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SPECTROPHOTOMETRIC STUDY ON THE FORMATION AND ANALYTICAL APPLICATION OF THE RHODIUM (III) CHELATE WITH 2-THIOXO-4-THIAZOLIDINONE

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ABSTRACT

The paper presents a spectrophotometric study of the binary system Rh(III) -2- thioxo - 4 -thiazolidinone. The formation conditions and the analytical application of the formed complex for spectrophotometric determination of Rh(III) were studied. The composition of the Rh(III) chelate with this particular ligand was determined by the continous variation method,its instability constant being $K_{inst} = 1,61 \cdot 10^{-8}$ mol^{2}L^{-2}.

KEYWORDS : rhodium (III), 2-thioxo-4-thiazolidinone, spectrophotometric study

RESUMO

O presente trabalho trata do estudo espectrofotométrico do sistema binário Rh(III)-2-tioxo-4-tiazolidinona. Foram estudadas as condições de formação e as aplicações do complexo para determinação analítica de Rh(III). A composição do quelato do Rh(III) com este ligante foi determinada usando o método de variação contínua e a constante de instabilidade, K_{inst}, foi $1,61x10^{-8}$ mol^{2}L^{-2}.

INTRODUCTION

Among all platinum metals, rhodium has the greatest number of oxidation states, namely eight positives and two negatives ones. The oxidation state for which the greatest diversity of complexes is found is (III). Ligands which are good σ-donors, but which have marked π-donor or π-acceptor properties are often associated with the oxidation state Rh (III). The methods based on the complex combinations formation with N-donor ligands (oxime, α-substituted dioxime, hydrazone) or S-donor ligands (NCS^-, thiokethone, thioamide) are much more used[1-6].

The present paper reports the study on the formation, the optical properties and the structure of the Rh (III) chelate with 2-thioxo-4-thiazolidinone (L). The chemical bond implies the participation of both a sulphur atom and a nitrogen of the ligand in coordination to the metal. This chelate was proposed for spectrophotometric determination of Rh (III).

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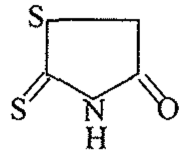


(L)

EXPRIMENTAL PROCEDURE

All the chemicals we used were of analytical grade: $RhCl_3 \cdot 3H_2O$ (Merk p.a.), 2-thioxo-4-thiazolidinone (L) (recrystallized).

The electronic spectra were performed in aqueous solutions using an Ocean Optics spectrometer(USA).

Experiments were done with an aqueous solution of $RhCl_3$ ($1 \cdot 10^{-3}$M, $1/2 \cdot 10^{-3}$M, $1/3 \cdot 10^{-3}$M) with the aqueous solution of L ($1 \cdot 10^{-3}$M, $1/2 \cdot 10^{-3}$M, $1/3 \cdot 10^{-3}$M) by solving the ligand. As a consequence of the reaction taking place between Rh (III) and the ligand L, yellow coloured complex compound was obtained, then the samples were heated for 10 minutes. The solutions were cooled and brought to 25 ml in calibrated fasks.

RESULTS AND DISCUSSIONS

Rh (III) reacts with 2-thioxo-4-thiazolidinone (L) at high temperature to form yellow complex compound.

The factors influencing the formation of the new compound are: the time period in which the colour of the new product stabilizes is about 10 minutes and the optimum pH for the formation is 5,5. The other pH values do not certify the formation in the studied system of the other more stable coloured compounds.

The electronic spectrum of the complex compound is presented in Figure 1. From the obtained data one can see that the most favourable wavelength in 460 nm (corresponding to 21739 cm^{-1}).

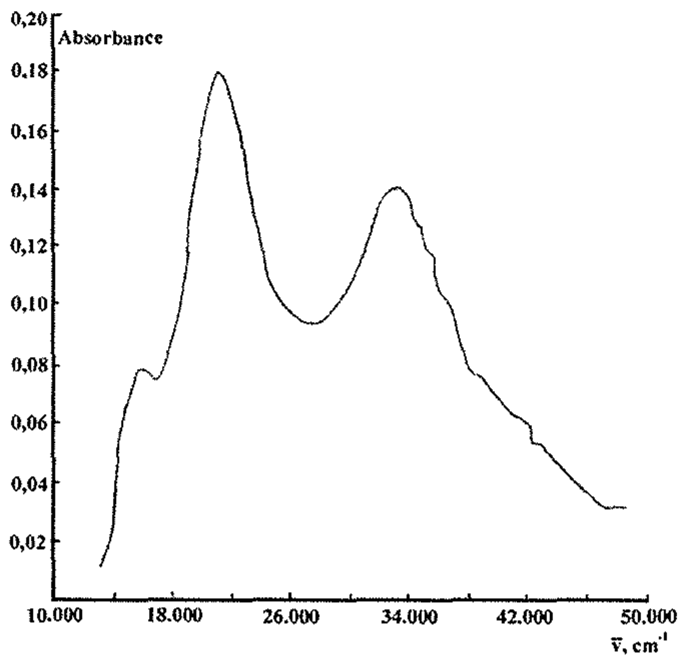


Figure 1. Electronic spectrum of the $RhCl_3$-L system at pH=5,5

The composition of the Rh (III) chelate was determined by the continous variation method. Figure 2 presents the results of the Job's method application for the three isomolar solution series ($1\cdot10^{-3}$M, $1/2\cdot10^{-3}$M, $1/3\cdot10^{-3}$M) at pH=5,5 and λ=460 nm. One can notice that each of the three curves reaches a single maximum value corresponding to the same molar ratio, which proves that a single complex compound was formed in the binary system and that its molar ratio is Rh (III):L = 1:2.

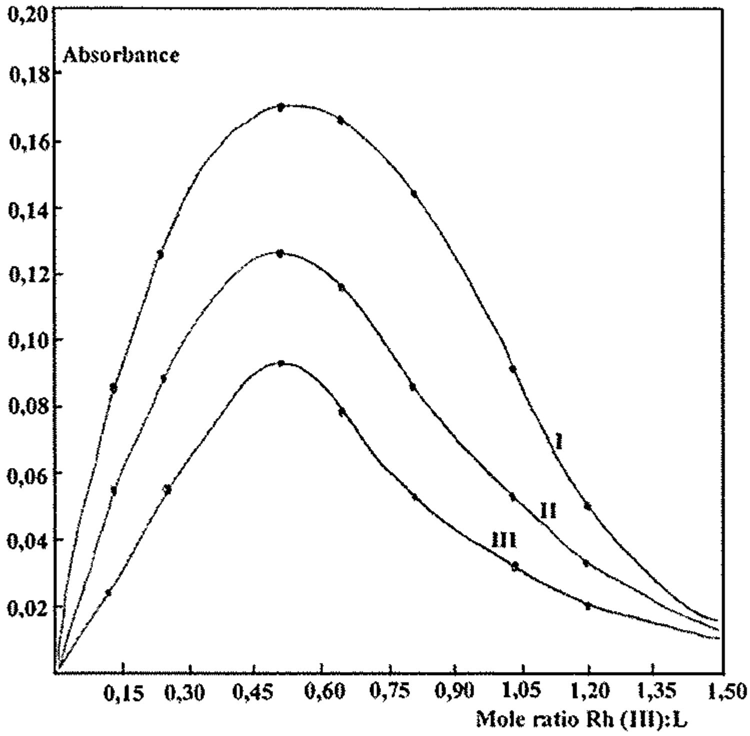


Figure 2. Variation of the absorbance for isomolar series.:
I-$1\cdot10^{-3}$M, II-$1/2\cdot10^{-3}$M, III-$1/3\cdot10^{-3}$M

To calculate the instability constant of the complex one has made use of the nonisomolar series method.

The general expression of the instability constant for equilibrium

$$mA + nB \rightleftharpoons A_mB_n \qquad (1)$$

is:

$$K_{inst} = \frac{C^{m+n-1}\, p^{n-1}[(pm+n)x-n]^{m+n}}{[m^{n-1}n^{m-1}(p-1)^{m+n-1}][n-(m+n)x]} \qquad (2)$$

in which m and n are molar index, C = the molar concentration of A, p = the molar concentration ratio of B and A, x = the mole ratio corresponding to maximum absorbance.

For the studied system, the molar index being m = 1 and n = 2 we obtain the following simplified expression:

$$K_{inst} = \frac{C^2\, p[(p+2)x-2]^3}{(p-1)^2(2-3x)} \quad (3)$$

Two series of nonisomolar solutions were prepared:

- the solution $RhCl_3$ ($1/2 \cdot 10^{-3}$M) – L (10^{-3}M);
- the solution $RhCl_3$ ($1/3 \cdot 10^{-3}$M) – L (10^{-3}M).

The results obtained are given in Figure 3.

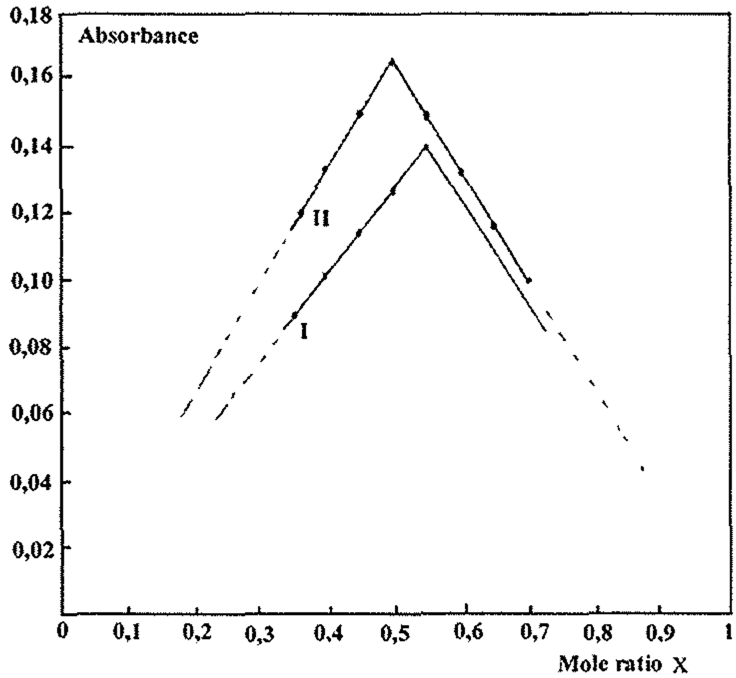


Figure 3. Variation of the absorbance in the nonisomolar series: I= Rh (III) ($1/2 \cdot 10^{-3}$M) – L (10^{-3}M); II= Rh (III) ($1/3 \cdot 10^{-3}$M) – L (10^{-3}M).

By introducing the practical results into the expression of the instability constant we obtain the values enclosed in Table 1.

Table 1
Values of the instability constant

C (mol · L^{-1})	p	x	K_{inst} (mol^2 · L^{-2})	$K_{m,inst}$ (mol^2 · L^{-2})
$1/2 \cdot 10^{-3}$	3	0,55	$1,14 \cdot 10^{-8}$	$1,61 \cdot 10^{-8}$
$1/3 \cdot 10^{-3}$	2	0,50	$2,07 \cdot 10^{-8}$	

The charge determination of the complex ion has been achieved by means of the electrophoretic migration method in presence of a weak solution of potassium nitrate. A small quantity of urea was introduced into the solution containing the complex compound corresponding to the molar ratio 1:2. After 15 minutes the displacement of the coloured complex ion towards the catode could be observed, thus proving the existence of its positive charge.

The results prove the following formula: $[RhL_2Cl_2]^+$, in which L acts as a bidentate ligand, using both a sulphur atom and a nitrogen in coordination to the metal.

In order to establish the coordination geometry and the symmetry for the new complex compound, a spectral analysis in the visible and UV range has been done. The correspondence between the absorption band occurring at 21739 cm^{-1} (460 nm) and 33335 cm^{-1} (299 nm) in the investigated complex $[RhL_2Cl_2]^+$ (Figure 1) and the ones found for the trans octahedral complexes of the type t-$[Rh(N_2S_2)Cl_2]^+$[7-9], leads us the conclusion that the coordinative compound that appears from the binary system Rh (III)-2- thioxo-4-thiazolidinone is stabilized by 2 L in equatorial plan and the monodentate Cl^- ligands are situated in trans to each other, so that $[RhL_2Cl_2]^+$ has an octahedral coordination geometry and a tetragonal symmetry, belonging to the $\mathbf{D_{2h}}$ point group[10] consequently (actually, the point group is either $\mathbf{C_{2h}}$ or $\mathbf{C_{2v}}$, but the internal structure of the ligand may be neglected).

Taking into account the results of the study above, which confirm high enough stability of this complex compound, it has been used for analytical purposes, namely for establishing a method of spectrometric determination of Rh (III).

The experimental results of the absorbance variation versus Rh (III) concentration are presented in Figure 4. The Beer`s law was respected over the concentration range 0,2-20,6 µg Rh (III)/mL.

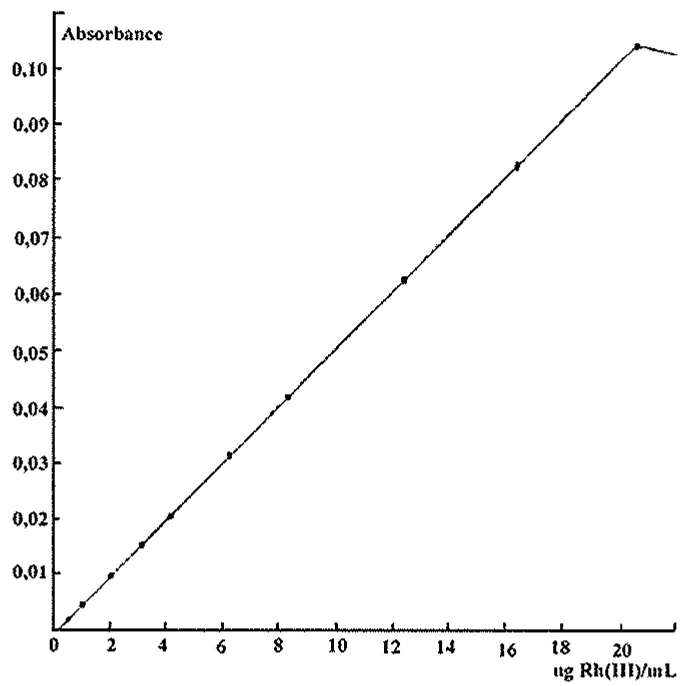


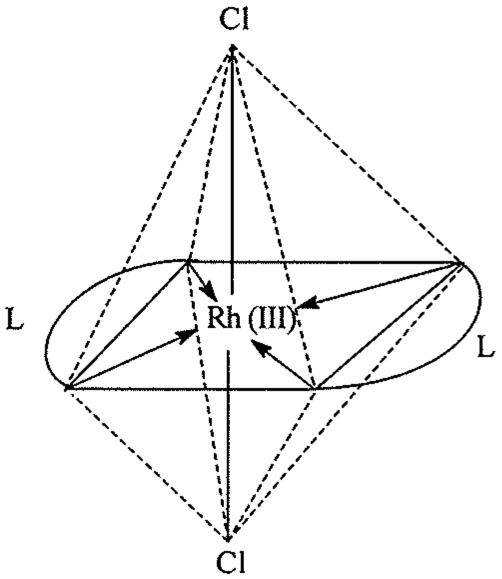
Figure 4. Variation of the absorbance versus Rh (III) concentration

In order to test the validity of the method, the experimental data were statistically interpreted. The error corresponding to eight determinations ($t_{0,95}$ = 2,447) is m = (30.414 ± 0,2334)·10^{-4}, meaning that the proposed method is reproducible and accurate and it is not affected by systematic errors, so that $[RhL_2Cl_2]^+$ can be used indeed for the spectrometric determination of Rh (III).

Other platinum metals (M = Pd, Pt) do not interfere in the spectrometric determination of rhodium in the $[RhL_2Cl_2]^+$ form. From the reaction`s feature between Rh (III) and L it has been ascertained that it is possible to recognize the Rh (III) in ruthenium`s presence up to the ratio Rh (III): Ru (III) = 1:18 and in gold`s presence up to the ratio Rh (III): Au (III) = 1:20.

CONCLUSIONS

On the basis of all the results obtained by this study, the following structure is proposed for the new complex compound, trans-$[RhL_2Cl_2]^+$:



It also has been proved that trans-$[RhL_2Cl_2]^+$ may be used for analytical purposes, namely for establishing a reproducible and accurate method of spectrometric determination of Rh (III).

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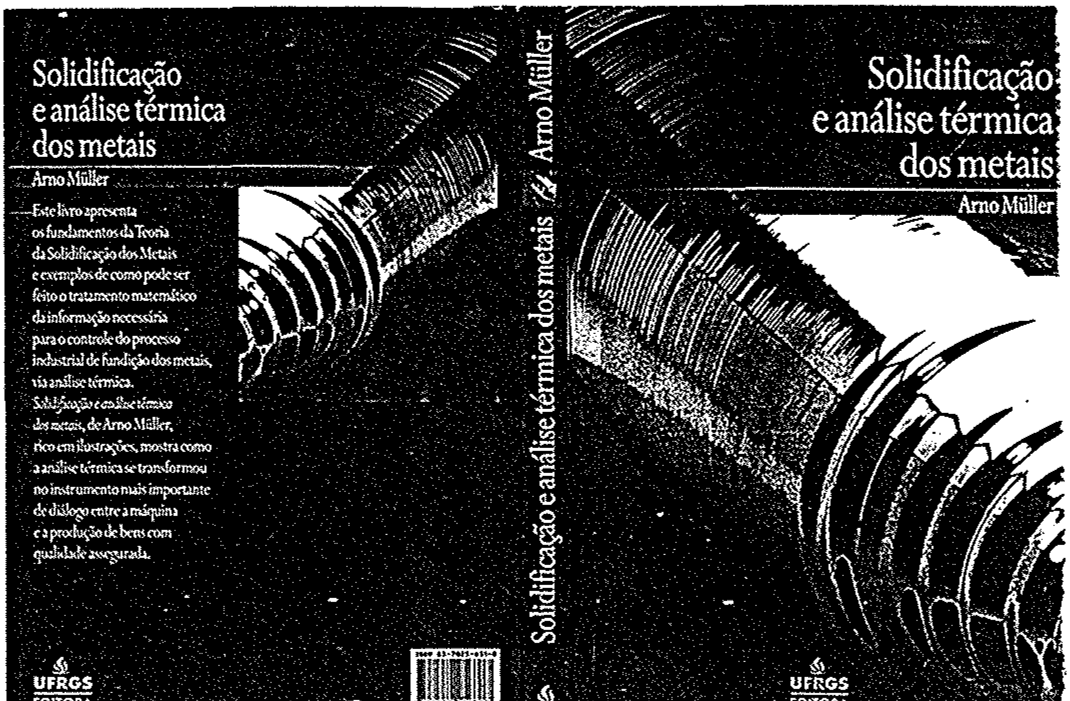
BOOKS / LIVROS

LIVROS

ARNO MÜLLER, *Solidificação e Análise Térmica dos Metais,* Editora da UFRGS, Porto Alegre, RS, Brasil, 2002, 278p.

Solidificação e Análise Térmica dos Metais trata de conceitos fundamentais que constituem a base para o entendimento dos processo e mecanismos de fabricação de bens industriais pelo uso da fundição. Por um lado a solidificação garante a qualidade das peças metálicas eliminando defeitos e a análise térmica, medindo as reações térmicas durante a solidificação assegura a qualidade e as propriedades mecânicas do produto da fundição.

O livro contém sete capítulos e um apêndice com anexos ricos em dados de interesse na metalurgia e apresenta a solidificação e a análise térmica da forma mais quantificada possível. O processo de solidificação, incluindo embriogênese de metais, termodinâmica, transformação e nucleação são tratados de maneira exemplar no Capítulo 1. A transferência de calor e a difusão de massa durante a solidificação são analisados nos Capítulos 2 e 3, respectivamente. O Capítulo 4 trata da estrutura de lingotes, o Capítulo 5 de defeitos de solidificação. Os fundamentos de análise térmica dos metais são apresentados no Capítulo 6 e as aplicações industriais são discutidas de maneira clara no Capítulo 7.



De certa forma, o livro reflete a personalidade, caráter e filosofia de vida do Professor Arno Müller. Ele é Engenheiro Metalúrgico formado pela UFRGS, Mestre em Ciência dos Materiais pelo Instituto Tecnológico da Aeronáutica (ITA) de São José dos Campos, São Paulo e Doutor em Engenharia pela Universidad Nacional de Rosário, República Argentina. Foi Professor Titular de Metalurgia da UFRGS, fundador do Laboratório de Fundição do Centro de Tecnologia da UFRGS e Diretor da Escola de Engenharia da mesma universidade.

Junto com outros pioneiros visionários e bandeirantes desbravadores, o Prof. Dr. Arno Müller foi também um dos fundadores do Programa de Doutorado em Engenharia Metalúrgica e dos Materiais da Escola de Engenharia da Universidade Federal do Rio Grande do Sul.

Atualmente ele ocupa os cargos de Professor e Coordenador do Programa de Pós-Graduação em Engenharia: Energia, Ambiente e Materiais da ULBRA – Universidade Luterana do Brasil.

Reproduzimos *ad integra* o frontispício do livro do Prof. Arno Müller.

"Duas visões do mundo tive comigo como engenheiro e pesquisador.

A primeira:
Fac quod in te est, ou faz aquilo que está ao teu alcance,
lema da Escola de Engenharia da UFRGS.

A segunda, a frase de Kant:
Alles Wissen stammt aus der Erfahrung
Ou seja, todo o conhecimento é proveniente da experiência.

Dedico este livro ao sofrido povo brasileiro, que custeou minha educação universitária em todos os níveis."

Recomendamos altamente este livro para todos os interessados em propriedades e uso de metais, incluindo alunos de graduação e pós-graduação em engenharia, física, química, mineralogia e ciência dos materiais. A sua tradução em outras línguas seria muito salutar.

Lavinel G. Ionescu, B.S., M.S., Ph.D. (Físico-Química)

ARNO MÜLLER, *Solidificação e Análise Térmica dos Metais*, Editora da UFRGS, Porto Alegre, RS, Brasil, 2002, 287p.

Solidification and Thermal Analysis of Metals (in Portuguese) treats fundamental concepts necessary for the understanding of metal casting and manufacturing of industrial metal products. The book consist of seven chapters and an appendix with physical data.

It includes solidification embryogenesis of metals, nucleation, solidification defects, thermodynamics, heat and mass difusion, thermal analysis and industrial applications. The book is the result of experience, reflection and practice of many decades of teaching and research in metallurgy. We recommend its translation to English and other languages.

Lavinel G. Ionescu, B.S., M.S., Ph.D.