October 1995 Notes Chem. Pharm. Bull. 43(10) 1791—1792 (1995) 1791

Stability Constants of Zn(II), Pb(II), Cd(II) and Cu(II) Complexes with Hematoxylin

Abdel-Monem El-Hosany EL-ASKALANY*,[a] and Ahmed Mohamed ABOU EL-MAGD[b]

Chemistry Department, Faculty of Science, Mansoura University,[a] Mansoura, Egypt and Faculty of Applied Sciences, Umm Al-Qura University,[b] Makkah Al Mukarrama, Kingdum of Saudi Arabia.

Received January 30, 1995; accepted June 2, 1995

The composition and stability constants of the complexes of Zn(II), Pb(II), Cd(II) and Cu(II) with hematoxylin have been studied using direct current polarography and differential pulse polarography. The results showed the formation of 1:2 (M:L) complexes for Zn(II) and Pb(II), and a 1:6 (M:L) complex for Cd(II). However, the formation of copper–hematoxylin complex is irreversible. The values of the formation constants for the above complexes at 298, 308 and 318 K were calculated as well as the relevant thermodynamic parameters.

Key words hematoxylin; complexes; zinc; lead; cadmium

Polyhydroxy compounds are used as complexing agents for the qualitative and quantitative analysis of metal ions. Their importance, as complexing agents, lies in the fact that they contains hydroxyl oxygen suitable for many elements which prefer this type of bonding. Hematoxylin has been used as a metalochromic indicator[1)] and reagent for the spectrophotometric determination of Al(III),[2—5)] gallium(III),[6)] molybdenum(VI),[7—10)] arsenic(V),[11)] vanadium(IV),[12)] and tin(IV).[13)] We now wish to report the effect of hematoxylin on some transition metal ions in aqueous sodium perchlorate solutions and the determination of their stability constants. The effect of temperature on the formation constants and the calculation of different thermodynamic parameters are described.

Experimental

Polarograms were obtained using a Metrohm polarecord E506 instrument connected with E505 polarography stand. An Ag/AgCl/KCl saturated reference electrode was used throughout the investigation. The capillary characteristics are $m=1.87\,\mathrm{mg\cdot s^{-1}}$ and $t=4.8\,\mathrm{s}$ at $h=40\,\mathrm{cm}$. In differential pulse polarography (DPP), a drop time of 1.0 s, a scan rate of $100\,\mathrm{mV\cdot s^{-1}}$ and a 50 mV pulse amplitude were used. The temperature was kept constant to within ±0.1 °C by Hake's thermostatic circulator and the ionic strength was kept constant at $0.6\,\mathrm{mol\,dm^{-3}}$ with sodium perchlorate as supporting electrolyte. The pH of the experimental solution under investigation was measured using a Hana pH meter model 8519. The concentration of metal ions was $5\times10^{-5}\,\mathrm{mol\,dm^{-3}}$. Hematoxylin was obtained from Aldrich while all other chemicals were of analytical reagent grade.

Theory The results of DPP have been used for determining the formation constants of formed complexes instead of conventional DC polarography.[14)] In this modificantion it is assumed that the shift in the half-wave potential $(E_{1/2})_s-(E_{1/2})_c$ is equal to the shift in the peak potential $(E_p)_s-(E_p)_c$. Thus, the Lingane equation[15)] can be expressed as follows:

$$(E_p)_s-(E_p)_c=\Delta E_p=(2.303RT/nF)\log\beta_{MX}+(2.303JRT/nF)\log C_X \quad (1)$$

where β_{MX} is the formation constant of the Jth. Complex, C_X is the analytical concentration of the ligand and ΔE_p is the shift in peak potential.

Results and Discussion

Addition of hematoxylin to $5\times10^{-5}\,\mathrm{mol\,dm^{-3}}$ Zn(II), Pb(II) and Cd(II) in the presence of $0.6\,\mathrm{mol\,dm^{-3}}$ sodium perchlorate at pH=2 ($E_{1/2}$ remains constant within the pH range 1—2) shifts the half-wave potential ($E_{1/2}$) towards more negative values. The limiting diffusion currents are not affected by increasing the concentration of hematoxylin ($i_d=ca.\ 3.5\,\mu\mathrm{A}$). This allows us to conclude that the number of electrons required by the metal ions and the formed complexes are the same. The splitting of the wave into two waves of equal height in the case of Cu(II) ion suggests the reduction of Cu(II) to Cu(I) and Cu(I) to Cu°. The half-wave potential for the first and second waves shifts from −0.29 and −0.58 V to −0.43 and −0.85 V respectively on raising the concentration of hematoxylin from 10^{-4} to $10^{-2}\,\mathrm{mol\,dm^{-3}}$.

Analysis of the polarographic waves by plotting $\log I/I_d-I$ *vs.* E gives straight lines with a slope of 30±2 mV. The half-width of the peak was 62±3 mV. These values indicate the reversible nature of the reduction process involving Zn(II), Cd(II) and Pb(II) and are in agreement with those calculated by Dillard and Hanck.[16)] However, in the case of the copper–hematoxylin complex, the irreversible nature of both waves was apparent with half-peak widths of 85 and 125 mV for the first and second waves, respectively. The plots of $\log i_l$ *vs.* $\log h$ give a stright line with a slope of 0.5±0.1 indicating that the current of the different waves is mainly controlled by diffusion.

The formation constants of the Zn(II), Pb(II) and Cd(II) complexes were calculated from Eq. 1. From the slope of the plots of ΔE_p *vs.* $\log C_x$ (Table 1), the coordination number J was found to be 2.0 for Zn(II) and Pb(II) and 6.0 for Cd(II). These results indicate the formation of 1:2 (M:L) complexes for Zn(II) and Pb(II) and a 1:6 (M:L) complex for Cd(II).

As shown in Table 2, the different values of $\log\beta$ for the complexes at different temperatures indicates that these values decrease as the ionic radii increase. Thus, for 1:2 (M:L) complexes $\log\beta_{Zn}>\log\beta_{Pb}$. The high value for the formation constant fo the Cd(II) complex is mainly due to the high coordination number. Thus, the order of decreasing formation constant for hematoxylin with metal ions is

Cd(II) > Zn(II) > Pb(II)

The thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ were calculated by standard methods (Table 2). Inspection of the values in Table 2 indicates that the formation of

---

* To whom correspondence should be addressed.

Table 1. Shift in ΔE_p with Increasing Hematoxylin Concentration at Different Temperatures

Temp. (K)	ΔE_p, *V. vs.* SCE Zn(II)			Pb(II)			Cd(II)		
	298	308	318	298	308	318	298	308	318
[X] mol dm^{-3}									
3×10^{-3}	0.100	0.090	0.080	0.030	0.020	0.010	0.020	0.012	0.010
5×10^{-3}	0.140	0.130	0.120	0.040	0.030	0.020	0.030	0.023	0.020
7×10^{-3}	0.190	0.160	0.150	0.050	0.040	0.025	0.040	0.033	0.029
1×10^{-2}	0.190	0.180	0.170	0.055	0.045	0.035	0.050	0.042	0.036
r	0.997	0.986	0.997	0.994	0.994	0.993	0.997	0.999	0.999
A	0.546	0.541	0.526	0.159	0.149	0.131	0.170	0.163	0.142
B	0.177	0.177	0.177	0.052	0.052	0.048	0.060	0.060	0.053
J	5.972	5.786	5.602	1.746	1.746	1.638	2.037	1.980	1.673

SCE = saturated calomel electrode. r = correlation coefficient, A = constant, B = regression coefficient and J = coordination number.

Table 2. Values of Formation Constants and Thermodynamic Parameters for the Zn(II), Pb(II) and Cd(II) Complexes

Temp. (K)	$\log \beta_{MXJ}$	$-\Delta G°$ (KJ mol^{-1})	$-\Delta H°$ (KJ mol^{-1})	$-\Delta S°$ (J mol^{-1})
ZN(II)				
298	5.750	32.81	113.14	276.9
308	5.338	31.48		
318	4.498	27.38		
Pb(II)				
298	5.387	30.74	111.80	271.0
308	4.885	28.81		
318	4.152	25.28		
Cd(II)				
298	18.476	105.42	161.12	185.5
308	17.736	104.59		
318	16.696	101.66		

the complexes are spontaneous, exothermic and entropically unfavorable. The value of $\Delta H°$, greater than $\Delta S°$, favors the reaction and, consequently gives a net negative value of $\Delta G°$. The entropy change of the complexes signifies a greater degree of order. The formation constants decrease with increasing temperature which means that the formation of complexes is favored at lower temperatures, as confirmed by the negative $\Delta H°$ values.

References

1) Taylor M. P., *Analyst*, **80**, 153 (1955).
2) Hatfield W. D., *Ind. Eng. Chem.*, **16**, 233 (1924).
3) Houghton G. U., *Analyst*, **68**, 208 (1943).
4) Dalal R. C., *Plant Soil*, **36**, 223 (1972).
5) Sarghie I., Sirghie E., *Rev. Chim.*, (Bucharest), **35**, 535 (1984).
6) Sarghie I., Sirghie E., *Rev. Chim.*, (Bucharest), **36**, 247 (1985).
7) Valero J., *Afindad*, **38**, 50 (1981).
8) Zhang Z., Chen T., Chen Y., *Huaxue Shiji*, **5**, 209, (1983) [*Chem. Abstr.*, **100**, 16893 (1984)].
9) Zhang Z., Qui J., Lin G., *Fenxi Hauaxe*, **11**, 591 (1983) [*Chem. Abstr.*, **100**, 79018 (1984)].
10) Zhang Z., Qui J., Lin G., *Gaodeng Xuexiao Huaxue Xuebao*, **5**, 39 (1984) [*Chem. Abstr.*, **100**, 184926 (1984)].
11) Croitrou V., Pirlog F., *Bull. Inst. Politech, Bucuresti, Ser. Chim. Metal*, **39** (1), 87 (1977) [*Chem. Abstr.*, **88**, 57991 (1978)].
12) Prakash O., Awasthi J. N., Mushran S. P., *Chim. Anal.* (Paris), **51**, 125 (1969).
13) Babko A. K., Karnaukhova N. N., *Zh. Anal. Khim.*, **22**, 868 (1976).
14) Heath G. A., Hefter C., *J. Electroanal. Chem.*, **84**, 295 (1977).
15) Lingane J. J., *Chem. Rev.*, **1**, 29 (1941).
16) Dillard J. M., Hanck K. W., *Anal. Chem.*, **48**, 216 (1976).