46. *Stability Constants of Zinc*(II)– *and Nickel*(II)–*2,2′-Bipyridyl Complexes.*

By S. Cabani and M. Landucci.

The formation constants of zinc(II)–2,2′-bipyridyl complexes have been determined, at different temperatures in both aqueous and aqueous-alcoholic solutions, by pH-metric and pAg-metric measurements; and the values of the thermodynamic functions corresponding to every formation step of the complexes have been calculated. Some values have then been verified by a competitive spectrophotometric technique which has then been employed to determine the formation constants of nickel(II) complexes with the same ligand at 20° in aqueous alcohol.

In earlier papers [1, 2] a study of the formation equilibria of chelate compounds of 2,2′-bipyridyl with some metallic ions was reported. In this paper the chelate compounds of zinc(II) and nickel(II) ions with the same ligand will be considered.

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[1] Cabani and Scrocco, *Ann. Chim.* (*Italy*), 1958, **48**, 85, 99; *J. Inorg. Nuclear Chem.*, 1958, **8**, 332.

[2] Cabani, Moretti, and Scrocco, *J.*, 1961, 88.

Stability constants of the zinc(II)–2,2'-bipyridyl system have been measured for aqueous and aqueous-alcoholic solution at different temperatures. For the nickel(II)–2,2'-bipyridyl system only the equilibria in aqueous-alcoholic solution were considered because the technique used did not give sufficiently accurate data to allow calculation of all the thermodynamic functions associated with the formation of the complexes.

TABLE 1.

Stability constants * of zinc(II)–2,2'-bipyridyl chelates.†

Temp.	log K_1	log K_2	log K_3	log β_2	log β_3	Temp.	log K_1	log K_2	log K_3	log β_2	log β_3
	Aqueous solutions					*Aqueous-alcoholic solutions* (EtOH 41·5% by wt.)					
10°	5·39	4·74	4·01	10·13	14·14	10°	5·08	4·43	3·28	9·51	12·79
20	5·20	4·50	3·83	9·70	13·53	17·5	5·00	4·22	3;18	9·22	12·40
25	5·16	4·46	3·74	9·62	13·36	20	4·95	4·17	3·13	9·12	12·25
	(5·40)	(4·40)	(3·50)	(9·80)	(13·30)	25	4·88	4·08	3·05	8·96	12·01
32	5·02	4·32	3·71	9·34	13·05	32·5	4·68	3·98	2·96	8·66	11·62
40	4·86	4·24	3·56	9·10	12·66	40	4·54	3·86	2·91	8·40	11·31

* The average error in log K is ±0·02.

† Values in parentheses were obtained by Yamasaki and Yasuda.[5]

TABLE 2.

	Aqueous solutions			Aqueous-alcoholic solutions		
	$\Delta F°$ (kcal./mole)	$\Delta H°$ (kcal./mole)	$\Delta S°$ (e.u.)	$\Delta F°$ (kcal./mole)	$\Delta H°$ (kcal./mole)	$\Delta S°$ (e.u.)
Zn + bip = Zn(bip)	$-7·04 \pm 0·03$	$-7·0 \pm 0·5$	$+0·1 \pm 1·8$	$-6·66 \pm 0·03$	$-7·6 \pm 0·5$	$-3·1 \pm 1·8$
Zn(bip) + bip = $Zn(bip)_2$	$-6·08 \pm 0·03$	$-6·7 \pm 0·6$	$-2·1 \pm 2·1$	$-5·57 \pm 0·03$	$-7·4 \pm 0·4$	$-6·1 \pm 1·4$
$Zn(bip)_2$ + bip = $Zn(bip)_3$	$-5·10 \pm 0·03$	$-5·8 \pm 0·6$	$-2·3 \pm 2·1$	$-4·16 \pm 0·03$	$-5·2 \pm 0·4$	$-3·5 \pm 1·4$
Zn + 2bip = $Zn(bip)_2$	$-13·12 \pm 0·03$	$-13·8 \pm 1·0$	$-2·3 \pm 3·4$	$-12·22 \pm 0·03$	$-15·0 \pm 0·2$	$-9·3 \pm 0·8$
Zn + 3bip = $Zn(bip)_3$	$-18·23 \pm 0·03$	$-19·6 \pm 0·8$	$-4·6 \pm 2·8$	$-16·38 \pm 0·03$	$-20·2 \pm 0·3$	$-12·8 \pm 1·1$

At neutral or acid pH the reaction between zinc(II) ions and 2,2'-bipyridyl involves the usual step process[3] until a normal trisbipyridyl complex is reached.[4] In 1956 Yamasaki and Yasuda[5] determined the stability constants, for aqueous solutions at 25°, of complexes containing 1, 2, and 3 molecules of ligand per metallic ion, but the thermodynamic functions ΔH and ΔS for the formation equilibria in solution were not reported.

To obtain these values the temperature coefficients of the equilibrium constants were measured. For measurements of the stability constants in aqueous-alcoholic solution the pAg-metric technique[1] was adopted but for aqueous solutions the pH-metric technique.[3] In both cases the constants were calculated by noting the pA values at the half-values of $\bar{n}$ in the formation curves and were improved by successive approximation equations as described by Carlson *et al.*[6] The final values listed in Table 1 were then examined by comparing the experimental with the calculated formation curves. At each temperature the divergence of the experimental points from the theoretical curves was very small for each $\bar{n}$ value. Table 1 gives also, for comparison, the values recorded by Yamasaky and Yasuda.[5] It should be noted that these authors did not specify whether their values were obtained directly from the formation curve or by successive iteration. Moreover, while in our calculation a $pK_{AH} = 4·40$ at 25° was used, they used $pK_{AH} = 4·44$. In Table 2 are reported values of the thermodynamic functions at 25° for the formation of zinc(II)–bipyridyl chelates in aqueous and aqueous-alcoholic solution.

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[3] Bjerrum, " Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[4] Jaeger and Van Dijik, *Proc. Akad. Sci.* (*Amsterdam*), 1934, **37**, 753; 1935, **38**, 235.

[5] Yamasaki and Yasuda, *J. Amer. Chem. Soc.*, 1956, **78**, 1324.

[6] Carlson, McReynold, and Verhoek, *J. Amer. Chem. Soc.*, 1945, **67**, 1334.

Much attention has been paid by many authors to the study of the nickel(II)–2,2′-bipyridyl system, but they were interested mainly in, for example, the separation of the optically active isomeric trisbipyridyl chelate compounds,[7] the kinetics and mechanism of dissociation and racemization,[8] the exchange rate,[9] and polarographic reduction.[10] We know of no previous attempt to determine the consecutive formation constants of these complexes and only indicative values of the overall constant have been found.[11] Actually the determination of the formation constants of nickel complexes is rather difficult. The potentiometric competitive technique was discarded because of the big differences between the stability constants of this system and of the available reference systems (bip–H$^+$) and (bip–Ag$^+$). So was the direct use of nickel electrodes because of the lack of reversibility and the kinetic characteristics of the reaction. We used instead indirect spectrophotometric measurements, choosing cupric as the antagonist ion. For this purpose spectra of solutions containing copper(II)-bipyridyl complexes, and copper(II)- and nickel(II)-bipyridyl complexes were recorded. The spectra reported in Fig. 1 are very similar until

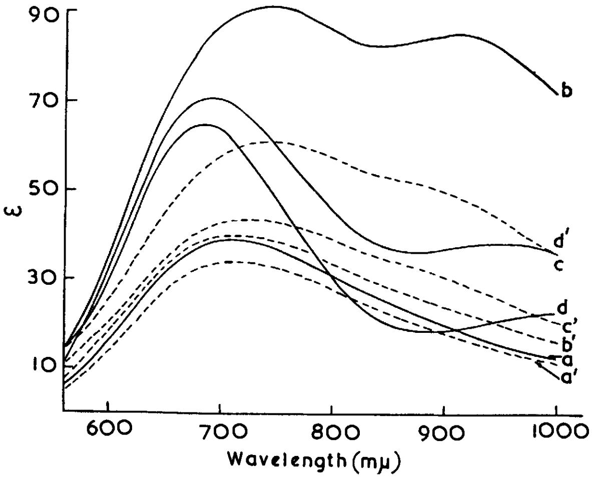

FIG. 1. Comparison of absorption curves of solutions containing Cu(II)–2,2′-bipyridyl complexes (——) with solutions containing both Cu(II)– and Ni(II)–2,2′-bipyridyl complexes (– – –) at various ratios $C_{\text{bip}}/C_{\text{Cu}}$ with C_{Cu} constant = 5 × 10^{-3}M.

(a) and (a′): $C_{\text{bip}}/C_{\text{Cu}} = 1$; (b) and (b′): $C_{\text{bip}}/C_{\text{Cu}} = 2$; (c) and (c′): $C_{\text{bip}}/C_{\text{Cu}} = 3$; (d) and (d′): $C_{\text{bip}}/C_{\text{Cu}} = 4$. In (a′), (b′), (c′), and (d′) $C_{\text{Ni}} = 5 \times 10^{-3}$M.

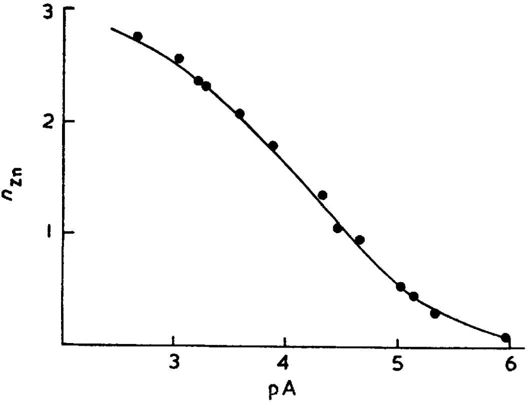

FIG. 2. Formation curve of the Zn(II)–2,2′-bipyridyl complexes in aqueous-alcoholic solution at 20°.

The full line is drawn from the formation constants obtained by potentiometric measurements ($\beta_1 = 8{\cdot}92 \times 10^4$; $\beta_2 = 1{\cdot}32 \times 10^9$; $\beta_3 = 1{\cdot}78 \times 10^{12}$). The points are experimental values obtained by competitive spectrophotometric measurements.

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[7] Morgan and Burstall, *J.*, 1931, 2213; Schweitzer and Lee, *J. Phys. Chem.*, 1952, **56**, 195; Davies and Dwyer, *Trans. Faraday Soc.*, 1953, **49**, 180; 1954, **50**, 24.

[8] Basolo, Hayes, and Neuman, *J. Amer. Chem. Soc.*, 1953, **75**, 5102.

[9] Johnson and Hall, *J. Amer. Chem. Soc.*, 1948, **70**, 2344.

[10] Vlček, *Nature*, 1956, **177**, 1043.

[11] Bjerrum and Jørgensen, *Rec. Trav. chim.*, 1956, **75**, 658; Irving, " International Conference on Co-ordination Chemistry," The Chemical Society, Burlington House, London, 1959, p. 16.

the ratio $C_{\text{bip}}/C_{\text{Cu}}$ is $\leqslant 1$ and rather different when the ratio becomes >1. It is deduced that, while for monobipyridyl complexes the stability of cupric chelate is higher than that of nickelous chelate, the contrary is the case for complexes containing two or three molecules of ligand in the co-ordination sphere. The values and the method used to determine the stability constants of nickel(II)-bipyridyl chelates from these spectrophotometric measurements are reported below.

The validity of the copper(II)-bipyridyl system as a reference system was verified by determining the stability constants of zinc(II)-bipyridyl chelates by similar indirect spectrophotometric measurements and comparing them with those from the potentiometric measurements. The curves $\varepsilon_\lambda = f(\bar{n}_{\text{Cu}})$ and $\bar{n}_{\text{Cu}} = f(\text{pA})$ reported in a previous paper[2] were used. In fact, since the zinc complexes have zero extinction coefficient in the wavelength range used, every ε_λ value of a solution containing known concentrations C_{Cu}, C_{Zn}, and C_{A} of copper(II) and zinc(II) salts and 2,2'-bipyridyl, respectively, yields a value of $\bar{n}_{\text{Cu}}$ and the corresponding p*A* value and the $\bar{n}_{\text{Zn}}$ value calculated by the equation

$$\bar{n}_{\text{Zn}} = [C_{\text{A}} - \bar{n}_{\text{Cu}}C_{\text{Cu}} - (\text{A})]/C_{\text{Zn}}, \qquad (1)$$

where (A) is the free-ligand concentration. The results agreed well with the potentiometric ones (Fig. 2), thus supporting the choice of copper(II)-2,2'-bipyridyl as a reference system for this kind of determination.

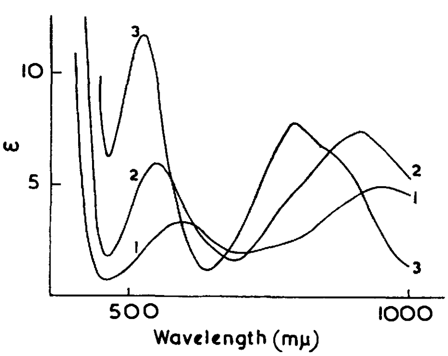

FIG. 3. Absorption curves of aqueous-alcoholic solutions of Ni(II)-2,2'-bipyridyl complexes ($C_{\text{Ni}} = 3 \times 10^{-2}$M).

(1) $C_{\text{bip}}/C_{\text{Ni}} = 1$; (2) $C_{\text{bip}}/C_{\text{Ni}} = 2$; (3) $C_{\text{bip}}/C_{\text{Ni}} \geqslant 3$.

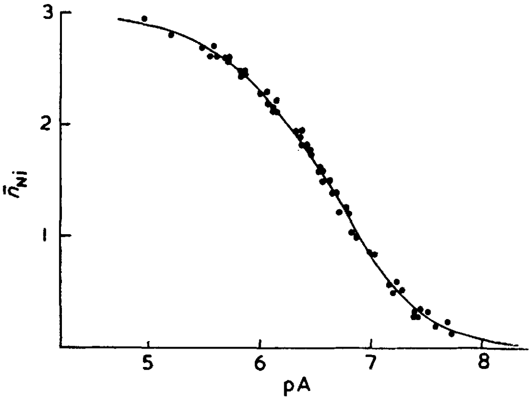

FIG. 4. Formation curve of Ni(II)-2,2'-bipyridyl complexes in aqueous-alcoholic solution at 20°.

The curve is drawn from the constants $\beta_1 = 8{\cdot}4 \times 10^6$, $\beta_2 = 4{\cdot}9 \times 10^{13}$, $\beta_3 = 3{\cdot}8 \times 10^{19}$ obtained by competitive spectrophotometric measurements.

The technique used to obtain the formation curve, $\bar{n}_{\text{Ni}} = f(\text{pA})$, was the same as described for zinc-bipyridyl complexes but modified to include ions having non-zero extinction coefficient. Spectra of nickel ions and alternatively of nickel(II)-bipyridyl complexes at a different step of formation in aqueous alcohol at 20° were recorded (Fig. 3). On the assumption that $\bar{n}_{\text{Ni}} = C_{\text{dip}}/C_{\text{Ni}}$,* curves $\varepsilon_\lambda = f(\bar{n}_{\text{Ni}})$ were drawn for each wavelength previously chosen for the reference system in the range 600—1000 mμ. So, once the curves $\varepsilon_\lambda = f(\bar{n}_{\text{Cu}})$ and $\varepsilon_\lambda = f(\bar{n}_{\text{Ni}})$ are known, it is possible to obtain the formation curve $\bar{n}_{\text{Ni}} = f(\text{pA})$ by a simple iterative proceeding.

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* This approximation is supported by the high value of the stability constants of nickel-bipyridyl complexes; moreover, for some of the chosen wavelengths (about 650 mμ), ε's of nickel complexes were almost constant for all ratios $C_{\text{bip}}/C_{\text{Ni}}$, so that the correction to be introduced in the calculations was constant independently of the $\bar{n}$ value.

Let $\varepsilon_\lambda{}^\circ$ be the molar absorption coefficient (at the wavelength λ and expressed with respect to the copper concentration) of a solution containing known amounts of copper(II) and nickel(II) salts and 2,2'-bipyridyl. Then the curve $\varepsilon_\lambda = f(\bar{n}_{\text{Cu}})$ yields a value of $\bar{n}^\circ{}_{\text{Cu}}$ from which it is possible to calculate an $\bar{n}^\circ{}_{\text{Ni}}$ of zero approximation. Then from the curve $\varepsilon_\lambda = f(\bar{n}_{\text{Ni}})$ a value for $\varepsilon_\lambda{}^\circ{}_{,\text{Ni}}$ is read and multiplied by the concentration ratio $C_{\text{Ni}}/C_{\text{Cu}}$; this product, subtracted from the $\varepsilon_\lambda{}^\circ$ of the solution, gives an $\varepsilon_\lambda{}'$ from which a new $\bar{n}'_{\text{Cu}}$ follows; and so on. The whole procedure must be repeated until constant values of ε_λ, $\bar{n}_{\text{Cu}}$, and $\bar{n}_{\text{Ni}}$ are obtained. Generally three iterations are more than sufficient to afford convergence. This procedure, if repeated for a series of solutions containing different amounts of bipyridyl for a given ratio $C_{\text{Ni}}/C_{\text{Cu}}$, allows one to obtain the formation curve of the nickel–bipyridyl complexes, from which the β_i's of the system can be obtained later. Several experiments have been made, with various ratios $C_{\text{Ni}}/C_{\text{Cu}}$.

The points in the formation curve, Fig. 4, refer to a series of experiments at 20° in aqueous-alcoholic solutions (EtOH,41·5% by wt.) in which the concentration of each metal ion was varied in the range $2{\cdot}5$—$7{\cdot}5 \times 10^{-3}$M and with the ratio $C_{\text{Ni}}/C_{\text{Cu}}$ 0·33—3·00. They represent the average values of results obtained at six wavelengths in the range 600—1000 mμ. The stability constants resulting from the iterative proceeding are: $\log \beta_1 = 6{\cdot}9 \pm 0{\cdot}3$; $\log \beta_2 = 13{\cdot}7 \pm 0{\cdot}1$; $\log \beta_3 = 19{\cdot}6 \pm 0{\cdot}1$. A more accurate value for β_1 of the nickel(II)-2,2'-bipyridyl complexes is difficult to obtain because the formation curve $\bar{n}_{\text{Ni}} = f(\text{pA})$ lies in a range of pA in which the corresponding formation curve of copper complexes has a very small slope $d\bar{n}/d\text{pA}$; a similar unfavourable situation is found in the curves $\varepsilon_\lambda = f(\bar{n}_{\text{Cu}})$. This causes sometimes appreciable differences in the values of $\bar{n}_{\text{Ni}}$ and pA even for small experimental errors in the absorption curves.

The results agree sufficiently with Bjerrum and Jørgensen's indicative value [11] ($\log \beta_3 = 20$ for the overall stability constant) and with those deducible from the formation curve reported by Irving [11] on the basis of distribution experiments (pA 7·5 for $\bar{n} = 0{\cdot}5$; 6·8 for $\bar{n} = 1{\cdot}5$; 6·0 for $\bar{n} = 2{\cdot}5$). Nevertheless, these values are hardly comparable with ours since the other authors cited give no information about their experimental conditions.

EXPERIMENTAL

The stock solution of zinc nitrate was prepared from recrystallised salt; to avoid hydrolysis small quantities of nitric acid were added. The solution was titrated with "Complexon" (cf. Schwarzenbach [12]). The stock solution of nickel nitrate was prepared from a Merck *extra pure* product and standardised by electrodeposition. The apparatus, purification of other products, and standardisation of other stock solutions are reported in previous papers.[1, 2]

For the pAg-metric measurements the concentration of silver nitrate was 2—6×10^{-3}M. In the pH-metric measurements the concentration of nitric acid was 1—2×10^{-3}M. The acid dissociation constant of 2,2'-bipyridyl was calculated, at different temperatures, by the equation $\text{p}K_{\text{AH}} = 755{\cdot}2/T + 1{\cdot}862$, obtained by applying the method of least squares to a set of six $\text{p}K_{\text{AH}}$ values determined in the temperature range 10—40°; the maximum deviation from the regression line was $\pm 0{\cdot}01$ pK unit. The concentration ranges in which the competitive spectrophotometric measurements were carried out have already been reported. The spectra were recorded 2—5 days after preparation of samples, to allow the solutions to reach complete equilibrium.

All the solutions contained potassium nitrate (0·1M) as indifferent electrolyte.

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PISA, ISTITUTO DI CHIMICA FISICA DELL'UNIVERSITA. [*Received, August 4th*, 1961.]

[12] Schwarzenbach, "Complexometric Titrations," Methuen & Co., London, 1957, p. 83.