Scientific paper

Extraction-Chromogenic System for Nickel(II) Based on 5-methyl-4-(2-thiazolylazo)resorcinol and Aliquat 336

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Abstract

A water–isobutanol extraction-chromogenic system for Ni^{II}, based on the azo dye 5-methyl-4-(2-thiazolylazo)resorcinol (MTAR; H_2L) and the ionic liquid Aliquat 336 (A336), was studied. Under the optimal conditions ($c_{MTAR} = 2.0 \times 10^{-4}$ mol dm^{-3}, $c_{A336} = 5.6 \times 10^{-3}$ mol dm^{-3}, pH 8.5 and extraction time t = 1 min), Ni^{II} is extracted as a ternary complex which can be represented by the formula $(A336^+)_2[Ni(L^{2-})_2]$. In the absence of A336, or in a slightly acidic medium, a binary complex, $[Ni(HL^-)_2]$, with an absorption maximum at λ = 548 nm and a shoulder at 590 nm is formed. The following extraction-spectrophotometric characteristics were determined at the above-mentioned optimal conditions: λ_{max} (545 nm), molar absorptivity (5.0×10^4 dm^3 mol^{-1} cm^{-1}), Sandell's sensitivity (1.2×10^{-3} μg cm^{-2}), Beer's law limits (0.05–3.1 μg cm^{-3}), constant of extraction (Log K = 6.1) and fraction extracted (99.2%). The effect of foreign ions was studied; the most serious interferences were caused by Co^{II}, Cu^{II} and Cr^{III}.

Keywords: Nickel(II); 4-(2-thiazolylazo)orcinol; ternary complex; solvent extraction; low-toxic solvent; spectrophotometry

1. Introduction

Nickel is a first-row transition metal with many industrial applications[1] and important functions in biology of microorganisms and plants.[2] It is involved in a variety of products, such as stainless steels, alloys, rechargeable batteries, guitar strings, green colored glasses, permanent magnets and catalysts for large-scale industrial processes. Most of the nickel produced is used in stainless steels, ferrous and non-ferrous alloys and nickel plating.[3] The chief criteria of use are its resistance to air oxygen, alkalis and acids, lustrous shine, ductility, malleability, and excellent ability to alloy with both ferrous and nonferrous metals. Over 3000 alloys containing nickel are known. They have more than 250 000 applications.[4]

In the earth's crust, nickel occurs most often in combination with sulfur, iron and arsenic. It is found in all types of soils, in fossil fuels, marine sediments, volcanic emissions and iron meteorites. Anthropogenic activities that contribute to nickel loadings in the environment include burning of fuel and residual oil, mining, smelting, refining, alloy processing, scrap metal reprocessing, waste incineration and disposal of sewage sludge or application of sludge as a fertilizer.[4–6]

It is known that nickel may have carcinogenic, mutagenic and allergic properties.[7] Negative health effects have been documented for respiratory, cardiovascular, gastrointestinal, hematological, musculoskeletal, hepatic, renal, dermal, ocular, immunological, developmental, neurological and reproductive systems.[6] An allergic skin reaction is a common problem for some people; it is often associated with the presence of nickel in daily-used objects, such as jewelry, keys, jean buttons, children's clothing and toys.[8,9]

Many analytical techniques, such as atomic absorption spectrophotometry, optical emission spectrometry, X-ray fluorescence analysis, neutron activation analysis, voltammetry and spectrophotometry, have been used for

nickel determination.[10–14] The methods involving spectrophotometry are simple and low-cost; they can be easily combined with procedures for preliminary separation and concentration, such as cloud point extraction,[13] solid phase extraction[14] and liquid-liquid extraction (LLE).[15–20]

5-methyl-4-(2-thiazolylazo)resorcinol (MTAR) is a well-known analytical reagent.[21-28] It has recently been used in our laboratory for LLE of $V^{IV,V}$.[29–32] Here, we describe investigations on a LLE-chromogenic system for Ni^{II} containing MTAR and the ionic liquid Aliquat 336 (A336). The selected organic solvent was isobutanol (2-methylpropan-1-ol). It is characterized by a low toxicity, volatility and corrosivity,[33,34] can be produced from renewable resources,[35] fulfills the so-called "CHON principle"[36] and is readily biodegradable and non-bioaccumulative.[33,37]

2. Materials and Methods

2. 1. Reagents and Apparatus

Stock solution of Ni^{II} (1.7×10^{-2} mol dm^{-3}; pH ~2) was prepared by dissolving $NiSO_4 \sim 7H_2O$ (Sigma-Aldrich, 99.999% trace metals basis) in distilled water containing H_2SO_4. Working solutions (2×10^{-4} mol dm^{-3}) were prepared by appropriate dilution of the stock solution. MTAR (95%, Sigma-Aldrich Chemie GmbH) was dissolved in the presence of KOH;[31] the obtained slightly alkaline aqueous solution (pH 8–9) was at concentration of 2×10^{-3} mol dm^{-3}. Aliquat 336 was purchased from Sigma-Aldrich Chemie and dissolved in isobitanol (p. a., Merck). Solutions with concentrations of 1.4×10^{-2} and 5.6×10^{-3} mol dm^{-3} were used; the calculations were based on the average molar mass of A336 (432 g mol^{-1}).[38] The acidity of the aqueous medium was set by the addition of buffer solution, prepared by 2 mol dm^{-3} solutions of CH_3COOH and ammonia. The pH of the buffers was measured by a WTW InoLab 7110 (Germany) pH meter with an accuracy of ±0.001 pH units. Absorbance measurements were made with a Camspec M508 and a Ultrospec3300 pro UV-Vis spectrophotometers (UK), equipped with 1 cm path-length glass cells. Distilled water was used throughout the work.

2. 2. Determination of the Optimum Conditions

Solutions of Ni^{II}, MTAR and buffer were placed into a separatory funnel. The aqueous phase volume was adjusted to 5 cm^3 or 10 cm^3 with water. A portion of the A336 solution was added and the organic phase was adjusted to 5 cm^3 with isobutanol. Then the funnel was shaken for a fixed time interval (between 5 and 300 seconds). After separation of the phases, the aqueous layer was discarded, and the organic layer was transferred into a beaker. A pinch of anhydrous Na_2SO_4 was added to remove any water and the colored solution was poured into the spectrophotometer cell. The absorbance was measured against isobutanol or simultaneously prepared blank sample.

2. 3. Determination of the Distribution Ratio

The distribution ratio D was calculated by the formula $D = A_1/(A_3 - A_1)$, where A_1 is the absorbance obtained after a single extraction under the optimal pH and reagents concentrations (Table 1) and A_3 is the absorbance obtained after a triple extraction.[30,31] The single extraction and the first stage of the triple extraction were performed with equal volumes of both phases (5 cm^3). The organic layers were transferred into two 25-cm^3 calibrated flasks and the flask for the single extraction was brought to volume with the isobutanol solution of A336 (5.6×10^{-3} mol dm^{-3}). The second stage of the triple extraction was performed by adding a 5-cm^3 portion of the A336 solution to the aqueous phase which remained after the first stage. The third stage was performed in the same manner. The two successive organic layers were transferred to the flask with the isobutanol extract obtained after the first stage. The volume was brought to the mark with the A336 solution. Absorbances A_1 and A_3 were measured against corresponding blanks.

2. 4. Investigation of the Influence of Foreign Ions

Solutions of Ni^{II} (1 cm^3, 2×10^{-4} mol dm^{-3}), foreign ion, MTAR (1 cm^3, 2×10^{-3} mol dm^{-3}) and buffer (1 cm^3, pH 8.5) were successively placed into a separatory funnel. The aqueous phase volume was adjusted to 10 cm^3 with

Table 1. LLE-spectrophotometric optimization of the Ni^{II} – MTAR – A336 – water – isobutanol system. The volume of the organic phase was 5 cm^3.

Parameter	Optimization range	Optimal value
Wavelength, nm	Visible range	545
pH	3.9–9.9	8.5
Volume of the aqueous phase, cm^{-3}	5 and 10	10
Concentration of MTAR, mol dm^{-3}	$(0–1.6) \times 10^{-3}$	2.0×10^{-4}
Concentration of A336, mol dm^{-3}	$(0–1.4) \times 10^{-2}$	5.6×10^{-3}
Extraction time, seconds	5–300	60

water. Then A336 solution (5 cm^3, 5.6 × 10^{-3} mol dm^{-3}) was added and the funnel was shaken for 1 min. The organic layer was transferred into a beaker, dried with a pinch of anhydrous Na_2SO_4 and poured into the spectrophotometer cell. The absorbance was measured at 545 nm against isobutanol. For control, samples prepared by the same procedure in the absence of the foreign ion or Ni^{II} were also run.

3. Results and Discussion

3. 1. Absorption Spectra of the Isobutanol-Extracted Complexes

Spectra of isobutanol-extracted Ni–MTAR complexes in the presence (1, 3) or absence (2, 4) of A336 are shown in Fig. 1. The spectra 1 and 2 are alike (1: λ_{max} = 545 nm; 2: λ_{max} = 548 nm), however in absence of A336 (2) the absorbance is lower, and a shoulder at about 590 nm is observed. Such a shoulder is slightly visible in spectrum 1. There is a tendency for it to become more and more imperceptible with increasing pH and decreasing the MTAR concentration.

At lower pH values (4.7; spectra 3 and 4), nickel is extracted to a negligible extent regardless of the presence or absence of A336. The absorbance of the blanks in the absence of A336 (2' and 4') is lower than that obtained in the presence of A336 (1' and 3', respectively). This can be explained by the formation of an extractable ion pair between the anion of the azo dye (HL^-)[31,39,40] and the cation of the ionic liquid ($A336^+$).

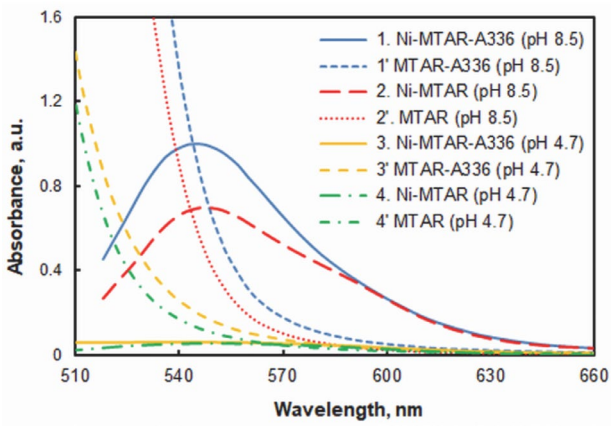

Figure 1. Absorption spectra in isobutanol of complexes against blanks (1 – 4; c_{Ni} = 2 × 10^{-5} mol dm^{-3}, c_{MTAR} = 2.7 × 10^{-4} mol dm^{-3}, c_{A366} = 5.6 × 10^{-3} mol dm^{-3}, $V_{aq.\ phase}$ = 10 cm^3, extraction time t = 60 sec) and corresponding blanks against isobutanol (1' – 4'). Samples 2, 2', 4 and 4' do not contain A336; pH is given in the legend.

3. 2. Effect of pH

The effect of pH on the absorbance obtained in the presence or absence of A336 is shown in Fig. 2. Ammonia-acetate buffer solutions, which have the best buffering action at pH 4.75 (the pK_a of acetic acid) and 9.25 (the pK_a of NH_4^+)[41] were used in all experiments. In the presence of A336 (series 1), maximal absorbance was obtained in slightly alkaline medium. The sharp decrease at pH < 6 can be attributed to incomplete complex formation due to the predominance of doubly protonated MTAR species.[42] In the absence of A336 (series 2), maximal absorbance was recorded in the slightly acidic region (pH *ca.* 6.5 – 7.0). It makes sense that the course of series 1 and series 2 is identical in the acidic region (up to pH *ca.* 6); probably the absorbance obtained in the presence of A336 is due to the simultaneous extraction of two complexes, Ni–MTAR–A336 and Ni–MTAR. However, with the increase in pH, the contribution of the ternary complex to the total absorbance becomes greater.

The decrease in absorbance at pH > *ca.* 9 (series 1) can be attributed to two factors: (i) presence of hydrolyzed $Ni(OH)^+$ species;[43] and (ii) a competitive extraction of the ($A336^+$)(HL^-) ion pair which reduces the effective concentrations of the reagents to a larger extent at higher pH values (see spectra 1' and 3' in Fig. 1).

One can conclude from Fig. 2, and from the above mentioned pK_a value of NH_4^+ (9.25), that the optimal pH range for the extraction of Ni^{II} is 8.3–9.0. We performed our further investigations at pH 8.5.

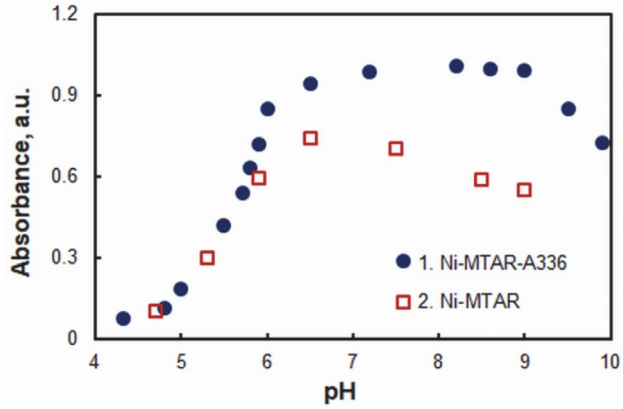

Figure 2. Absorbance of the complex in presence (1) or absence (2) of A336 vs. pH of the aqueous phase. c_{Ni} = 2 × 10^{-5} mol dm^{-3}, c_{MTAR} = 2 × 10^{-4} mol dm^{-3}, c_{A366} = 5.6 × 10^{-3} mol dm^{-3}, $V_{aq.\ phase}$ = 10 cm^3, extraction time t = 60 sec.

3. 3. Effect of the Reagents Concentrations, Volume of the Aqueous Phase and Shaking Time

The effect of the MTAR concentration on the absorbance is shown in Fig. 3 for two different sets of conditions. There is a maximum in both series; at high concentrations of MTAR, the absorption decreases. With a 2:1 volume ratio (series 2; 10 cm^3 aqueous phase / 5 cm^3 isobutanol phase), the apparent molar absorptivity is high-

er. The optimal reagent concentration for this volume ratio appears to be $c_{MTAR} = 2.0 \times 10^{-4}$ mol dm^{-3}. It is considerably lower (by almost an order of magnitude) than the MTAR concentration required for the extraction of V^{V}.[31]

The effect of the A336 concentration on the absorbance is shown in Fig. 4. The optimal concentration is $c_{A336} = 5.6 \times 10^{-3}$ mol dm^{-3}. It is also lower than that required for the extraction of V^{V};[31] this indicates that the Ni^{II}–MTAR–A336 complex is more stable than the corresponding V^{V} complex.

The effect of shaking time was studied under the optimal pH and reagents concentrations (Table 1). It was found that 50 seconds are enough for a quantitative extraction of Ni^{II}. To avoid accidental errors, induced by the combination of short shaking times and different shaking rates, we shook for 60 seconds in our further experiments.

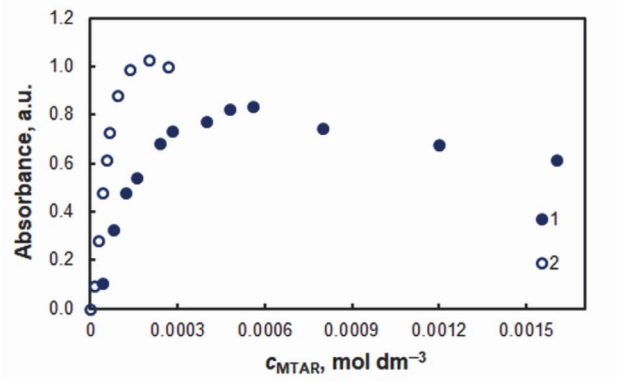

Figure 3. Absorbance vs. concentration of MTAR. (1) $c_{Ni} = 4 \times 10^{-5}$ mol dm^{-3}, $c_{A366} = 1.4 \times 10^{-2}$ mol dm^{-3}, pH 6, $V_{aq.\ phase} = 5$ cm^3, extraction time t = 60 sec; (2) $c_{Ni} = 2 \times 10^{-5}$ mol dm^{-3}, $c_{A366} = 5.6 \times 10^{-3}$ mol dm^{-3}, pH 8.5, $V_{aq.\ phase} = 10$ cm^3, extraction time t = 60 sec.

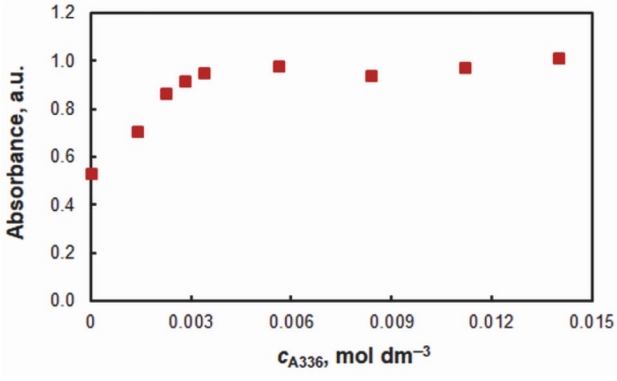

Figure 4. Absorbance vs. concentration of A336. $c_{Ni} = 2 \times 10^{-5}$ mol dm^{-3}, $c_{MTAR} = 2.0 \times 10^{-4}$ mol dm^{-3}, pH 8.5, $V_{aq.\ phase} = 10$ cm^3, extraction time t = 60 sec.

3. 4. Molar Ratios, Structure and Equations of Complex Formation and Extraction

It is known that thiazolylazo- and pyridylazo dyes form 1:1[44] or 1:2[45–48] complexes with Ni^{II}. In aqueous medium, at least two different 1:2 Ni-to-PAR complex species (PAR = H_2L = 4-(2-pyridylazo)resorcinol) exist, $[Ni(HL)L]^-$ and $[NiL_2]^{2-}$.[49] In the presence of a quaternary ammonium salt (tetradecyldimethylbenzylammonium chloride; Q^+Cl^-),[50] two kinds of complexes can be extracted in chloroform, $[Ni(HL)_2] \cdot n(Q^+Cl^-)$ and $(Q^+)_2[NiL_2]$; the second one has a higher molar absorptivity. Karipcin et al. isolated in solid state water-insoluble octahedral 1:2 binary complexes with PAR[47] or 4-(2-thiazolylazo)resorcinol (TAR);[48] they can be represented by the general formula $[Ni(HL)_2]$. The TAR complex is partially soluble in chloroform and readily soluble in alcohols; in ethanol, it shows an absorption maximum at 543 nm and a shoulder at 586 nm.[48]

It is clear from our investigations (see Fig. 1, Fig 2 and Fig. 4) that at least two different Ni^{II} – MTAR isobutanol-extractable complexes exist: (i) a binary Ni–MTAR complex; it is extracted in the absence of A336 (Fig. 1, spectrum 1); and (ii) a ternary Ni–MTAR–A336 complex (Fig. 1, spectrum 2). The MTAR:Ni^{II} and A336:Ni^{II} molar ratios in the ternary complex were determined by the straight-line method of

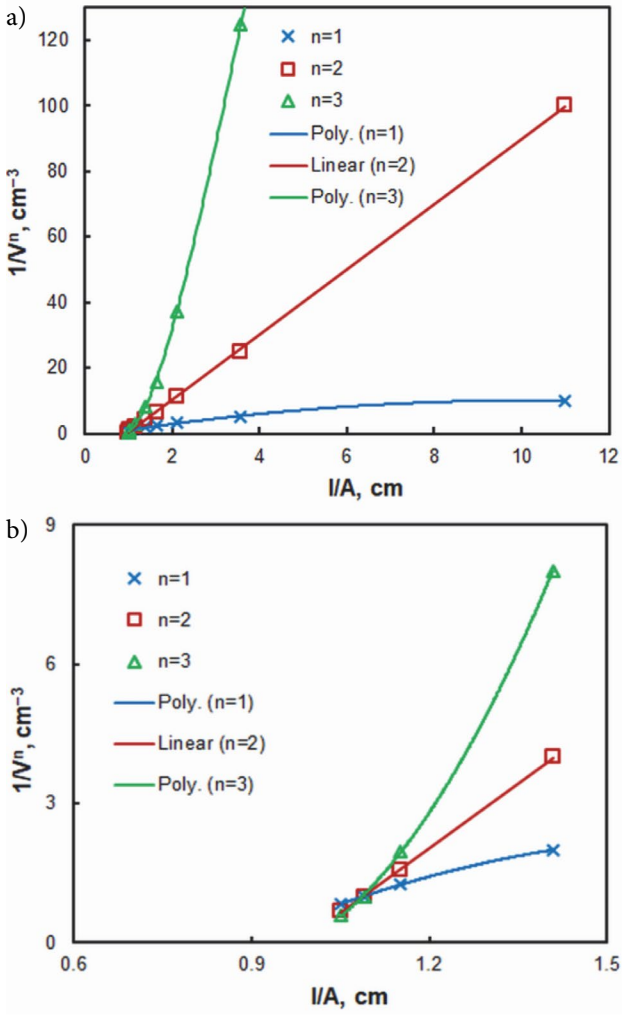

Figure 5. Determination of the MTAR/Ni^{II} (**a**) and A336/Ni^{II} (**b**) molar ratios by the straight-line method of Asmus. The experimental conditions are given in Fig. 3 (series 2) and Fig. 4, respectively.

Asmus[51] (Fig. 5) and the mobile equilibrium method[52] (Fig. 6). Its formation and extraction can be represented by Eq. 1.

$$Ni^{2+}_{(aq)} + 2HL^{-}_{(aq)} + 2A336^{+}_{(org)} \rightleftarrows (A336^{+})_2[Ni(L)_2]_{(org)} + 2H^{+}_{(aq)} \quad (1)$$

In the absence of A336, a neutral $[Ni(HL)_2]$ complex is formed (Eq. 2).

$$Ni^{2+}_{(aq)} + 2HL^{-}_{(aq)} \rightleftarrows [Ni(HL)_2]_{(org)} \quad (2)$$

As mentioned above, a complex with the same formula (which is insoluble in water and soluble in alcohols) has been prepared with TAR.[48] The MTAR complex obtained by us has similar spectral characteristics (an absorption maximum of 548 nm and a shoulder at about 590 nm), indicating that it probably has a similar structure. Most likely, both MTAR complexes, $[Ni(HL)_2]$ and $(A336^{+})_2[Ni(L)_2]$, have an octahedral geometry which is common for Ni^{II} centers.[47,48,53,54] Donor atoms of each of the tridentate MTAR units should be the o-hydroxyl oxygen (relative to the azo-group) and the two nitrogens (from the thiazole ring and azo-group).[47,48,55]

As shown in Eqs. 1 and 2, MTAR at the operating conditions exists mainly in its HL^{-} form (with a proton in the OH-group in ortho-position relative to the azo-group).[42,56] It is known that this form dominates (in aqueous medium) at the pH range of 5.7–11.8.[42]

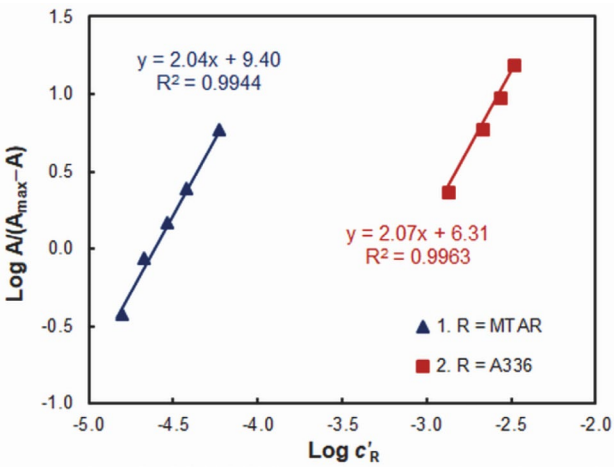

Figure 6. Determination of the MTAR/Ni^{II} (1) and A336/Ni^{II} (2) molar ratios by the mobile equilibrium method. The experimental conditions are given in Fig. 3 (series 2) and Fig. 4, respectively.

3. 5. Beer's Law and Analytical Characteristics

The dependence between the concentration of Ni^{II} in the aqueous phase and the absorbance of the extract was studied under the optimal conditions (Table 1). A good linearity was obtained in the range of 0.05 – 3.1 μg cm^{-3} (R^2 = 0.9993, N = 9). The linear regression equation was $A = 0.845\gamma - 0.006$, where A is the absorbance and γ is the concentration ($\mu g\ cm^{-3}$) of Ni^{II}. The standard deviations of the slope and intercept were 0.008 and 0.013, respectively. The limits of detection (LOD) and quantitation (LOQ), calculated as 3- and 10-times standard deviation of the intercept divided by the slope, were LOD = 46 ng cm^{-3} and LOQ = 153 ng cm^{-3}. The molar absorptivity (ε) and Sandell's sensitivity (S) at λ_{max} = 545 nm were $\varepsilon = 5.0 \times 10^4$ $dm^3\ mol^{-1}\ cm^{-1}$ and $S = 1.2 \times 10^{-3}\ \mu g\ cm^{-2}$, respectively.

Table 2. Effect of foreign ions in determination of 11.7 μg of Ni^{II}.

Foreign ion (FI) added	Added salt	FI : Ni^{II} mass ratio	Amount of Ni^{II} found (μg)	(%)
Al^{III}	$Al_2(SO_4)_3 \cdot 18H_2O$	8.5	11.4	97.4
Br^{-}	NaBr	850	11.7	100
Cd^{II}	$CdCl_2$	5	12.3	105
Cl^{-}	NH_4Cl	850	11.8	101
Co^{II}	$CoSO_4 \cdot 7H_2O$	1	17.0	146
Cr^{III}	$Cr_2(SO_4)_3$	1	8.42	72.0
Cr^{VI}	K_2CrO_4	500	11.9	101
Cu^{II}	$CuSO_4 \cdot 5H_2O$	1	16.1	138
F^{-}	NH_4F	850	10.6	99.4
Fe^{III}	$Fe_2(SO_4)_3$	5	12.3	105
HPO_4^{2-}	Na_2HPO_4	500	11.8	101
I^{-}	KI	250	11.1	95.1
Mg^{II}	$MgSO_4$	500	11.7	100
Mn^{II}	$MnSO_4 \cdot 5H_2O$	5	11.7	100
Mo^{VI}	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	100	11.7	100
NO_3^{-}	NH_4NO_3	850	10.4	97.2
Re^{VII}	NH_4ReO_4	400	11.5	98.2
V^{V}	NH_4VO_3	5	12.0	103
W^{VI}	$Na_2WO_4 \cdot 2H_2O$	500	12.0	103
Zn^{II}	$ZnSO_4 \cdot 7H_2O$	1	12.5	107

The distribution ratio D was calculated from the absorbances obtained after single and triple extractions as described above: $D = 121 \pm 3$ (six replicate measurements). The fraction extracted, $E = 99.2\%$, was found by the formula $E\% = 100 \times D/(D+1)$. The conditional equilibrium constant characterizing Eq. 1 was calculated by the mobile equilibrium method[52] (Fig. 5, straight line 2; abscissa intercept). The obtained value was $\log K = 6.1 \pm 0.2$.

3. 6. Effect of Foreign Ions

Various salts were used to test the selectivity of the developed procedure. Their effect is summarized in Table 2. The most significant interferences were those of Co^{II}, Cu^{II} and Cr^{III} which form intensively colored complexes under the specified conditions. Cr^{III} causes a negative error, while Co^{II} and Cu^{II} cause positive errors. Zn^{II} also causes positive errors, however its interfering effect is smaller. A 250-fold excess of I^-; 100-fold excess of Mo^{VI}; 8.5-fold excess of Al^{III}; and 5-fold excess of V^V, Fe^{III}, Cd^{II} and Mn^{II} are tolerable. The determination of Ni^{II} is not affected by high concentrations of alkali and alkaline-earth ions, NH_4^+, Cl^-, Br^-, F^-, NO_3^-, SO_4^{2-}, CrO_4^{2-}, WO_4^{2-}, ReO_4^- and HPO_4^{2-}.

4. Conclusions

The described investigations shed light on the complex formation between Ni^{II} and MTAR in the presence or absence of A336. The conditions of existence of the two main extracted complexes, $(A336^+)_2[Ni(L)_2]$ and $[Ni(HL)_2]$, have been outlined and the differences in their spectra have been highlighted. In a slightly alkaline medium, Ni^{II} predominantly forms a ternary complex. It is intensively colored and readily extractable into isobutanol. This solvent is less toxic than the diluents commonly applied to improve the physico-chemical characteristics of the ionic liquid A336 (e.g., benzene,[57] carbon tetrachloride,[58] chloroform,[58] toluene,[59] xylene[60] and kerosene[61]) and the organic solvents typically used for LLE-spectrophotometric determination of Ni^{II} (e.g., chloroform).[17-20]

Acknowledgments

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5. References

1. K. K. Chatterjee, Uses of Metals and Metallic Minerals, New Age International (P) Ltd. Publishers, New Delhi, India, **2007**, pp. 272–275.
2. P. H. Brown, in: A. V Barker, D. J. Pilbeam (Ed.): Handbook of Plant Nutrition, CRC Press, Boca Raton, USA, **2007**, pp 395–409.
3. A. Apostolikas, E. Frogoudakis, J. Bakallbashi, in: Nickel, World Production and Demand: Proceedings of the 3rd Balkan Mining Congress (Balkanmine 2009), The Chamber of Mining Engineers of Turkey, Turkey, **2009**, pp. 29–34.
4. Y. Chau, O. Kulikovsky-Cordeiro, *Environ. Rev.* **1995**, *3*, 95–120. **DOI:**10.1139/a95-004
5. S. Sikdar, M. Kundu, *ChemBioEng Rev.* **2018**, *5*, 18–29. **DOI:**10.1002/cben.201700005
6. R. Eisler, Nickel hazards to fish, wildlife, and invertebrates: a synoptic review; Geological Survey Washington DC1998, https://www.pwrc.usgs.gov/eisler/CHR_34_Nickel.PDF, (assessed: June 05, 2019)
7. S. Dzugkoev, I. Mozhaeva, O. Margieva, A. Tedtoeva, F. Dzugkoeva, *Sciences of Europe* **2017**, *2*, 78–81.
8. Position Statement on Nickel Sensitivity (August 22, 2015), https://www.aad.org/Forms/Policies/Uploads/PS/PS-Nickel%20Sensitivity.pdf (assessed: June 05, 2019)
9. J. P. Thyssen, *Contact Dermatitis* **2011**, *65*, 1–68. **DOI:**10.1111/j.1600-0536.2011.01957.x
10. M. Ghaedi, *Spectrochim. Acta A* **2007**, *66*, 295–301. **DOI:**10.1016/j.saa.2006.02.055
11. S. K. Kumar, P. S. Rao, L. Krishnaiah, B. Jayaraj, P. Chiranjeevi, *Anal. Sci.* **2004**, *20*, 951–953. **DOI:**10.2116/analsci.20.951
12. Z. Li, J. Pan and J. Tang, *Anal. Lett.* **2002**, *35*, 167–183. **DOI:**10.1081/AL-120002369
13. Y. Bazel, A. Tupys, Y. Ostapiuk, O. Tymoshuk, V. Matiychuk, *J. Mol. Liq.* **2017**, *242*, 471–477. **DOI:**10.1016/j.molliq.2017.07.047
14. D. Rekha, J. Kumar, B. Jayaraj, Y. Lingappa, P. Chiranjeevi, *Bull. Korean Chem. Soc.* **2007**, *28*, 373–378. **DOI:**10.5012/bkcs.2007.28.3.373
15. C. Ramachandraiah, J. Rajesh Kumar, K. Janardhan Reddy, S. Lakshmi Narayana, A. Varada Reddy, *J. Environ. Manage.* **2008**, *88*, 729–736. **DOI:**10.1016/j.jenvman.2007.03.033
16. L. S. Sarma, J. R. Kumar, K. J. Reddy, T. Thriveni, A. V. Reddy, *J. Trace Elem. Med. Bio.* **2008**, *22*, 285–295. **DOI:**10.1016/j.jtemb.2008.06.003
17. C. Ravichandran, D. Benzil, C. Ramachandraiah, K. Chandrasekhar, *Int. J. Bioassays* **2015**, *4*, 4468–4472. **DOI:** 10.21746/ijbio.2015.11.005.
18. K. Kuliev, N. Verdizade, S. Aliev, G. Suleymanova, *World J. Pharmaceut. Res.* **2018**, *7*, 61–73. **DOI:** 10.20959/wjpr201819-13762.
19. S. G. Aliyev, R. A. Ismailova, E. I. Suleymanova, L. M. Magarramova, S. S. Sultanzadeh, Z. G. Asgerova, A. Z. Zalov, *Int. J. Innovat. Sci., Eng. Technol.* **2018**, *5*, 192–206.
20. N. A. Verdizadeh and K. A. Kuliev, *Izv. Saratov Univ. (N.S.), Ser. Chemistry. Biology. Ecology* **2017**, *17*, 247–262. **DOI:**10.18500/1816-9775-2017-17-3-247-262
21. M. Tuzen, M. Soylak, D. Citak, H. S. Ferreira, M. G. A. Korn, M. A. Bezerra, *J. Hazard. Mat.* **2009**, *162*, 1041–1045. **DOI:**10.1016/j.jhazmat.2008.05.154

22. W. N. L. dos Santos, D. D. Cavalcante, H. S. Ferreira, C. F. das Virgens, A. R. Borges, M. M. Silva, M. G. R. Vale, *Int. J. Environ. Anal. Chem.* **2011**, *91*, 1447–1452. **DOI:**10.1080/03067319.2010.484885
23. M. Soylak, M. Tuzen, *J. Hazard. Mat.* **2008**, *152*, 656-661. **DOI:**10.1016/j.jhazmat.2007.07.027
24. S. A. Rocha and S. L. Ferreira, *Eurasian J. Anal. Chem.* **2007**, *2*, 1–11. **DOI:**10.12973/ejac/77011
25. Y.-S. Chung, W.-S. Chung, *Bull. Korean Chem. Soc.* **2003**, *24*, 1781–1784.
26. M. A. Zaitoun, A. K. El-Qisairi, K. A. Momani, H. A. Qaseer, W. Alhalasah, *J. Environ. Occup. Sci.* **2014**, *3*, 154–161. **DOI:**10.5455/jeos.20140909071020
27. M. Zaitoun, K. Momani, Q. Jaradat, I. Momani, I. Qurashi, *Jordan J. Chem.* **2014**, *9*, 81–96. **DOI:**10.12816/0026472
28. Y. Erdogdu, Ü. C. Başköse and S. Sağlam, *Chem. Pap.* **2019**. **DOI:**10.1007/s11696-019-00739-4
29. K. B. Gavazov, T. S. Stefanova, *Croat. Chem. Acta* **2014**, *87*, 233–240. **DOI:**10.5562/cca2436
30. K. B. Gavazov, V. B. Delchev, K. T. Mileva, T. S. Stefanova, G. K. Toncheva, *Acta Chim. Slov.* **2016**, *63*, 392-398. **DOI:**10.17344/acsi.2016.2431
31. G. K. Toncheva, N. P. Milcheva, K. B. Gavazov, *Acta Chim. Slov*. **2018**, *65*, 847–852. **DOI:**10.17344/acsi.2018.4491
32. K. B. Gavazov, V. B. Delchev, N. P. Milcheva, G. K. Toncheva, *Open Chem.* **2019**, *17*, 599–608. **DOI:**10.1515/chem-2019-0071
33. J. Patocka, K. Kuca, *Mil. Med. Sci. Lett.* **2012**, *81*, 142–163. **DOI:**10.31482/mmsl.2012.022.
34. A. Pal, V. Manish, S. Gupta, N. Kumar, *SAE Tech. Pap.* **2013**, *2013-24-0151*. **DOI:**10.4271/2013-24-0151
35. S. Atsumi, T. Hanai and J. C. Liao, *Nature* **2008**, *451*, 86–90. **DOI:**10.1038/nature06450
36. E. Löfström-Engdahl, On the diluent and solvent effects in liquid-liquid extraction systems based on bis-triazine-bipyridine (BTBP) ligands, PhD thesis, Chalmers University of Technology, Gothenburg, Sweden 2014, http://publications.lib.chalmers.se/records/fulltext/203658/203658.pdf (assessed: June 05, 2019)
37. C. E. Schaefer, X. Yang, O. Pelz, D. T. Tsao, S. H. Streger, R. J. Steffan, *Chemosphere* **2010**, *81*, 1111–1117. **DOI:**10.1016/j.chemosphere.2010.09.002
38. J.-P. Mikkola, P. Virtanen, R. Sjoholm, *Green Chem.* **2006**, *8*, 250–255. **DOI:**10.1039/b512819f
39. K. B. Gavazov, G. K. Toncheva, *Russ. J. Gen. Chem.* **2015**, *85*, 192–197. **DOI:**10.1134/S1070363215010338
40. K. B. Gavazov, G. K. Toncheva, *J. Adv. Chem.* **2013**, *5*, 641–651.
41. L. Konermann, *J. Am. Soc. Mass Spectrom.* **2017**, *28*, 1827–1835. **DOI:**10.1007/s13361-017-1739-3
42. N. Menek, E. Eren, S. Topçu, *Dyes Pigm.* **2006**, *68*, 205–210. **DOI:**10.1016/j.dyepig.2005.01.010
43. D. D. Perrin, *J. Chem. Soc. (Resumed)* **1964**, 3644–3648. **DOI:**10.1039/jr9640003644
44. A. S. Amin, *Quim. Anal.* **2001**, *20*, 145–151. **DOI:**10.1023/A:1008799422509
45. A. S. Amin, M. S. Ibrahim, *Ann. Chim.* (*Rome)* **2001**, *91*, 103–110.
46. K. Ohshita, H. Wada, G. Nakagawa, *Anal. Chim. Acta* **1981**, *124*, 193–200. **DOI:**10.1016/S0003-2670(01)83913-1
47. F. Karipcin, E. Kabalcilar, *Acta Chim. Slov.* **2007**, *54*, 242–247.
48. F. Karipcin, B. Dede, S. Percin-Ozkorucuklu, E. Kabalcilar, *Dyes Pigm.* **2010**, *84*, 14–18. **DOI:**10.1016/j.dyepig.2009.06.010
49. D. Nonova and B. Evtimova, *Anal. Chim. Acta* **1972**, *62*, 456–461. **DOI:**10.1016/0003-2670(72)80058-8
50. H. Hoshino, T. Yotsuyanagi, K. Aomura, *Anal. Chim. Acta* **1976**, *83*, 317–328. **DOI:**10.1016/S0003-2670(01)84658-4
51. E. Asmus, *Fresenius' J. Anal. Chem.* **1960**, *178*, 104–116. **DOI:**10.1007/BF00467200
52. Z. Zhiming, M. Dongsten, Y. Cunxiao, *J. Rare Earths* **1997**, *15*, 216–219.
53. R. Vafazadeh, M. Namazian, B. Shahpoori-Arani, A. C. Willis, P. D. Carr, *Acta Chim. Slov.* **2018**, *65*, 372–379. **DOI:**10.17344/acsi.2017.4096
54. X.-N. Fang, J. Li, X.-G. Yi, Q. Luo, J.-Y. Chen and Y.-X. Li, *Acta Chim. Slov.* **2019**. **DOI:**10.17344/acsi.2018.4885
55. H. R. Hovind, *Analyst* **1975**, *100*, 769–796. **DOI:**10.1039/an9750000769
56. K. Pytlakowska, V. Kozik, M. Dabioch, *Talanta* **2013**, *110*, 202–228. **DOI:**10.1016/j.talanta.2013.02.037
57. W. Wei, C.-W. Cho, S. Kim, M.-H. Song, J. K. Bediako, Y.-S. Yun, *J. Mol. Liq*. **2016**, *216*, 18–24. **DOI:**10.1016/j.molliq.2016.01.016
58. M. Atanassova, I. L. Dukov, *Separ. Purif. Technol*. **2004**, *40*, 171–176. **DOI:**10.1016/j.seppur.2004.02.007
59. V. Gardoňová, M. Labaška, I. Antalík, J. Kuruc, *J. Radioanal. Nucl. Chem*. **2013**, *295*, 1353–1360. **DOI:**10.1007/s10967-012-1955-z
60. A. G. Gaikwad, A. D. Damodaran, *J. Radioanal. Nucl. Chem*. **1992**, *163*, 277–288. **DOI:**10.1007/BF02034801
61. J. A. López-López, B. Herce-Sesa, C. Moreno, *Talanta* **2016**, *159*, 117–121. **DOI:**10.1016/j.talanta.2016.06.018

Povzetek

Proučevali smo kromogen sistem ekstrakcije voda-izobutanol za Ni^{II} na osnovi azo barvila 5-metil-4- (2-tiazolilazo) resorcinola (MTAR;H_2L) in ionske tekočine Aliquat 336 (A336). Pri uporabi optimalnih pogojev ekstrakcije (c_{MTAR} = 2,0 · 10^{-4} mol dm^{-3}, c_{A336} = 5,6 ·10^{-3} mol dm^{-3}, pH 8,5 in čas ekstrakcije t = 1 min), se Ni^{II} ekstrahira kot ternarna kompleksna spojina, ki jo lahko zapišemo s formulo $(A336^+)_2[Ni(L^{2-})_2]$. V odsotnosti A336 ali v rahlo kislem mediju pride do nastanka binarne kompleksne spojine $[Ni(HL^-)_2]$, ki ima absorpcijski maksimum pri λ = 548 nm, v spektru pa je opaziti tudi ramo pri λ = 590 nm. Značilne ekstrakcijske in spektrofotometrične parametre smo določili pri optimalnih pogojih ekstrakcije: λ_{max} (545 nm), molarna absorptivnost (5,0 · 10^4 dm^3 mol^{-1} cm^{-1}), Sandellova občutljivost (1,2 · 10^{-3} μg cm^{-2}), omejitve Beerovega zakona (0,05–3,1 μg cm^{-3}), konstanta ekstrakcije (Log K = 6,1) in delež ekstrahirane frakcije (99,2 %). Preučevali smo tudi vpliv dodanih ionov. Namočnejši vpliv v preučevanem sistemu so imeli Co^{II}, Cu^{II} in Cr^{II}.

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