

**ՀԱՅԱՍՏԱՆԻ ՀԱՆՐԱՊԵՏՈՒԹՅԱՆ ԳԻՏՈՒԹՅՈՒՆՆԵՐԻ
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НАЦИОНАЛЬНАЯ АКАДЕМИЯ НАУК РЕСПУБЛИКИ
АРМЕНИЯ**

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**FURTHER STUDY OF BETA-CORRECTION PRINCIPLE
FOR ANALYSIS OF METAL CHELATE SOLUTIONS**

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Further study of Beta-correction Principle has been made for the determination of metal chelates' characteristic parameters. The step stability constants for the chelates were formulized and determined. The reactions of nickel (II) and cobalt (II) with PAR at pH 9 have been used for the determination of the above parameters with the acceptable results.

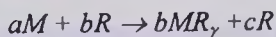
Fig. 3, table 1, ref. 5.

In chelate chemistry the determination of a chelate characteristic parameters involves the following spectroscopic methods in spectrophotometry: Molar Ratio¹⁾, Continuous Variation²⁾, Equilibrium Movement³⁾, Yatzimirsky⁴⁾, etc. They are usually confined because of their empiric character. The recent principle named Beta-correction theory was developed and applied for the determination of traces of metals (5a,b). In this paper this new principle has been further studied for the development of the equation for metal chelates' stability constant calculation and is reported for the first time here. The two reactions of nickel and cobalt with PAR at pH 9 was used as example for the determination of the chelates' characteristic parameters. The results are satisfactory.

PRINCIPLE

Beta-correction Equations

The dual-wavelength principle can be illustrated by the following reaction of ligand (*R*) with metal (*M*).



where, a is the added molar concentration of M at the reaction initial stage and b is that for R ; c is the concentration of the excess of R at the reaction equilibrium; γ is the composition ratio of the formed chelate MR_{γ} . Figure 1 shows that at the wavelength λ , the real absorbance (A_c) of chelate MR_{γ} should be equal to the interval of curve 2 and 3. Its equation is:

$$A_c = \frac{\Delta A - \beta \cdot \Delta A'}{1 - \beta \cdot \alpha} \quad (1)$$

where ΔA and $\Delta A'$ are the absorbances of the above coloured solution, respectively, against a reagent at λ_2 and λ_1 . We see that $\Delta A = MN$ and $-\Delta A' = QP$. Both α and β are so called correction coefficients and their equations are as follows:

$$\beta = A_o/A_o' \quad (2)$$

and

$$\alpha = A'_{\alpha}/A_{\alpha} \quad (3)$$

where A_o , A_o' , A'_{α} and A_{α} are all measurable absorbances (Figure 1).

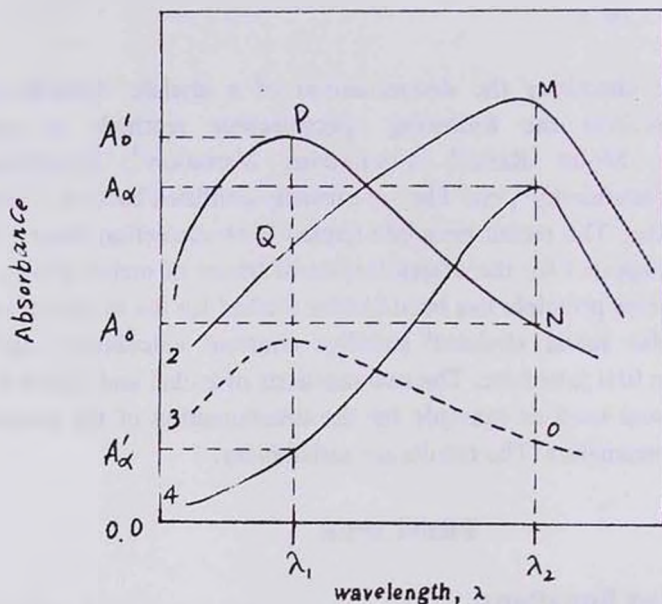


Figure. 1. Spectra of R , MR_{γ} and their mixture: 1, R (b amount); 2, $R(b) + M(a)$; 3, $R(c)$; 4, MR_{γ} . All against water.

The effective ratio (η) of R for complexation is expressed by ^{5b)}

$$\eta = (Ac - \Delta A)/Ao \times 100\% \quad (4)$$

Its simplified equation is

$$\eta = \frac{\alpha \cdot \Delta A - \Delta A'}{(1 - \alpha \cdot \beta)Ao'} \times 100\% \quad (5)$$

From a value the complexation ratio (γ) can be determined according to the following equation in case if added M will react completely.

$$\gamma = 0,01 \eta \cdot b/a \quad (6)$$

where a and b have the same meanings as the above reaction.

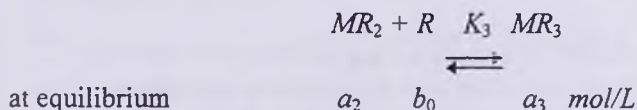
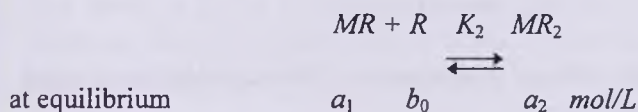
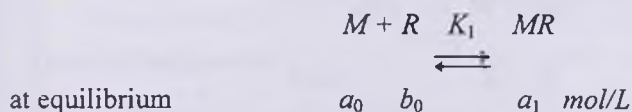
When γ value will reach maximum and remain constant, the complexation will be completed, and this reaction will reach the maximal sensitivity. Therefore, this maximal γ value presents the composition ratio of chelate MR_γ .

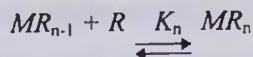
Development of Stability Constant Equation

In order to calculate the stability constant or the instability constant of chelate MR_γ , the following reaction solution, containing a mol/L of M and b mol/L of R at the start was used.



The possible equilibrium involves the following reactions where n corresponds to the maximal complexation ratio of R to M:





at equilibrium $a_{n-1} \quad b_0 \quad a_n \text{ mol/L}$

We calculate the n-th step stability constant, k_n , by the following equation:

$$k_n = \frac{a_n}{a_{n-1} b_0}$$

where $b_0 = b - a_1 - 2a_2 - 2a_3 - \dots - (n-1)a_{n-1}$. $na_n = b - \sum a_i$ and $a = a_0 + a_1 + a_2 + \dots = \sum a_i$.

Because $(b-b_0)/b = \eta$, from the above equation,

$$k_n = \frac{a_n}{a_{n-1} b_{(1-\eta)}} \quad (7)$$

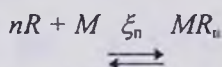
We think if γ average, calculated by Eqn 6, is more than $(n-0,2)$ the coloured solution is considered to contain the excess of R , MR_n and MR_{n-1} with the yield ratio to MR_{n-1} over 5, other chelates' concentrations should be omitted, for example MR_{n-2} , MR_{n-3} , ... MR , M , etc. If so,

$$a \approx a_{n-1} + a_n \quad (8)$$

and

$$\eta = \frac{na_n + (n-1)a_{n-1}}{b} \quad (9)$$

From the above equations 7,8 and 9 we may calculate k_n . Under the above condition, $\gamma > n-0.1$ the equation of the total stability constant (ξ_n) should be established by the following equilibrium:



at the start $b \quad a \quad 0 \text{ mol/L}$

at equilibrium $(b - na_n) \quad (a - a_n) \quad a_n$

where a_n is the formed chelates' concentration. We may calculate ξ value from the following equation:

$$\xi_n = \frac{a_n}{(a - a_n)(b - na_n)^n} \quad (10)$$

Because $na_n / b \approx \eta$, the instability constant of chelate MR_n may be expressed by

$$\xi_n \approx b^{1-n} (\eta)(a_n - b_\eta)^{-1} (1 - \eta)^{-n} \quad (11)$$

$$\xi_n = k_1 \cdot k_2 \cdot k_3 \dots k_n \quad (12)$$

The step stability, $k_{n-1}, k_{n-2} \dots k_1$, may be calculated by Eqns 11 and 12.

EXPERIMENTAL

Apparatus and Reagents

Visible spectra were recorded with Model 722 spectrophotometer (Made in Shanghai Third Analytical Instrument, CHINA).

The following reagent solution are necessary: standard Co(II) and Ni(II) solutions, both 5,00 mg/L dissolved in distilled water, EDTA, 5% used for masking other metal ions from distilled water, for example, Ca(II), etc, PAR, 1,00 mmol/L dissolved in ethanol for complexing Co(II); ammonia buffer solution, pH 9 for controlling the acidity of chelating.

Recommended Procedure

The reaction solutions of Ni(II) and Co(II) with PAR were prepared by the following procedure, Add 10,0 g of Ni(II) or Co(II) (mol/L) in a 25 ml volumetric flask. Then add 2 ml of ammonia buffer solution (pH 9) and 1,00 ml of 1,00 mmol/L PAR. Dilut up to the mark. After 10 min, add 1,0 ml of 5% EDTA and mix well. Measure absorbances at 410 and 510 nm (Ni-PAR) or 410 and 510 nm (Co-PAR), respectively.

RESULT AND DISCUSSION

Absorption spectra

The absorption spectra of PAR and its Ni and Co coloured solutions have been shown in Figure 2. From curve 3, $\lambda_1 = 410$ (or 400) and $\lambda_2 = 500$ nm should be selected because of the maximal sensitivity. Both β and α values have been calculated from curves 1 and 2, respectively.

Determination of γ

Vary the concentrations of PAR in its Ni and Co coloured solutions and measure their absorbances. Calculate both η and γ and draw up their curves (Figure 3). From curve 1 we see that when the concentration of PAR exceeds $1.54 \cdot 10^{-5}$ mol/L, γ remains constant and reaches its maximal

value. The γ values present the chelate composition ratio of to Co. The formed chelates may be expressed by: $\text{Ni}(\text{PAR})_2$ and $\text{Co}(\text{PAR})_2$.

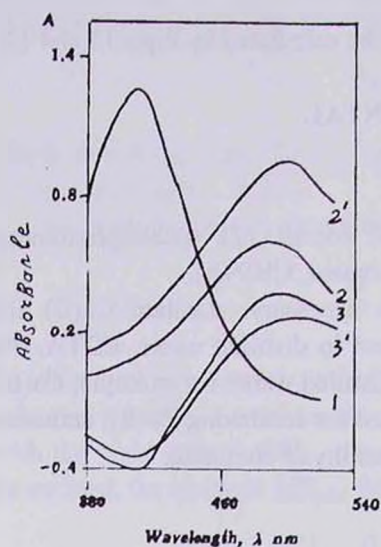


Figure 2. Absorption spectra: 1, PAR solution against water; 2, Ni-(2',Co-) chelate against water; 3, Ni coloured solution (3', that of Co) against a reagent blank.

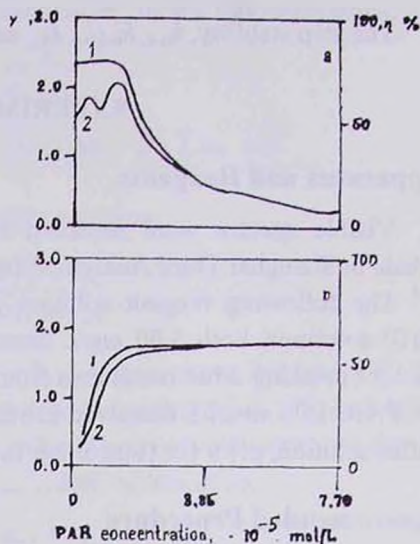


Figure 3. Curves of γ and α : a- 1, γ of Ni-PAR chelate; b-1, γ of Co-PAR chelate; a-2, of PAR in Ni solution; b-2, of PAR in Co coloured solution.

Calculation of stability constant

From the above Figures we selected the suitable coloured solution to calculate the chelates' total stability constant and its second-step one from Eqns 7,8,9 and 11 under the above described conditions. Their first-step stability constant has been also calculated from Eqn 12. The results (for 6 determinations) have been listed in Table. One can notice that $\text{Co}(\text{PAR})_2$ is more stable than Ni at pH 9 by comparing their ξ_n values. Figure 3 (b) shows that PAR added up to $1.15 \cdot 10^{-5}$ mol/L concentration remains by 100% in Co solution. It shows that the added PAR is in $\text{Co}(\text{II})$ chelate form, and the first-step chelate reaction has very high stability constant. Because η is less than 89% and its peaks appears at $5.77 \cdot 10^{-6}$ and $1.15 \cdot 10^{-5}$ mol/L of PAR, Figure 3 (a) shows that excess of PAR always exists in Ni coloured solution. This also proves that the first-step stability constant of $\text{Co}(\text{PAR})_2$ is much greater than that of $\text{Ni}(\text{PAR})_2$.

Table

Determination of stability constant of $\text{Ni}(\text{PAR})_2$ and $\text{Co}(\text{PAR})_2$

PAR concentration selected	n, η and γ	k_2 , ξ_2 and k_1	a_2 , a_1 and a_0 (mol/L)	precision of ξ_2
$6.54 \cdot 10^{-6}$ mol/L $\text{Ni}(\text{II})^+$	$n=2$ $\eta=0.630$ $\gamma=1.9$	$k_2=9.41 \cdot 10^5$ $\xi_2=2.19 \cdot 10^{11}$ $k_1=2.33 \cdot 10^5$	$a_2=5.56 \cdot 10^{-6}$ $a_1=9.84 \cdot 10^{-7}$ $a_0=5.94 \cdot 10^{-7}$	17%
$1.92 \cdot 10^{-5}$ mol/L PAR				
$6.54 \cdot 10^{-6}$ mol/L $\text{Co}(\text{II})^+$	$n=2$ $\eta=0.811$ $\gamma=1.91$	$k_2=3.46 \cdot 10^6$ $\xi_2=2.50 \cdot 10^{12}$ $k_1=7.23 \cdot 10^5$	$a_2=5.95 \cdot 10^{-6}$ $a_1=5.91 \cdot 10^{-7}$ $a_0=2.81 \cdot 10^{-7}$	12%
$1.54 \cdot 10^{-5}$ mol/L PAR				

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ԽՈՆԳՎԵՆ ԳԱՈ

Մետաղների քելատների ընդլայնման պարամետրերի որոշման նպատակով իրականացվել է բետա-շտկման սկզբունքի հետազոտումնախրումը: Ձևակերպվել է որոշվել են կայունության կոնստանտները: Վերը նշված պարամետրերի որոշման համար օգտագործվել են նիկելի (II) և կոբալտի (II) ռեակցիաները ՊԱՐ-ի հետ pH 9-ի դեպքում:

ДАЛЬНЕЙШЕЕ ИССЛЕДОВАНИЕ ПРИНЦИПА
БЕТТА-КОРРЕКЦИИ ДЛЯ АНАЛИЗА РАСТВОРОВ
ХЕЛАТОВ МЕТАЛЛОВ

ХОНГ-ВЕН ГАО

Проведено дальнейшее исследование принципа бетта-коррекции для определения характерных параметров хелатов металлов.

Сформулированы и определены константы стабильности. Реакции никеля (II) и кобальта (II) с ПАР при pH 9 применены для определения вышеуказанных параметров.

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