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ANTAZOLİN ve Ni(dtp)$_2$'den OLUŞAN KATIM ÜRÜNLERİNİN TERMODINAMIK SABİTELERİ

THERMODYNAMIC CONSTANTS OF THE ADDUCTS FORMED WITH ANTAZOLINE AND NICKEL (II) DIETHYLDITHIOPHOSPHATE [Ni(dtp)$_2$]

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SUMMARY

In this study, two simple and sensitive spectrophotometric procedures were developed for determination of the stepwise equilibrium constants of 1:1 and 2:1 adduct formation of Ni(dtp)$_2$ with antazoline in toluene. One is based on the measurement of absorbances of series of solutions, which contained constant total concentration of Ni(dtp)$_2$ and antazoline at 455 nm, and the straight line plot of Rose-Drago equation in this special case. This method was applied for the determination of the formation constant and molar absorptivity of 1:1 adduct and they were found to be 3073±40 and 308.5, respectively.

The other is based on the spectrophotometric measurement of the solutions in constant Ni(dtp)$_2$ concentration with increasing antazoline concentration. From the slope and the intercept values of the derived equation, the equilibrium constant and the molar absorptivity of 2:1 adduct were calculated and they were found to be 152 ± 2 and 51.9 ± 2.6, respectively.

ÖZET

Bu çalışmada, Antazolin ile Ni(dtp)$_2$'nin toluende 1:1 ve 2:1 katım ürünlerinin denge sabitelerinin tayini için iki basit ve hassas spektrofotometrik yöntem geliştirildi. Biri, sabit toplam konsantrasyondaki bir seri Ni(dtp)$_2$ ve antazoline çözeltilerinin 455 nm'deki absorbanslarının ölçülmesine ve bu özel durumda Rose-Drago denklemindeki doğrunun kullanılmasına dayanmaktadır. Bu metod 1:1 katım ürününün teşekkül sabitesinin ve molar absorptivitesinin tayini için uygulandı ve sırasıyla 3073 ± 40 ve 308.5 bulundu.

Diğeri, artan antazolin konsantrasyonlarına karşı sabit konsantrasyonda Ni(dtp)$_2$ ihtiva eden çözeltilerin spektrofotometrik ölçümlerine dayanmaktadır. Meydana gelen eşitliğin eğim ve intersept değerlerinden, 2:1 katım ürününün denge sabiti ve molar absorptivitesi hesaplandı ve sırasıyla 152 ± 2 ve 51.9 ± 2.6 bulundu.

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INTRODUCTION

Dialkyldithiophosphates $[(RO)_2PS_2H_2]$ (LH) form planar four coordinate molecules, soluble in organic solvents, in which the nickel atom has the low-spin configuration (1). They react with heterocyclic bases, B, to form bis adducts, $NİL_2B_2$, in which the metal atom has the high-spin configuration (2). Bidentate bases, Bb, such as bipyridyl, 1,10-phenantroline, also form high-spin adducts, $NİL_2Bb$, with cis-octahedral nature (3). The sterically hindered base 2,9-dimethyl - 1,10-phenantroline forms a very interesting five-coordinate adduct, NiL_2Bb, with nickel (II) diethyldithiophosphate, $Ni(dtp)_2$, in which both nitrogen atoms are coordinated to the nickel atom but one of the 4 membered chelate ring has opened by rapture of a Ni-S bond (3-5).

Thermodynamic data have been obtained by Marshall T. and Fernando Q. (6) for the reaction of bisdimethyl– and bisdiethyldithiophosphate nickel (II), with several heterocyclic bases.

Dakternieks D.R. and Graddon D.P. (7) have studied the reaction of nickel(II) dialkyldithiophosphates with heterocyclic bases calorimetrically and obtained values both the equilibrium constant and enthalpies in benzene solution by thermometric titration.

The reaction of nickel(II) dialkyldithiophosphates with bases in benzene solution have also been studied spectrophotometrically (4, 8, 9).

In this work equilibrium constants for the stepwise addition of two molecules of antazoline base to $Ni(dtp)_2$ were calculated by spectrophotometric method in toluene solution.

EXPERIMENTAL

Chemicals

The metale chelate, $Ni(dtp)_2$, was prepared by published method and purified by recrystallization (11).

The solvents employed in the experiments were of analytical grade and used without further purification.

Antazoline base was obtained from its hydrochloride salt by alkaline ether extraction and purified by recrystallization.

Apparatus

The measurements were made on a Zeiss PMQ II spectrophotometer.

Determination of the equilibrium constants :

(a) Procedure for the determination of equilibrium constant of 1:1 adduct : Total concentration of antazoline and $Ni(dtp)_2$ was kept constant (0.005 M). 5-7 ml of 0.005 M $Ni(dtp)_2$ solution in toluene was mixed with 5-3 ml of 0.005 M antazoline solution in the same solvent (total volume of 10 ml). The absorbance of the mixture was read at 455 nm (10) against toluene, at 10°, 15°, 20°, and 25°C. Blank determinations were also performed taking pure toluene instead of antazoline solution.

The same experiment was also performed in chloroform at 20°.

(b) Procedure for the determination of equilibrium constant of 2:1 adduct : 0.5-2 ml of 0.15 M antazoline solution in toluene was added to 1 ml of 0.015 M $Ni(dtp)_2$ solution in the same solvent and the volume was made up to 10 ml with toluene. The absorbance of the mixture was read at 455 nm at 13.5°C.

CALCULATIONS

1:1 Adduct formation between antazoline base, (D), and $Ni(dtp)_2$, (A), represented with the following eequation (eq. 1):

$$\underset{(\epsilon_A)}{A} + \underset{(\epsilon_D)}{D} \rightleftharpoons \underset{(\epsilon_{AD})}{AD} \qquad (1)$$

Rose-Drago equation (eq.2) (11) was used to calculate equilibrium constant, K, and molar absorptivity, ϵ_{AD}, of 1:1 adduct.

$$\frac{C^\circ_A \times C^\circ_D}{a - \epsilon_A \times C^\circ_A} = \frac{C^\circ_A + C^\circ_D}{(\epsilon_{AD} - \epsilon_A)} + \frac{1}{K \times (\epsilon_{AD} - \epsilon_A)} - \frac{a - \epsilon_A \times C^\circ_A}{(\epsilon_{AD} - \epsilon_A)^2} \qquad (2)$$

Where A, D and AD represents $Ni(dtp)_2$, antazoline and 1:1 adduct, respectively. C°'s are the initial concentrations, ϵ_A, ϵ_D and ϵ_{AD} are the molar absorptivities of the species exist in solution. K is the equilbrium constant and «a» is the total absorbance of the mixture.

There is no graphical solution of this equation if C°_D and C°_A were both varied. In the case of constant total concentration of C°_A and C°_D ($C^\circ = C^\circ_A + C^\circ_D$) graphical solution of eq. 2 becomes possible.

$$\frac{C^\circ_A \times C^\circ_D}{a - \epsilon_A \times C^\circ_A} = \frac{K \times C^\circ + 1}{K \times (\epsilon_{AD} - \epsilon_A)} - \frac{a - \epsilon_A \times C^\circ_A}{(\epsilon_{AD} - \epsilon_A)^2} \qquad (3)$$

Plot of $C^\circ_A \times C^\circ_D/(a - \epsilon_A \times C^\circ_A)$ vs $(a - \epsilon_A \times C^\circ_A)$ gives a straight line with a slope of $1/(\epsilon_{AD} - \epsilon_A)^2$ and intercept of $(K \times C^\circ + 1)/[K \times (\epsilon_{AD} - \epsilon_A)]$. When Ni(dtp)$_2$, A, was in excess, the donor, D, forms almost exclusively 1:1 adduct (10), thus form the slope and the intercept values ϵ_{AD} and K can easily be calculated.

Successive addition of the base to Ni(dtp)$_2$ represented by eq.4 :

$$AD + D \rightleftharpoons D_2A \qquad (4)$$

and the formation constant K′ of the 2:1 adduct is given by eq. 5 :

$$K' = \frac{[D_2A]}{[AD]\ [D]} \qquad (5)$$

When the base concentration is large enough, the second addition to the 5-coordinated 1:1 adduct becomes important and it should be taken into account on the equilibrium constant calculations. In this case initial concentrations of Ni(dtp)$_2$ and antazoline are :

$$C^\circ_A = [A] + [AD] + [D_2A] \qquad (6)$$

and

$$C^\circ_D = [D] + [AD] + 2[D_2A] \qquad (7)$$

Paranthetical values are the equilibrium concentrations of donor, acceptor, 1:1 and 2:1 adducts. Since the donor concentration is much larger than the acceptor concentration ($C^\circ_D \gg C^\circ_A$), equilibrium concentration of acceptor, Ni(dtp)$_2$, should be close to zero, thus in eq. 6 initial concentration of acceptor, C°_A, becomes sum of the equilibrium concentrations 1:1 and 2:1 adducts (eq.8).

$$C^{\circ}_{A} = [AD] + [D_2A] \tag{8}$$

Substitution for [AD] from eq.8 in eq.7 gives eq.9;

$$C_D^{\circ} = C_A^{\circ} + [D] + [D_2A] \tag{9}$$

Since equilibrium concentration of 2:1 adduct is much less than (C_A° + [D]), in eq.9 [D_2A] term could be omitted.

$$C^{\circ}_{D} \simeq C^{\circ}_{A} + [D] \tag{10}$$

Combination of eq. 5, eq. 8 and eq. 10 and solution for [D_2A] gives eq. 11;

$$[D_2A] = \frac{K' \times C^{\circ}_{A} \times (C^{\circ}_{D} - C^{\circ}_{A})}{1 + K' \times (C^{\circ}_{D} - C^{\circ}_{A})} \tag{11}$$

The absorbance, a′, of a solution in 1 cm cell containing $Ni(dtp)_2$, base, 1:1 and 2:1 adducts at a wavelength at which $Ni(dtp)_2$, 1:1 and 2:1 adducts are the absorbing species is given by eq.12 :

$$a' = \epsilon_{AD} \times [AD] + \epsilon_{D_2A} \times [D_2A] \tag{12}$$

Where ϵ_{D_2A} is the molar absorptivity of 2:1 adduct. When the base concentration is relatively large with respect to $Ni(dtp)_2$, free acceptor will be nearly zero in the solution, so the absorption term for this species has been omitted from the eq. 12 :

Substitution the values of eq.8 and eq.11 in eq.12 gives eq.13 :

$$\frac{C^{\circ}_{A}}{a' - \epsilon_{AD} + C^{\circ}_{A}} = \frac{1}{K' \times (\epsilon_{D_2A} - \epsilon_{AD})} \times \frac{1}{(C^{\circ}_{D} - C^{\circ}_{A})} + \frac{1}{(\epsilon_{D_2A} - \epsilon_{AD})} \tag{13}$$

When acceptor concentration, C°_{A}, is taken constant, this equation becomes straight line with the slope of $1/[K' \times (\epsilon_{D_2A} - \epsilon_{AD})]$ and the intercept of $1/(\epsilon_{D_2A} - \epsilon_{AD})$. When ϵ_{AD} is known,

ϵ_{D_2A} and K′ values could be calculated from the slope and the intercept of this line.

The free energy, ΔG°, for 1:1 adduct formation is calculated using eq.14;

$$\Delta G^\circ = -R \times T \times \mathrm{Ln}\, K \qquad (14)$$

and enthalpy value, ΔH°, is calculated from the slope of the least square line for a plot of Ln K vs 1/T. The entropy, ΔS°, values are obtained from eq.15 :

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \qquad (15)$$

RESULTS AND DISCUSSION

Four coordinated planar nickel complex, Ni(dtp)$_2$, forms five coordinated adduct with an imidazoline base antazoline (10). The

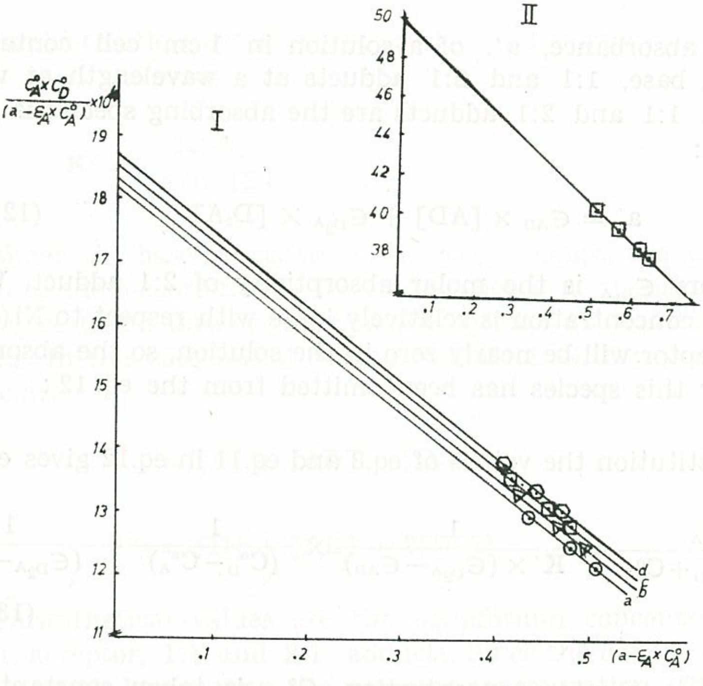

Fig. 1 — Plot of Rose-Drago equation in the case of constant total concentration of antazoline and Ni(dtp)$_2$. I. in toluene at a) 10°, b) 15°, c) 20°, d) 25°, II. in chloroform at 20°

existance of the complex is deduced from the analysis of some change in the absorption spectrum of the mixture when compared to the spectrum of the individual components. From the study of these changes as a function of concentration of the components, values of stepwise equilibrium constants K and K′ and molar absorptivities (ϵ_{AD} and ϵ_{D_2A}) of 1:1 and 2:1 adducts can be determined separately.

Molar absorptivity and equilibrium constant for 1:1 adduct were calculated from the slope and the intercept of eq.3. Fig. 1 represents the plot of $C^{\circ}_{A} \times C^{\circ}_{D}/(a - \epsilon_{A} \times C^{\circ}_{A})$ vs $(a - \epsilon_{A} \times C^{\circ}_{A})$ for antazoline at four different temperatures. The experiment was designed according to the procedure (a) described in the experimental section, using least-squares regression, the slope and the intercept values of the eq. 3 were found, then K and ϵ_{AD} values were calculated. Table I. represents the results together with the standard deviations. The data which was obtained in chloroform was also included in the same table. As it is noticed, equilibrium constant in chloroform is much less than that of in toluene.

Table I. Thermodynamic constants of 1:1 adduct of antazoline-Ni(dtp)$_2$ in a) toluene b) chloroform. $\epsilon_A = 18.5$, $\lambda = 455$ nm.

t°C	ϵ_{AD}	K	$1/T \times 10^{-3}$	$-\Delta G^{\circ}$ kcal/mol	$-\Delta S^{\circ}$ cal/mol	ΔH° kcal/mol	
10	308.5	3706 ± 69	35.34	4.621	2.399	5.300	(a)
15	308.5	3073 ± 40	34.72	4.603	2.416	—	
20	309.1	2635 ± 64	34.13	4.585	2.440	—	
25	309.3	2316 ± 14	33.56	4.587	2.399	—	
20	258.5	536 ± 3	34.13	3.659	—	—	(b)

The values of ΔG°, ΔH° and ΔS° together with estimated standard deviations were also summarized in table I. The non-weighed least-squares straight line plots of Ln K vs 1/T for 1:1 adduct is shown in Fig. 2.

The equilibrium constant, K′, and molar absorptivity, ϵ_{D_2A} for 2:1 adduct were calculated in the concentration range where appreciable amount of D_2A exist in the mixture. When the constant concentration of Ni(dtp)$_2$ solution in toluene was spect-

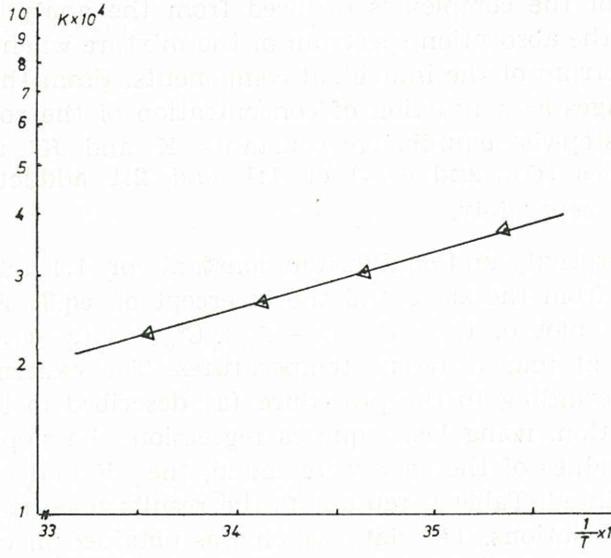

Fig. 2 — Linear least-squares plots of Ln K vs 1/T for the formation of 1:1 adduct of $Ni(dtp)_2$ and antazoline.

rophotometrically titrated with antazoline solution in toluene, the absorbance at 455 nm, which belong to 1:1 adduct, was increased, then slowly decreased with the increasing antazoline cc

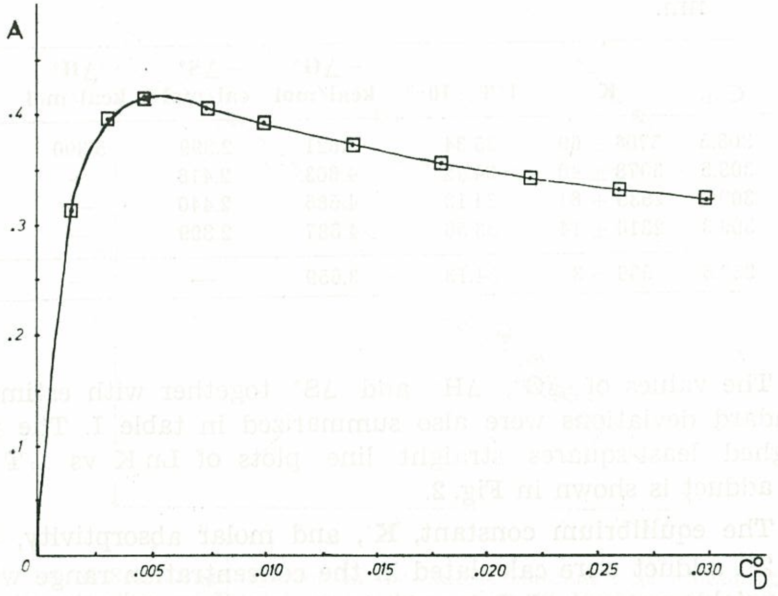

Fig. 3 — Variation of absorbance of the adducts as a function of increasing concentration of donor. ($C°_A = 1.5 \times 10^{-3}$ M, $\lambda = 455$ nm)

centration (Fig. 3). This indicated formation of a second adduct which has lower absorptivity than that of the first one. The formation constant was also smaller for 2:1 adduct since the decrease in absorbance was not large when the base concentration increased. Fig. 4 represents the plot of $C^\circ_A/(a' - \epsilon_{AD} \times C^\circ_A)$ vs $1/(C_D^\circ - C_A^\circ)$ for antazoline in toluene according to eq.13, where ϵ_{AD} was taken 308.From the slope and the intercept values ϵ_{D_2A} and K′ were found to be 152 ± 2 and 51.9 ± 2.6, respectively.

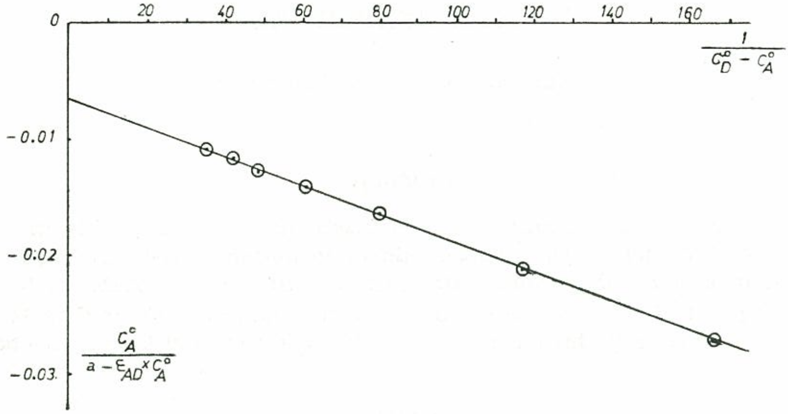

Fig. 4 — Plot of eq. 13 for the adducts of antazoline with $Ni(dtp)_2$ in toluene ($\epsilon_{AD} = 308$, $\epsilon_A = 18.5$)

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