



COMPLEX FORMATION IN A LOW TOXIC ORGANIC SOLVENT-BASED LIQUID-LIQUID EXTRACTION-CHROMOGENIC SYSTEM FOR VANADIUM(V), NICKEL(II) AND CUPRUM(II)



Galya K. Toncheva¹, Nikolina P. Milcheva², Siana K. Chobanova¹, Mariela G. Kalendarska¹ and Kiril B. Gavazov²

¹ – Department of General and Inorganic Chemistry with Methodology of Chemical Education, University of Plovdiv Paisii Hilendarski, 24 Tsar Assen St., Plovdiv 4000, Bulgaria

² – Department of Chemical Sciences, Medical University of Plovdiv, 120 Buxton Brothers St., Plovdiv 4004, Bulgaria

Abstract

Liquid-liquid extraction-chromogenic systems for vanadium(V), nickel(II) and copper(II) containing azo dye {4-(2-thiazolylazo)orcinol, TAO}, quaternary ammonium salt (Aliquat 336) and low-toxic organic solvent (isobutanol) were studied. The optimum conditions for extraction of the mentioned metal ions were found. The following extraction and spectrophotometric characteristics were determined: absorption maxima, molar absorptivities, Sandell's sensitivities, constants of extraction, constants of distribution, fractions extracted, and Beer's law limits. The stoichiometry of the extracted binary and ternary complexes was established by different methods.

Acknowledgements: This work was supported by the Plovdiv University Scientific Fund (grant No SP19-009).

1. Experimental Procedure

1.1. Reagents and apparatus

Vanadium(V) solution (2×10^{-4} mol dm⁻³) was prepared by dissolving NH₄VO₃ (puriss. p.a., VEB Laborchemie Apolda, Germany) in water. Nickel(II) solution (2×10^{-4} mol dm⁻³) was prepared by dissolving NiSO₄·6H₂O (puriss. p.a., Sigma-Aldrich Chemie GmbH, Germany) in water. Copper(II) solution (2×10^{-4} mol dm⁻³) was prepared by dissolving CuSO₄·5H₂O (puriss. p.a., Sigma-Aldrich Chemie GmbH, Germany) in water.

TAO (95%, Sigma-Aldrich Chemie GmbH) was dissolved in the presence of KOH (1–2 pellets per 100 cm³); the obtained slightly alkaline aqueous solution (pH 8–9) was at concentration of 5.3×10^{-3} mol dm⁻³. Aliquat 336 was purchased from Sigma-Aldrich Chemie and dissolved in isobutanol (p. a. Merck).

2. Results and Discussion

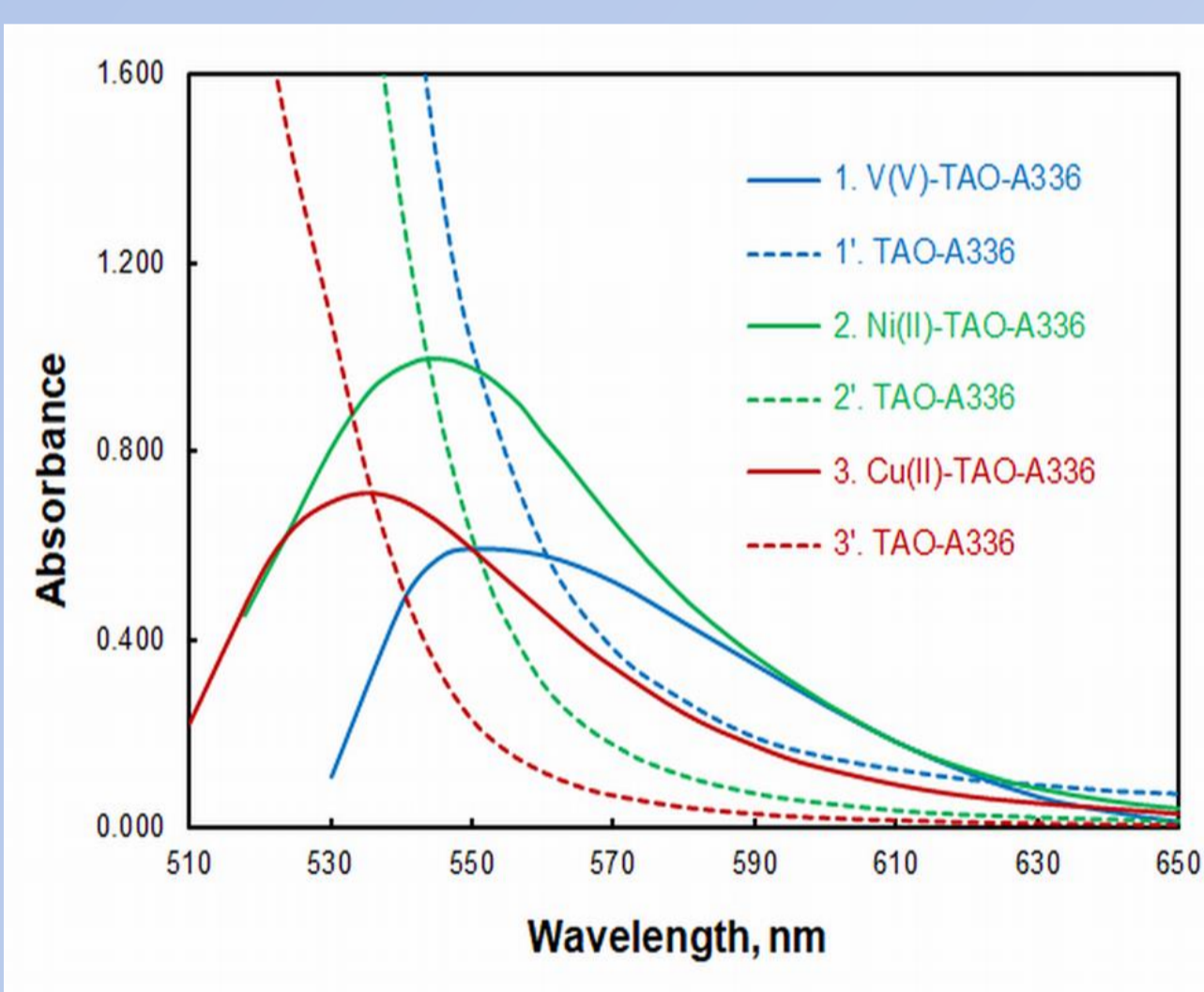


Figure 1. Spectra of the complexes (1–3) and blanks (1'–3') at the optimum conditions. $c_M = 2 \cdot 10^{-5}$ mol L⁻¹

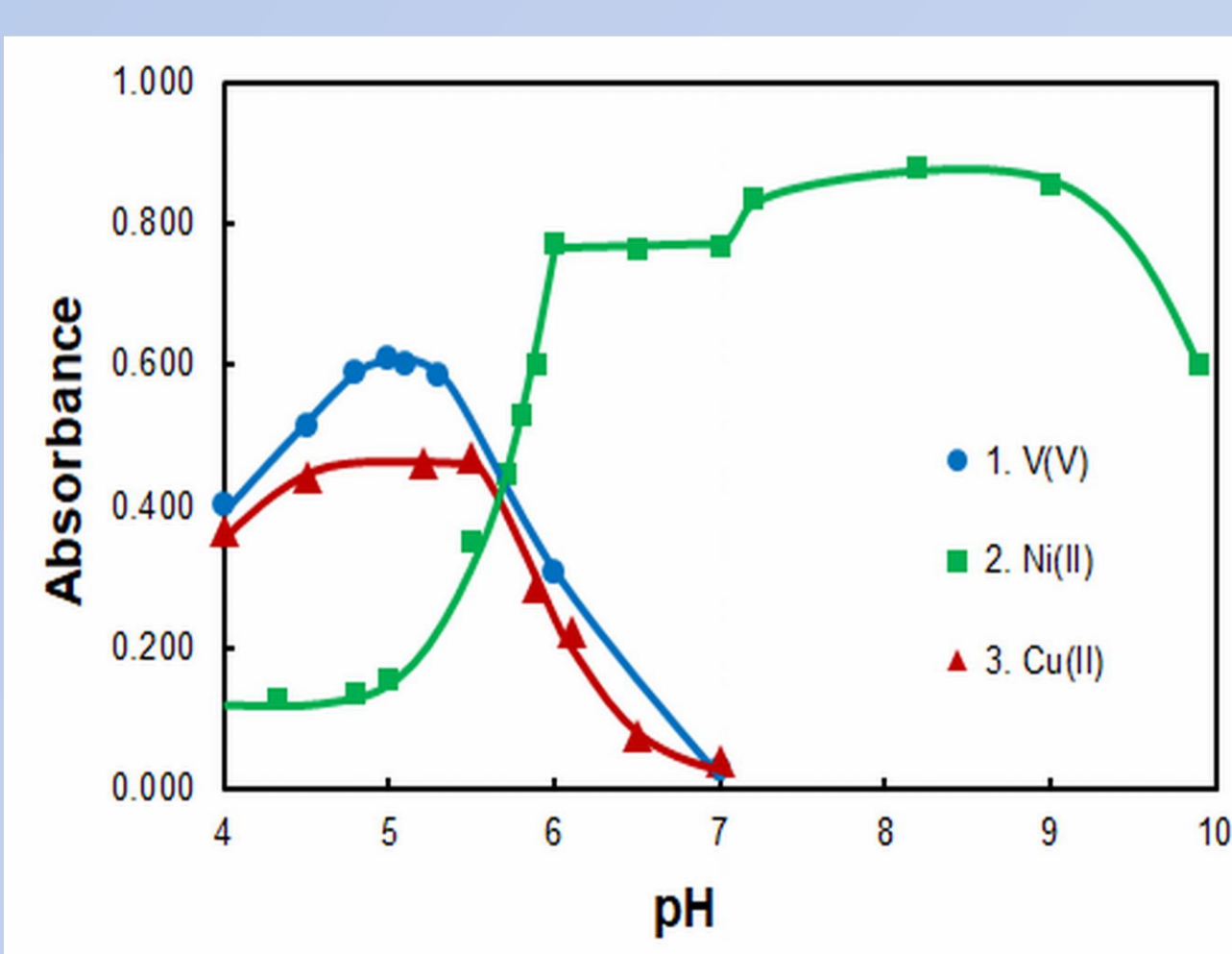


Figure 2. Effect of pH on the absorbance

Parameter	Value		
	V ^v	Ni ^{II}	Cu ^{II}
Wavelength, nm	547	545	535
pH	5.0	8.5	5.5
Concentration of TAO, mol L ⁻¹	1.6×10^{-3}	2.7×10^{-4}	1.6×10^{-4}
Concentration of Aliquat 336, mol L ⁻¹	1.3×10^{-2}	5.6×10^{-3}	6.0×10^{-2}
Extraction time, s	30	60	60

* The volumes of the aqueous phase and organic phase were 10 mL and 5 mL, respectively

Table 1. Optimum extraction-spectrophotometric conditions*

Analytical characteristics	Value		
	V ^v	Ni ^{II}	Cu ^{II}
Adherence to Beer's law, $\mu\text{g cm}^{-3}$	0.084 – 2.0	0.054 – 3.1	0.19 – 2.3
Linear regression equation	$A = 0.615y - 0.0067$	$A = 0.845y + 0.0064$	$A = 0.632y - 0.0093$
Squared correlation coefficient (R^2)	0.9994 (N = 9)	0.9993 (N = 9)	0.9976 (N = 11)
Molar absorptivity, L mol ⁻¹ cm ⁻¹	3.1×10^4	5.0×10^4	4.0×10^4
Sandell's sensitivity, $\mu\text{g cm}^{-2}$	1.6×10^{-3}	1.2×10^{-3}	1.6×10^{-3}
Limit of detection (LOD), $\mu\text{g cm}^{-3}$	0.025	0.016	0.056
Limit of quantification (LOQ), $\mu\text{g cm}^{-3}$	0.084	0.054	0.187
Fraction extracted, %	90.2	99.0	–
Coefficient of distribution (Log D)	0.97	2.0	–
Constant of extraction (Log K)	2.8	–	–

Table 2. Analytical characteristics

Extraction system	Determined composition (M : TAO : A336)	Suggested formula
V(V) – TAO – A336 – H ₂ O – isobutanol	1 : 1 : 1	(A336 ⁺)[VO ₂ (TAO)]
Ni(II) – TAO – A336 – H ₂ O – isobutanol	1 : 2 : 2	(A336 ⁺) ₂ [Ni(TAO) ₂]
Cu(II) – TAO – A336 – H ₂ O – isobutanol	1 : 2 : 1	(A336 ⁺)[Cu(TAO)(HTAO)]

Table 3. Ternary complexes extracted under the optimum conditions

3. Conclusions

1. V(V) is extracted in isobutanol as complex which can be represented by the formula (R₄N⁺)[VO₂(TAO²⁻)] with $\lambda_{\text{max}} = 547$ nm.
2. Nickel(II) is extracted as a ternary 1:2:2 ion-association complex, which can be represented by the formula (R₄N⁺)₂[Ni(TAO²⁻)₂] with $\lambda_{\text{max}} = 547$ nm.
3. Cu(II) is extracted as a 1:2:1 ion-association complex, represented by the formula (R₄N⁺)[Cu(TAO)(HTAO)] with $\lambda_{\text{max}} = 530$ nm.

4. Acknowledgment

This work was supported by the Research Fund of the Plovdiv University (Grant No SP19-HF009)

References

1. 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.
2. E. Papp, J. Inczedy, *Talanta* **1980**, *27*, 49–51. DOI: 10.1016/0039-9140(80)80011-7.
3. G. L. Lee, R. W. Cattrall, H. Daud, J. F. Smith, I. C. Hamilton, *Anal. Chim. Acta* **1981**, *123*, 213–220. DOI: 10.1016/S0003-2670(01)83173-1.
4. Y. Bal, K. E. Bal, G. Cote, A. Lallam, *Hydrometallurgy* **2004**, *75*, 123–134. DOI: 10.1016/j.hydromet.2004.07.004.
5. K. T. Stojnova, K. B. Gavazov, V. D. Lekova, *Acta Chim. Slov.* **2013**, *60*, 390–396.
6. K. B. Gavazov, G. K. Toncheva, V. B. Delchev, *Open Chem.* **2016**, *14*, 197–205. DOI: 10.1515/chem-2016-0022.
7. G. G. Shalamova, *Tr. Perm. Med. Inst.* **1972**, *108*, 48–53.
8. O. I. Karpova, V. V. Lukachina, A. T. Pilipenko, *Ukr. Khim. Zh.* **1973**, *39*, 194–195.
9. J. J. Arias, F. Jimenez, F. Garcia Montelongo, *An. Qulth., Ser. B* **1980**, *76*, 452–459.
10. L. Konermann, *J. Am. Soc. Mass Spectrom.* **2017**, *28*, 1827–1835. DOI: 10.1007/s13361-017-1739-3.
11. N. Menek, E. Eren, S. Topcu, *Dyes Pigm.* **2006**, *68*, 205–210. DOI: 10.1016/j.dyepig.2005.01.010.
12. K. Toei, *Anal. Sci.* **1987**, *3*, 479–488. DOI: 10.2116/analsci.3.479.
13. K. B. Gavazov, *Chemistry* **2013**, *22*, 222–253.