Scientific paper

Study on the Equilibria of the Complex Formation of Anionic Chelate of Zn(II) with Tridentate Ligand and the Cation of 3-(2-naphtyl)-2,5-diphenyl-2*H*-tetrazolium chloride

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Abstract

The equilibria of the complex formation between the anionic chelate of zinc(II) with the tridentate ligand of 4-(2-pyridylazo)-resorcinol (PAR) and the bulky organic tetrazolium cation of 3-(2-naphtyl)-2,5-diphenyl-2*H*-tetrazolium chloride (TV) in the liquid-liquid extraction system Zn(II)–PAR–TV–H_2O–2-methyl-1-propanol was studied by spectrophotometric method. The molar ratio of the reagents was determined by independent methods under the optimum condition for ion-association and for extraction. The validity of Beer's law was checked and some analytical characteristics were calculated. The constants, describing the association process in aqueous phase and the extraction equilibria, were calculated. Based on this, a reaction scheme, a general formula and a structural formula of the complex were suggested. The zinc(II) cation is six coordinated with the tridentate ligand through the following atoms: the azo nitrogen, the pyridine nitrogen and the oxygen atom from the phenolic group, which is in *ortho* position relative to the azo group, each of them forming two five-membered chelate rings.

Keywords: zinc(II); tridentate ligand; chelate formation; extraction equilibria

1. Introduction

The zinc is a typical transition, complex forming metal essential from biochemical point of view. It is an important trace element needed by plants,[1] animals,[2] and microorganisms.[3] In the human body the zinc content amounts to 2–4 g.[4] Zinc is the second most abundant metal in the human body[5] and is a cofactor for more than 300 enzymes involved in many processes, including the cellular respiration, immunity, DNA and protein synthesis, metabolism, cell division, etc.[6–10] It is known that zinc can be toxic when exposures exceed physiological needs. Negative health effects have been documented after short-term exposure to concentrations of zinc in water and beverages between 1.0 and 2.5 mg L^{-1}, e.g. poisoning incidents with symptoms of gastrointestinal distress, nausea and diarrhea.[11]

The zinc forms metal complexes with potential application in the fields of medicine, pharmacy, catalysis, photoluminescence, or as semiconductor materials.[12–16] Zinc(II) complexes with ligands, containing [S,S], [O,O], [N,O], [N,N] donor atoms, like 1,10-phenantroline, 2,2´-bipyridene,[17] 2-(2´-aminophenyl)benzothiazole,[18] *N*-benzoyl-glycine, *N*-acetyl amino acids and their amine adducts,[19] *N*-ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone,[20] tetraphenylporphyrin, *meso*-tetrakis(4-sulfophenyl)porphyrin,[21] 1-[(5-benzyl-1,3-thiazol-2-yl) diazenyl]naphthalene-2-ol,[22] 1-(2-pyridylazo)-2-naphthol,[23] Schiff bases[24], were synthesized and structurally characterized. Zinc(II) gives colored chelates with polyphenols and their functional derivatives, containing azo groups and two or more hydroxyl groups in *ortho* position relative to each other, such as 2-(*N*-acetylamino)-6-methylpyridine,[25] 8-hydroxyquinoline and its derivatives,[26] xylenol orange[27], methylthymol blue, 1-(2-pyridilazo)-2-naphtol, 2-(4,6-dimethyl-2-pyrimidylazo)-1-naphthol-4sulphonate sodium salt.[28]

Colored anionic chelates of zinc(II) can form ion-associated complexes with bulky organic cations, like tetra-

zolium salts. The structure and properties of tetrazolium salts determine their ability to form ion-associated complexes.[29,30] The bulky hydrophobic organic substituents in the molecules of the tetrazolium salts increase the extractability of the ion-associated complexes. The presence of a quaternary nitrogen atom in the molecules of the tetrazolium salts determines the ability to form ionic associates with chelates of metals in aqueous phase without protonation, as opposed to the amines. Tetrazolium salts are used as reagents for the preparation of various ion-associated complexes of metals, e.g. Ga(III), Co(II), Ge(IV), Mo(-VI).[29, 31–39]

The liquid-liquid extraction is a part of the chemistry of the solutions and the coordination compounds. It is applied to study the processes of complex formation and the extraction equilibria.[40–43] The extraction spectrophotometry is a relatively simple, convenient, sensitive, selective, rapid to perform and inexpensive method for preparation and characterization of new complex compounds as well as for their application in the chemical analysis.[44–49]

This present work aims to study the extraction equilibria for complex formation between the anionic chelate of Zn(II) with the tridentate ligand of 4-(2-pyridylazo)-resorcinol (PAR) and the cation of 3-(2-naphthyl)-2,5-diphenyl-2*H*-tetrazolium chloride (TV) in the liquid-liquid system Zn(II)–PAR–TV–H_2O–*i*-BuOH by spectrophotometric method. The selected organic solvent *i*-BuOH is characterized by a low volatility and toxicity, it is readily biodegradable and non-bioaccumulative, and can be produced from renewable resources.[50,51] The final goal was to evaluate the possible applications of the system for the determination of the traces of zinc(II) in biological, medical, and pharmaceutical samples.

2. Experimental

2. 1. Reagents and Apparatus

Zinc(II) chloride, anhydrous ($ZnCl_2$) (Alfa Aesar, 98%): an aqueous 1.53×10^{-2} mol L^{-1} solution was prepared. 4-(2-Pyridyazo)-resorcinol (PAR) (Sigma–Aldrich, 96%): PAR was dissolved in slightly alkaline distilled water to give a 2.0×10^{-3} mol L^{-1} solution. 3-(2-Naphtyl)-2,5-diphenyl-2*H*-tetrazolium chloride (Tetrazolium Violet, TV) (Loba Feinchemie, p. a.): an aqueous 3.0×10^{-3} mol L^{-1} solution was prepared. The alkalinity of the aqueous medium was determined using an aqueous sodium hydroxide solution. As organic solvent 2-methyl-1-propanol (isobutyl alcohol, i-BuOH) (Chempur, p.a.) was used. The pH was checked by HI 83140 pH meter (Romania). A Camspes M 508 spectrophotometer (United Kingdom), equipped with 10 mm path length cells, was employed for reading of the absorbance.

2. 2. Procedure for Establishment of the Optimum Conditions for Chelate Formation and Ion-association

Aliquots of the solutions of Zn(II), PAR, TV and sodium hydroxide (pH = 7.0–10.0) were filled into 100 mL separatory funnels. The resulting solutions were diluted with distilled water to a total volume of 10 mL. Then 10 mL of isobutyl alcohol was added and the funnels were shaken for a fixed time (up 180 s). A portion of the organic extract was filtered through a filter paper into a cell. The absorbance was read against a blank sample, which was prepared in the same manner, but in the absence of zinc(II).[39]

3. Results and Discussion

3. 1. Optimum Conditions for Chelate Formation and Ion-association

The absorption spectra of the extract of ion-associated complex, formed between the orange-colored anionic chelate of zinc(II) with 4-(2-pyridyazo)-resorcinol and the cation of the tetrazolium salt, and the blank sample, containing 4-(2-pyridyazo)-resorcinol and 3-(2-naphtyl)-2,5-diphenyl-2*H*-tetrazolium chloride, are shown in Figure 1. The absorption maximum of the complex appears in the visible range at 510 nm, where the blank sample absorbs insignificantly. The maximum and constant extraction of the ion-associated complex is achieved in the pH range from 7.0 to 10.0 and aqueous sodium hydroxide solution was used in all further experiments. The extraction equilibrium of the ion-associated complex is established for shaking time not less than 90 s and for this reason the experiments were performed for 2 min. To

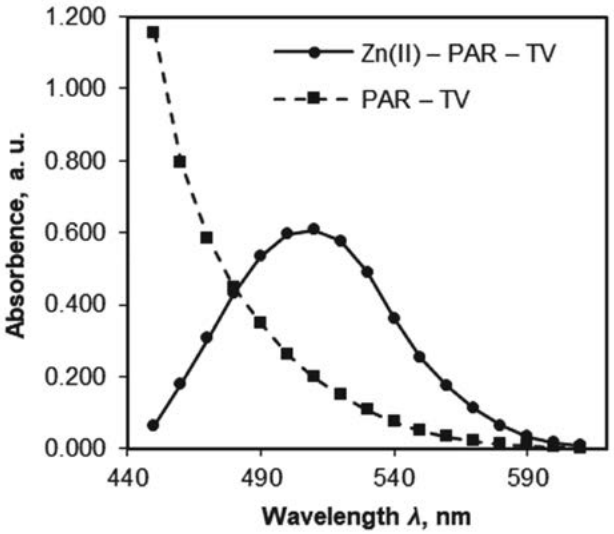


Figure 1. Absorption spectra of the complex of Zn-PAR-TV and the bank sample PAR-TV in *i*-BuOH; $C_{Zn(II)} = 1.53\times10^{-5}$ mol L^{-1}; $C_{PAR} = 2.0\times10^{-4}$ mol L^{-1}; $C_{TV} = 3.0\times10^{-4}$ mol L^{-1}, $\tau = 2$ min

determine the influence of the concentration of reagents on the extraction equilibrium, the fold excess of the reagents was calculated. The chelate formation of Zn(II)-PAR requires 13.7-fold excess of PAR ($C_{PAR} \geq 1.8 \times 10^{-4}$ mol L^{-1}) and 19.61-fold excess of TV ($C_{TV} \geq 2.7 \times 10^{-4}$ mol L^{-1}) for maximum association and extraction.

The optimum experimental conditions for the chelate formation and extraction of the ion-associated complex are summarized in Table 1, column 1.

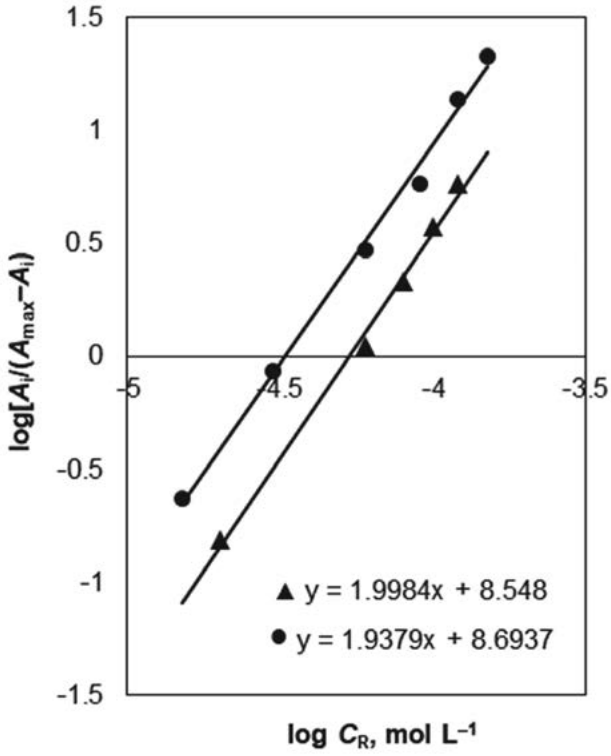
3. 2. Beer's Law, Molar Absorptivity and Other Analytical Characteristics

The linear relationship between the zinc(II) concentration ($C_{Zn(II)}$, μg mL^{-1}) in the aqueous phase and the absorbance of the ion-associated complex in the organic phase after extraction was studied using regression analysis under the optimum conditions for complex formation. The range of obedience to Beer's Law, i.e. the linearity, is observed for concentration up to 2.80 μg mL^{-1} Zn(II). The equation of a straight line was found to be Y = 0.6102 X + 0.0013 with a correlation coefficient squared 0.9999. Further analytical characteristics, such as apparent molar absorptivity ε´, Sandell's sensitivity, limit of detection and limit of quantification, are shown in Table 1, column 2.

On the basis of the analytical characteristics of the extraction system Zn(II)–PAR–H_2O–*i*-BuOH, it can be concluded that the ion-associate formed between the anionic chelate of Zn(II)-PAR and the tetrazolium cation allows determination of Zn(II) with a high sensitivity.

3. 3. Molar Ratios of the Ion-associated Complex, Reaction Scheme and Suggested General Formula

The molar ratios of the components of the ion-associated complex were determined by three independent methods: the mobile equilibrium method, the straight-line method of Asmus and the method of continuous variations.[52] The results from the application of the mobile equilibrium method to prove the molar ratios Zn(II):PAR and Zn(II):TV are presented in Figure 2.



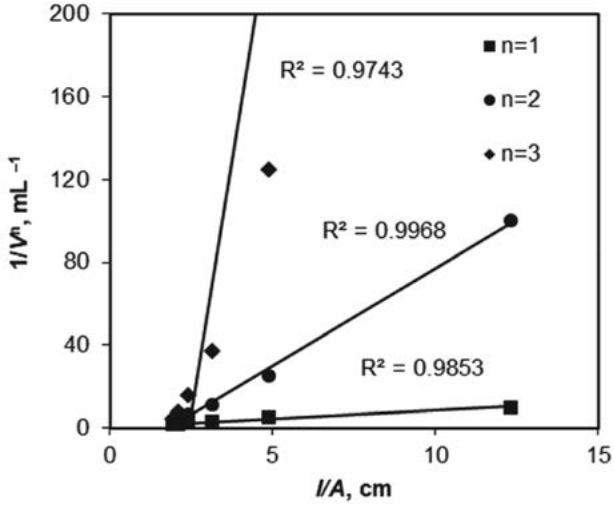
Figures 2. Straight line by the mobile equilibrium method for determination of the molar ratio Zn(II):PAR and Zn(II):TV; $C_{Zn(II)} = 1.53 \times 10^{-5}$ mol L^{-1}; λ = 510 nm; τ = 2 min; ▲ Zn(II):PAR; $C_{TV} = 3.0 \times 10^{-4}$ mol L^{-1}; • Zn(II):TV; $C_{PAR} = 2.0 \times 10^{-4}$ mol L^{-1}

The results from the application of the straight-line method of Asmus to prove the molar ratios Zn(II):PAR and Zn(II):TV are shown in Figure 3 and Figure 4, respectively.

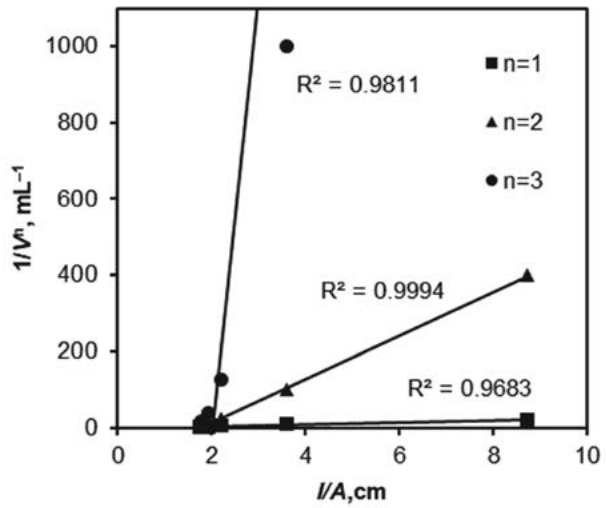
The results from the application of the mobile equilibrium method and the straight-line method of Asmus reveal that the molar ratio for chelate formation between

Table 1. Optimum extraction-spectrophotometric conditions and analytical characteristics of the system Zn(II)–PAR–H_2O–*i*-BuOH

Optimum Conditions	Analytical Characteristic
Absorption maximum (λ_{max}) 510 nm	Apparent molar absorptivity (ε´) $(3.94 \pm 0.06) \times 10^4$ L $mol^{-1}cm^{-1}$
Volume of the aqueous phase 10 cm^3	True molar absorptivity (ε) $(3.86 \pm 0.06) \times 10^4$ L $mol^{-1}cm^{-1}$
Volume of the organic phase 10 cm^3	Sandell's sensitivity (SS) 1.66 ng cm^{-2}
pH of the aqueous phase 7.0 ÷10.0	Adherence to Beer's law up to 2.80 μg cm^{-3}
Shaking time (τ) 2 min	Relative standard deviation (RSD) 1.66%
Concentration of PAR $\geq 1.8 \times 10^{-4}$ mol L^{-1}	Limit of detection (LOD) 0.04 μg cm^{-3}
Concentration of TV $\geq 2.7 \times 10^{-5}$ mol L^{-1}	Limit of quantification (LOQ) 0.13 μg cm^{-3}



Figures 3. Determination of molar ratio (n) Zn(II):PAR by the method of Asmus; $C_{Zn(II)} = 1.53 \times 10^{-5}$ mol L^{-1}; $C_{TV} = 3.0 \times 10^{-4}$ mol L^{-1}; λ = 510 nm; τ = 2 min



Figures 4. Determination of molar ratio (n) Zn(II):TV by the method of Asmus; $C_{Zn(II)} = 1.53 \times 10^{-5}$ mol L^{-1}; $C_{PAR} = 2.0 \times 10^{-4}$ mol L^{-1}; λ = 510 nm; τ = 2 min

Zn(II) and PAR is 1:2 and the ion-associated complex Zn(II)–PAR–TV is formed in the molar ratio 1:2:2, respectively.

The application of the method of continuous variations confirmed the molar ratio Zn(II):TV = 1:2 (Figure 5).

Zincates containing $[Zn(OH)_3]^-$, $[Zn(OH)_4]^{2-}$, $[Zn(OH)_3(H_2O)]^-$, $[Zn(OH)_6]^{4-}$ $[Zn(OH)_4(H_2O)_2]^{2-}$ in alkaline solutions are already described in the literature.[53,54] In the pH range from 1.5 to 6.5, functional azo derivatives of polyphenols, such as TAR or PAR are presented in a molecular form (H_2R). The deprotonation (HR^-) starts at pH = 4.0, while a complete deprotonation (R^{2-}) is achieved in the alkaline range (pH >11).[33]

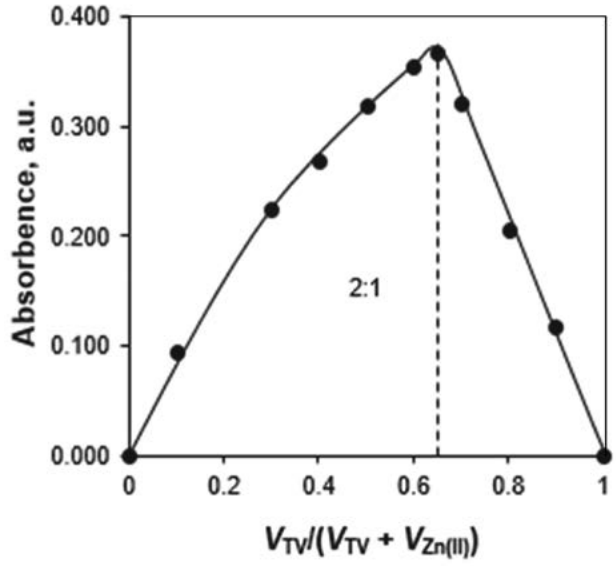


Figure 5. Determination of the molar ratio (*n*) Zn(II):TV by the method of continuous variations $C_{Zn(II)} + C_{TV} = 3.06 \times 10^{-5}$ mol L^{-1}; $C_{PAR} = 2.0 \times 10^{-4}$ mol L^{-1}; λ = 510 nm; τ = 2 min

The carried out experiments showed that the complex formation and the extraction of the ion-associated complex have occurred in the pH range from 7.0 to 10.0. Under these conditions, an equilibrium between the monoprotonated form (HR^-) and the deprotonated form (R^{2-}) exists in the solution. Therefore, the complex formation of anionic chelate of zinc(II) with 4-(2-pyridyazo)-resorcinol ($C_{11}H_9N_3O_2$) can be given by equation (1):

$$[Zn(OH)_4(H_2O)_2]^{2-}(aq) + [C_{11}H_7N_3(OH)O]^-(aq) + [C_{11}H_7N_3O_2]^{2-}(aq) \rightarrow [Zn(C_{11}H_7N_3O_2)_2]^{2-}(aq) + 3OH^- + 3H_2O \quad (1)$$

The formation of the ion-associate in aqueous phase, its distribution between the aqueous and the organic phases and its extraction in *i*-BuOH can be given the following equations (2–4):

$$[Zn(C_{11}H_7N_3O_2)_2]^{2-}(aq) + 2(TV^+)(aq) \leftrightharpoons \{(TV)_2[Zn(C_{11}H_7N_3O_2)_2]\}(aq) \quad (2)$$

$$\{(TV)_2[Zn(C_{11}H_7N_3O_2)_2]\}(aq) \leftrightharpoons \{(TV)_2[Zn(C_{11}H_7N_3O_2)_2]\}(org) \quad (3)$$

$$2(TV)^+(aq) + [Zn(C_{11}H_7N_3O_2)_2]^{2-}(aq) \leftrightharpoons \{(TV)_2[Zn(C_{11}H_7N_3O_2)_2]\}(org) \quad (4)$$

Therefore, the ion-associated complex formed between the anionic chelate $[Zn(C_{11}H_7N_3O_2)_2]^{2-}$ and the cation of monotetrazolium salt can be represented by the general formula $(TV)_2[Zn(C_{11}H_7N_3O_2)_2]$.

3. 4. Equilibrium Constants, True Molar Absorptivity, Recovery Factor and Suggested Structural Formula of the Ion-associated Complex

The association process in aqueous phase and the extraction equilibria were investigated and quantitatively characterized with respect to the following key constants: association constant β, distribution constant K_D and extraction constant K_{ex}, as well as the recovery factor *R*%.

The ion-association in the aqueous phase between the anionic chelate $[Zn(C_{11}H_7N_3O_2)_2]^{2-}$ and the tetrazolium cation $(TV)^+$ is given with the association constant (β) by the equation (5):

$$\beta = \{(TV)_2[Zn(C_{11}H_7N_3O_2)_2]\}(aq) / \{\{TV^+\}^2(aq) \times \{[Zn(C_{11}H_7N_3O_2)_2]^{2-}\}(aq)\} \quad (5)$$

The association constant β was determined by two independent methods: Komar–Tolmachev method[52] and Holme–Langmyhr method[55] and the obtained values (logβ) are given in Table 2, column 2.

The association constant β was calculated by the equation (6)[52]:

$$\beta = (l/n)^n / [\varepsilon (tg\ \alpha)^{n+1}] \quad (6)$$

where l *is* the cuvette thickness (l = 1 cm); n is the molar ratio between the components independently determined (e.g. by the mobile equilibrium method, the straight-line method of Asmus or the method of continuous variations) (n = 2); ε is the true molar absorptivity.

The true molar absorptivity ε was determined by the method of Komar-Tolmachev from the equation of a straight line Y = 0.3879 X + 2.5940; $\varepsilon = 1/(2.594\times10^{-5})$ L mol^{-1} cm^{-1} (Figure 6).

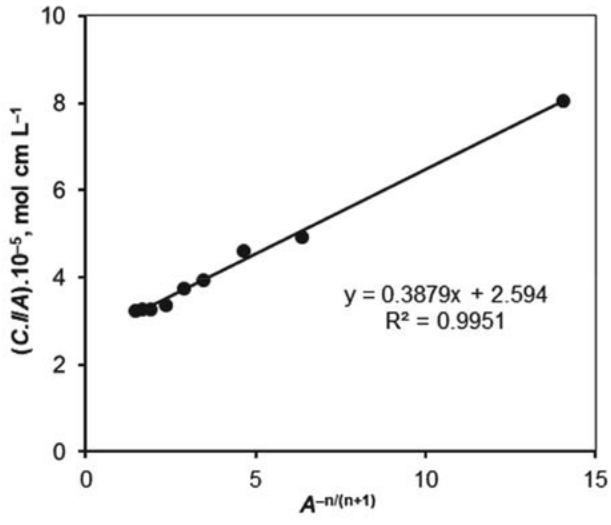


Figure 6. Dependency of $(C\times l / A)$ on $A^{-n/(n+1)}$ (method of Komar–Tolmachev); $C_{Zn(II)} = 2C_{TV} = C$, mol L^{-1}; $C_{PAR} = 2.0\times10^{-4}$ mol L^{-1}; *A* – absorbance; *l* – cell thickness, *l* = 1 cm; *n* = 2; λ = 510 nm; τ = 2 min

The distribution of the ion-associated complex between the aqueous and the organic phase is given by the distribution constant K_D of the equation (7):

$$K_D = \{(TV)_2[Zn(C_{11}H_7N_3O_2)_2]\}(org) / \{(TV)_2[Zn(C_{11}H_7N_3O_2)_2]\}(aq) \quad (7)$$

The distribution constant K_D was calculated by the equation (8):

$$K_D = A_1/(A_3 - A_1) \quad (8)$$

where A_1 is the light absorbance obtained after a single extraction at the optimum conditions; A_3 is the absorbance obtained after a triple extraction under the same conditions.[56]

The recovery factor was determined by the equation (9):

$$R\% = 100\ K_D / (K_D + 1) \quad (9)$$

The extraction equilibrium of the ion-associate between the aqueous and the organic phases is given by the extraction constant K_D for the equation (10)

$$K_{ex} = \{(TV)_2[Zn(C_{11}H_7N_3O_2)_2]\}(org) / \{\{TV^+\}^2(aq)\times\{[Zn(C_{11}H_7N_3O_2)_2]^{2-}\}(aq)\} \quad (10)$$

The extraction constant K_{ex} was calculated by two independent methods:

(i) from the equation $\log K_{ex} = \log K_D + \log \beta$ (11)

where β was calculated by the method of Komar–Tolmachev.[52]

(ii) by the method of Likussar-Boltz:[57]

The method of Likussar-Boltz uses the data from the method of continuous variations (Figure 5). The extraction constant K_{ex} was calculated by the equation of Likussar-Boltz for molar ratio 1:2 (equation 12):

$$\log K_{ex} = 0.3522 - 2 \log K + \log Y_{max} - 3 \log (1 - Y_{max}) \quad (12)$$

where K is the total concentration of reagents ($K = C_{Zn(II)} + C_{TV} = 3.06 \times 10^{-5}$ mol L^{-1}); Y_{max} and $(1–Y_{max})$ are determined from the additionally plotted normalized absorption curve (Y_{max} = 0.8852; $(1 - Y_{max}) = 0.1148$).

The values of the equilibrium constants and the recovery factor, obtained by the independent methods, are statistically similar (Table 2). They indicate that the ion-associated complex, formed between the anionic chelate Zn(II) and the tridentate ligand (PAR) in the presence of the bulky organic cation of the tetrazolium salt, is characterized by sufficiently high stability and good extractability. Therefore, the ion-associated complex Zn(II)–PAR–TV

Table 2. Values of the equilibrium constants and the recovery factor

Equilibrium Constant and Recovery Factor	Value
Equilibrium (equation 2)-Association constant β	
$\beta = \{(TV)_2[Zn(C_{11}H_7N_3O_2)_2]\}(aq) / \{\{TV^+\}^2(aq) \times \{[Zn(C_{11}H_7N_3O_2)_2]^{2-}\}(aq)\}$	$\log\beta = (11.05 \pm 1.08)$[a]
	$\log\beta = (11.04 \pm 0.95)$[b]
Equilibrium (equation 3) - Distribution constant K_D	
$K_D = \{(TV)_2[Zn(C_{11}H_7N_3O_2)_2]\}(org) / \{(TV)_2[Zn(C_{11}H_7N_3O_2)_2]\}(aq)$	$\log K_D = (1.32 \pm 0.01)$[c]
Equilibrium (equation 4)-Extraction constant K_{ex}	
$K_{ex} = \{(TV)_2[Zn(C_{11}H_7N_3O_2)_2]\}(org) /\{\{TV^+\}^2(aq) \times \{[Zn(C_{11}H_7N_3O_2)_2]^{2-}\}(aq)\}$	$\log K_{ex} = (12.37 \pm 1.09)$[d]
	$\log K_{ex} = (12.15 \pm 0.10)$[e]
Recovery factor, R%	$R = (95.48 \pm 0.01)\%$[f]

[a] Calculated by Komar-Tolmachev method (equation 6); [b] Calculated by Holme-Langmyhr method;[55] [c] Calculated by equation 8; [d] Calculated by equation 11, where β is determined by the Komar-Tolmachev method; [e] Calculated by Likussar-Boltz method (equation 12); [f] Calculated by equation 9.

can be successfully applied for determination of zinc(II) in alloys, medical, biological and pharmaceutical samples.

The results obtained by the independent methods, confirm the proposed reaction scheme of the process of chelate formation of the ion-associate in the aqueous phase, its distribution between the aqueous and the organic phases and its extraction into *i*-BuOH (equations 1-4). Based on this, the proposed structural formula of the ion-associated complex is represented in Figure 7. The zinc(II) cation is six coordinated with the tridentate ligand through the following atoms: the azo nitrogen, the pyridine nitrogen and the oxygen atom from the phenolic group, which is in *ortho* position relative to the azo group, each of them forming two five-membered chelate rings.

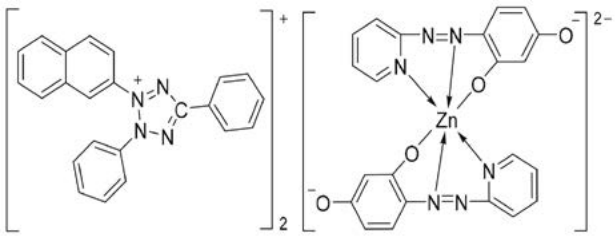


Figure 7. Structural formula of the ion-associated complex Zn(II)-PAR-TV

4. Conclusion

The equilibria of the complex formation between the orange-colored anionic chelate of zinc(II) with the tridentate ligand of 4-(2-pyridylazo)resorcinol (PAR) and the bulky organic tetrazolium cation of 3-(2-naphtyl)-2,5-diphenyl-2H-tetrazolium chloride (TV) in the liquid-liquid extraction system Zn(II)-PAR-TV-H_2O-*i*-BuOH was studied by spectrophotometric method. The optimum conditions for the ion-association in aqueous phase and for the extraction of the ion-associated complex Zn(II)-PAR-TV into *i*-BuOH were established. The validity of Beer's law was checked and some analytical characteristics were calculated: the apparent molar absorptivity (ε′), the true molar absorptivity (ε), the limit of detection (LOD), the limit of quantification (LOQ) and the Sandell's sensitivity (SS). From the analytical characteristics of the extraction system Zn(II)-PAR-TV-H_2O-*i*-BuOH, it can be concluded that the ion-associate, formed between the anionic chelate of Zn(II)-PAR and the tetrazolium cation, allows determinations of Zn(II) with a high sensitivity. The following key constants, needed for the quantitative assessment of the association process in aqueous phase and the extraction equilibria, were also calculated: the association constant (β), the distribution constant (K_D), the extraction constant (*Kex*), as well as the recovery factor (*R*). The molar ration of the reagents, determined by independent methods, showed that the ion-associated complex can be represented with the general formula $(TV)_2[Zn(C_{11}H_7N_3O_2)_2]$, which corresponds to the suggested reaction scheme. A structural formula of the complex also was proposed. The zinc(II) cation is six coordinated with the tridentate ligand through the following atoms: the azo nitrogen, the pyridine nitrogen and the oxygen atom from the phenolic group, which is in *ortho* position relative to the azo group, each of them forming two five-membered chelate rings.

5. References

1. M. R. Broadley, P. J. White, J. P. Hammond, I. Zelko, A. Lux, *New Phytol.* **2007**, *173*, 677–702. **DOI:**10.1111/j.1469-8137.2007.01996.x
2. A. S. Prasad, *Mol. Med.* **2008**, *14*, 353–357. **DOI:**10.2119/2008-00033.Prasad
3. B. Sugarman, *Rev. Infect. Dis.* **1983**, *5*, 137–147. **DOI:**10.1093/clinids/5.1.137
4. L. Rink, Ph. Gabriel, *P. Nutr. Soc.* **2000**, *59*, 541–552. **DOI:**10.1017/S0029665100000781
5. K. A. Mccall, C. Huang, C. A. Fierke, *J. Nutr.* **2000**, *130*, 1437S–1446S. **DOI:**10.1093/jn/130.5.1437S

6. M. Jarosz, M. Olbert, G. Wyszogrodzka, K. Młyniec, T. Librowski, *Inflammopharmacol* **2017**, *25*, 11–24. **DOI:**10.1007/s10787-017-0309-4
7. P. Bonaventura, G. Benedetti, F. Albarède, P. Miossec, *Autoimmun. Rev*. **2015**, *14*, 277–285. **DOI:**10.1016/j.autrev.2014.11.008
8. P.-H. Lin, M. Sermersheim, H. Li, P. H. U. Lee, S. M. Steinberg, J. Ma, *Nutrients* **2018**, *10*, 16. **DOI:**10.3390/nu10010016
9. L. Rochette, S. Ghibu, *J. Mol. Sci*. **2021**, *22*, 7979. **DOI:**10.3390/ijms22157979
10. L. L. Rus, A. M. Juncan, V. I. Craciun, A. Frum, S.-C. Heghes, A. Butuca, C. M. Dobrea, A. A. Chis, A. C. Muntean, A. L. Vonica-Tincu, C. Morgovan, *Appl. Sci*. **2022**, *12*, 4476. **DOI:**10.3390/app12094476
11. M. Hernick, C. A. Fierke, *Arch. Biochem. Biophys*. **2005**, *443*, 71–84. **DOI:**10.1016/j.abb.2004.08.006
12. W. H. Zhao, V. Ferro, M. V. Baker, *Coord. Chem. Rev.* **2017**, *339*, 1–16. **DOI:**10.1016/j.ccr.2017.03.005
13. M. Hu, X. Z. Ai, Z. M. Wang, Z. J. Zhang, H. L. Chong, W. M. Zhang, J. Lin, H. H. Yang, B. G. Xing, *Nano Res.* **2018**, *11*, 5474–5498. **DOI:**10.1007/s12274-018-2138-1
14. H. J. Chen, G. Y. Lyu, Y. F. Yue, T. W. Wang, D. P. Li, H. Shi, J. N. Xing, J. Y. Shao, R. Zhang, J. Liu, *J. Mater. Chem. C*. **2019**, *7*, 7249–7258. **DOI:**10.1039/C9TC01520E
15. L. H. Abdel-Rahman, A. M. Abu-Dief, R. M. Shehata, F. M. Atlam, *Appl. Organomet. Chem.* **2019**, *33*, E4699–4700. **DOI:**10.1002/aoc.4699
16. X.-G. Yi, X.-N. Fang, J. Guo, J. Li, Z.-P. Xie, *Acta Chim. Slov.* **2020**, *67*, 507–515. **DOI:**10.17344/acsi.2019.5532
17. E. A. Ermakova, J. A. Golubeva, K. S. Smirnova, L. S. Klyushova, I. V. Eltsov, A. A. Zubenko, L. N. Fetisov, A. E. Svyatogorova, E. V. Lider, *Polyhedron* **2023**, *230*, 116213. **DOI:**10.1016/j.poly.2022.116213
18. T. S. Sukhikh, D. S. Kolybalov, E. K. Pylova, S. N. Konchenko, *Inorganics* **2022**, *10*, 138. **DOI:**10.3390/inorganics10090138
19. A. B. Corradi, *Coord. Chem. Rev.* **1992**, *117*, 45–98. **DOI:**10.1016/0010-8545(92)80020-R
20. K. J. Reddy, J. R. Kumar, C. Ramachandraiah, T. Thriveni, A. V. Reddy, *Food Chem*. **2007**, *101*, 585–591. **DOI:**10.1016/j.foodchem.2006.02.018
21. M. Biesaga, K. Pyrzynska, M. Trojanowicz, *Talanta* **2000**, *51*, 209–224. **DOI:**10.1016/S0039-9140(99)00291-X
22. M. Fizer, V. Sidey, A. Tupys, Y. Ostapiuk, O. Tymoshuk, Y. Bazel, *J. Mol. Struct*. **2017**, *1149*, 669e682. **DOI:**10.1016/j.molstruc.2017.08.037
23. G. Supriyanto, J. Simon, *Talanta* **2005**, *68*, 318–322. **DOI:**10.1016/j.talanta.2005.08.052
24. H. Keypour, F. Forouzandeh, S. Salehzadeh, F. Hajibabaei, S. Feizi, R. Karamian, N. Ghiasi, R. W. Gable, *Polyhedron* **2019**, *170*, 584–592. **DOI:**10.1016/j.poly.2019.06.023
25. A. S. Berezin, O. V. Antonova, E. V. Lider, A. I. Smolentsev, V. A. Nadolinny, M. S. Mel'gunov, *J. Lumin*. **2017**, *190*, 261–266. **DOI:**10.1016/j.jlumin.2017.05.024
26. D. N. Konshina, I. A. Lupanova, S. E. Efimenko, V. V. Konshin, *Solvent Extr. Ion Exch*. **2022**, *40*, 236–250. **DOI:**10.1080/07366299.2021.1910271
27. M. Benamor, K. Belhamel, M. T. Draa, *J. Pharmaceut. Biomed*. **2000**, *23*, 1033–1038. **DOI:**10.1016/S0731-7085(00)00366-6
28. I. Singh, *Indian J. Chem*. **2000**, *39A*, 545–547. http://nopr.niscpr.res.in/handle/123456789/21128
29. K. Gavazov, A. Dimitrov, V. Lekova, *Russ. Chem. Rev*. **2007**, *76*, 169–179. **DOI:**10.1070/RC2007v076n02ABEH003655
30. H. Şenöz, *Hacettepe J. Biol. & Chem*. **2012**, *40*, 293–301.
31. K. Stojnova, K. Gavazov, V. Lekova, *Acta Chim. Slov.* **2013**, *60*, 390–396.
32. K. T. Stojnova, V. V. Divarova, P. V. Racheva, V. D. Lekova, *J. Appl. Spectrosc.* **2015**, *82*, 853–856. **DOI:**10.1007/s10812-015-0193-x
33. V. Divarova, K. Stojnova, P. Racheva, V. Lekova, *Acta Chim. Slov.* **2016**, *63*, 97–103 **DOI:**10.17344/acsi.2015.1987
34. V. Divarova, K. Stojnova, P. Racheva, V. Lekova, *Russ. J. Inorg. Chem*. **2018,** *63,* 974–977. **DOI:**10.1134/S0036023618070057
35. P. Racheva, K. Stojnova, V. Divarova, V. Lekova, *Acta Chim. Slov.* **2017**, *64*, 365–372. **DOI:**10.17344/acsi.2017.3214
36. K. Stojnova, V. Lekova, *Acta Chim. Slov.* **2019**, *66*, 360–366. **DOI:**10.17344/acsi.2018.4862
37. K. Stojnova, V. Divarova, P. Racheva, K. Bozhinova, V. Lekova, *Acta Chim. Slov.* **2016**, *63*, 654–660. **DOI:**10.17344/acsi.2016.2513
38. K. Stojnova, V. Divarova, P. Racheva, K. Bozhinova, V. Lekova, *Acta Chim. Slov.* **2018**, *65*, 213–220. **DOI:**10.17344/acsi.2017.3860
39. K. Stojnova, P. Racheva, V. Divarova, P. Yanev, V. Lekova, *Acta Chim. Slov.* **2020**, *67*, 594–601. **DOI:**10.17344/acsi.2019.5612
40. A. N. Turanov, V. K. Karandashev, O. I. Artyushin, E. V. Sharova, *Solvent Extr. Ion Exch*. **2015**, *33*, 540–553. **DOI:**10.1080/07366299.2015.1067052
41. A. N. Turanov, V. K. Karandashev, V. E. Baulin, E. V. Kirillov, S. V. Kirillov, V. N. Rychkov, A. Yu. Tsivadze, *Russ. J. Inorg. Chem*. **2016**, *61*, 1335–1338. **DOI:**10.1134/S0036023616100211
42. G. Kristian: Analytical Chemistry, BINOM, Moscow, Russia, **2009,** pp. 113–121.
43. A. N. Turanov, V. K. Karandashev, V. E. Baulin, D. V. Baulin, A. Y. Tsivadze, *Acta Chim. Slov*. **2020**, *67*, 246–252. **DOI:**10.17344/acsi.2019.5380
44. A. K. Babko, A. T. Pilipenko: Photometric Analysis, Khimiya, Moscow, Russia, **1968,** pp. 159–164.
45. V. V. Divarova, K. T. Stojnova P. V. Racheva, V. D. Lekova, *J. Appl. Spectrosc.* **2017,** *84,* 231–236. **DOI:**10.1007/s10812-017-0456-9
46. P. V. Racheva, D. G. Hristov, K. B. Gavazov, *Russ. J. Gen. Chem*. **2020**, *90*, 1351–1356. **DOI:**10.1134/S1070363220070245
47. D. Tomov, G. Bocheva, V. Divarova, L. Kasabova, D. Svinarov, *J. Med. Biochem*. **2021**, *40*, 10–16. **DOI:**10.5937/jomb0-24746
48. P. V. Racheva, N. P. Milcheva, F. Genc, K. B. Gavazov, *Spectrochim. Acta A* **2021**, *262*, 120106. **DOI:**10.1016/j.saa.2021.120106
49. D. G. Hristov, V. V. Divarova, R. D. Mancheva, K. B. Gavazov, *Russ. J. Gen. Chem*. **2019**, *89*, 2136–2142.

DOI:10.1134/S1070363219100232
50. A. Pal, V. Manish, S. Gupta, N. Kumar, *SAE Tech. Pap*. **2013**, *2013-24-0151*. **DOI:**10.4271/2013-24-0151
51. G. K. Toncheva, D. G. Hristov, N. P. Milcheva, K. B. Gavazov, *Acta Chim. Slov.* **2020,** *67,* 151–158. **DOI:**10.17344/acsi.2019.5299
52. M. I. Bulatov, I. P. Kalinkin: Practical Handbook on Photometric Methods of Analysis, Khimiya, Leningrad, Russia, **1986**, pp. 174–264.
53. F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann: Advanced Inorganic Chemistry, Wiley Publishers, New Jersey, **1999**, pp. 599–606.
54. H. Remy: Inorganic chemistry, Mir, Moscow, Russia, **1966**, pp. 464–476.
55. A. Holme, F. J. Langmyhr, *Anal. Chim. Acta* **1966**, *36*, 383–391. **DOI:**10.1016/0003-2670(66)80066-1
56. K. T. Stojnova, V. D. Lekova, *Russ. J. Inorg. Chem*. **2019**, *64*, 1235–1241. **DOI:**10.1134/S0036023619100152
57. W. Likussar, D. F. Boltz, *Anal. Chem.* **1971**, *43*, 1265–1272. **DOI:**10.1021/ac60304a006

Povzetek

S spektrofotometričnimi metodami smo raziskali ravnotežno reakcijo tvorbe kompleksa med anionskim kelatom zgrajen iz cinka(II) in tridentatnega liganda 4-(2-piridilazo)-resorcinolom (PAR) in organskim tetrazolijevim kationom 3-(2-naftil)-2,5-difenil-2H-tetrazolijevim kloridom (TV) v tekoče-tekoče ekstrakcijskem sistemu Zn(II)-PAR-TV-H_2O-2-metil-1-propanol. Molsko razmerje reagentov je bilo določeno z neodvisnimi metodami pri optimalnih pogojih za ionsko asociacijo in ekstrakcijo. Preverili smo veljavnost Beerovega zakona in izračunali nekatere analizne značilnosti. Izračunane so bile konstante, ki opisujejo proces asociacije v vodni fazi in ekstrakcijsko ravnotežje. Na podlagi tega so bili predlagani reakcijska shema, splošna formula in strukturna formula kompleksa. Cinkov(II) kation je šestvezno koordiniran s tridentatnim ligandom prek naslednjih atomov: azo dušik, piridinski dušik in kisikov atom iz fenolne skupine, ki je v orto položaju glede na azo skupino, vsak od njih pa tvori dva petčlenska kelatna obroča.