, the number of bands and their intensity sharply increases in the region 1300–1700 cm^{-1} , suggesting a possible substitution of hydrogen in the hydroxyl group by Ni(II). When NiSO_4 in solution for complex formation was substituted by NiCl_2 , the strong feature at $\sim 1100 \text{ cm}^{-1}$ decreased indicating that this band was also associated with stretching vibration of C–O–Me. Similar results have been obtained by other authors [9, 10].

Assignment	$\text{Na}_3\text{citrate}$	Ni(II)-citrate complex	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$
ν OH	3450 s.	3636 s. (Ni–OH)	3450 s. (H_2O)
	3233 s.	3420 v.s (H_2O)	3423 s. (H_2O)
ν CH (CH_2)	2970–2919 m.	2970–2910 m.	
ν_{as} COO^-	1609 v.s.	1590 v.s.	
ν_{s} COO^-	1402 s.	1400 s.	
δ CH (CH_2)	1480 w.	1490 w.	
δ CH_2 -(CH_2 -COOH)	1260	1256 m.	
δ OH(C–OH)	1290; 1210; 1136; 1079 m.	1076 m.	
ν C–C(CH_2 -COO $^-$)	920; 894 m.	910; 879 m.	
ν_{as} SO_4		1122 s-m.	1110 v.s.
δ SO_4			664 – 612 s.

v. s. – very strong; s. – strong; m. – medium; w. – weak.

The intensity of the band characteristic of $-\text{OH}$ in $\text{Ni}(\text{OH})_2$ increases with an increase in the solution pH, confirming the results of chemical analysis (Table 1).

Dissolution of the precipitate formed depends on its age, pH and the volume of the solvent used for the treatment. There are conditions when Ni(II)–citrate dissolves and the excess of $\text{Ni}(\text{OH})_2$ remains as a precipitate. This peculiarity of Ni(II)–citrate- OH^- precipitate enables to remove Ni(II)–citrate complex from spent solutions and to reuse them.

CONCLUSIONS

The insoluble Ni(II)–citrate compound forms at the excess of Ni(II) in alkaline solutions. Investigations suggest that the precipitate is composed of the insoluble nickel citrate complex and $\text{Ni}(\text{OH})_2$. The content of $\text{Ni}(\text{OH})_2$ in the precipitate depends on the initial concentrations of Ni(II) and citrate and the solution pH. Ni(II) is bound by the three COO^- groups and $-\text{OH}$ group of citrate into an insoluble compound. The insoluble compound also contains SO_4^{2-} and OH^- groups.

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NETIRPIŲ POLIBRANDUOLINIŲ NI(II)–CITRATINIŲ KOMPLEKSŲ SUSIDARYMAS ŠARMINĖJE TERPĖJE

S a n t r a u k a

Kai į šarminius tirpalus Ni(II) pridedama kelis kartus daugiau nei jame yra citrato, iš jų nusėda ir Ni(II), ir citratas. Nikelio ir citrato santykis nuosėdose bei iš tirpalų nusėdęs jų kiekis priklauso nuo į tirpalą pridėtų nikelio ir citrato santykio bei pH. Nuosėdose yra Ni(II)–citrato kompleksas ir $\text{Ni}(\text{OH})_2$.

Nuosėdų cheminės analizės, potenciometrinio titravimo, FT-IR ir matomosios šviesos spektrofotometriniai tyrimai įgalina manyti, kad Ni(II) į netirpų kompleksą yra surištas su citrato trimis $-\text{COOH}^-$ grupėmis ir $-\text{OH}$ grupe. Nuosėdose taip pat yra sulfatų ir hidroksidų.