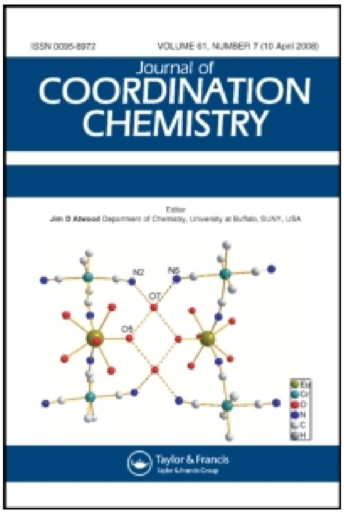

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SHORT COMMUNICATION
The Stability Constant of the Manganese(II) Monoazide Complex in Aqueous Solution

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INTRODUCTION

The stability constants of the monoazide complexes of cobalt(II),[1,2] nickel(II),[1,3,4,5] copper(II)[6–10] and zinc(II)[11,12] have been determined by various authors and some of them[1,4,6] concluded that the azide ligand obeys the Irving–Williams rule.[13] The purpose of this work is to determine the stability constant of the corresponding manganese(II) complex which has so far not been studied. The method employed is based on the use of competitive reactions through the use of copper(II) ions as an auxiliary species. The method is based in the measurement of absorbance due to the copper(II) monoazide species on solutions containing manganese(II) ions. The stability constant and molar absorption coefficients of CuN_3^+ species at certain wavelengths which are necessary for our calculations were initially determined by us.

EXPERIMENTAL

Copper(II) and manganese(II) perchlorates were prepared from corresponding C.P. carbonates and C.P. perchloric acid, a slight excess of the former being employed. Standardization of stock solutions of copper(II) and manganese(II) was carried out volumetrically by titration with EDTA.[14] The preparation, purification and standardization of stock solutions of sodium perchlorate and sodium azide was performed as described previously.[1] Spectrophotometric measurements were made with a Zeiss, model PMQII, spectrophotometer with cells of 1.00 cm. The pH values were measured as described previously.[1]

EQUATIONS

In the determination of the stability constant of copper(II) monoazide complex we used the following equations:

$$\frac{C_{Cu}\,C_L}{A(1+hK)} = \frac{C_{Cu}+C_L}{\epsilon(1+hK)} + \frac{1}{\epsilon\beta_{1,Cu}} \tag{1}$$

$$\frac{C_{Cu}\,C_L}{A(1+hK)} = \frac{C_{Cu}+C_L-A/\epsilon}{\epsilon(1+hK)} + \frac{1}{\epsilon\beta_{1,Cu}} \tag{2}$$

where the notation is the same used in a recent paper.[15] By plotting

$$\frac{C_{Cu}\,C_L}{A(1+hK)}$$

as a function of

$$\frac{C_{Cu}+C_L-A/\epsilon}{(1+hK)}$$

a straight line is obtained whose slope is $1/\epsilon$ and whose intercept is $1/\epsilon\beta_{1,Cu}$. For the application of Eq. (2) it is necessary to know the value of A/ϵ. The value of ϵ is obtained in a first calculation by using Eq. (1). Eq. (2) is valid if the monoazide complex is the only one formed which is achieved by choosing $C_{Cu} \gg C_L$. As moreover $[CuL] = A/\epsilon \ll C_{Cu} + C_L$, also Eq. (1) is valid with good approximation.

The formation constant of maganese(II) monoazide complex has been evaluated for each solution from the values of [Mn], [L] and [MnL].

As in our experimental conditions $C_{Mn} \gg C_L$, then

$$[Mn] \simeq C_{Mn} \tag{3}$$

The value of [L] has been calculated by the

TABLE I
Values of the molar absorption coefficients of CuN_3^+ species.

Wavelength, nm	350	360	365	370	375	380	390
$\epsilon.10^{-3}$	1.49	1.74	1.78	1.79	1.73	1.63	1.33

TABLE II
Experimental data for the calculation of $\beta_{1,Mn}$ $C_L = 5.060.10^{-4}$; I = 1.0 M; t = 25°C.

$C_{Cu}.10^3$	$C_{Mn}.10^2$	pH	350	360	365	370	375	380	390	β_1
2.648	14.72	5.37	0.137	0.163	0.167	0.166	0.160	0.152	0.123	4.8
4.237	14.72	5.26	0.199	0.234	0.241	0.240	0.234	0.220	0.179	4.6
5.296	7.360	5.21	0.266	0.312	0.322	0.322	0.313	0.296	0.243	4.3
5.296	11.04	5.29	0.246	0.289	0.298	0.298	0.289	0.272	0.222	4.9
5.296	14.72	5.19	0.231	0.272	0.279	0.277	0.270	0.255	0.207	4.7
5.296	18.40	5.18	0.217	0.256	0.262	0.262	0.254	0.240	0.196	4.3
5.296	22.08	5.15	0.208	0.240	0.250	0.249	0.243	0.228	0.187	4.4
5.296	25.76	5.24	0.196	0.231	0.237	0.235	0.228	0.215	0.177	4.7
7.944	14.72	5.29	0.306	0.359	0.370	0.370	0.358	0.337	0.275	4.5
9.533	14.72	5.21	0.337	0.394	0.406	0.404	0.392	0.370	0.301	4.6
13.24	14.72	5.09	0.390	0.458	0.471	0.471	0.457	0.429	0.352	4.8
13.24	22.08	5.12	0.360	0.425	0.438	0.436	0.424	0.398	0.324	4.7
13.24	25.76	5.07	0.347	0.404	0.418	0.418	0.406	0.382	0.312	4.7
15.89	14.72	4.97	0.422	0.498	0.510	0.511	0.498	0.468	0.384	4.3

equation

$$[L] = \frac{A}{\epsilon\beta_{1,Cu}(C_{Cu} - A/\epsilon)} \qquad (4)$$

which can be obtained by substituting the expressions $[CuL] = A/\epsilon$ and $[Cu] = C_{Cu} - A/\epsilon$ in the equilibrium constant expression for $\beta_{1,Cu}$.

Finally, by solving the equation of the mass balance on azide for [MnL] and taking into account that $[CuL] = A/\epsilon$ and $[HL] = hK\,[L]$, we obtain

$$[MnL] = C_L - [L](1 + hK) - A/\epsilon \qquad (5)$$

The equations (3), (4) and (5) are valid when $C_{Mn} \gg C_L$ and $C_{Cu} \gg C_L$ since under such conditions the monoazide complexes of copper(II) and manganese(II) are the only ones formed.

RESULTS

The stability constant of manganese(II) monoazide complex has been determined in ionic strength 1.0 and at 25°C. The values of the association constant of hydrazoic acid and the stability constant of copper(II) monoazide complex used in the calculations were $2.75.10^4$ [5,10] and $1.61.10^2$ respectively. This value of $\beta_{1,Cu}$, which was determined in this work, is in accordance to data obtained by Neves and Oliveira.[9] The values of the molar absorption coefficients obtained for the species CuN_3^+ at some wavelengths are shown in Table I. The experimental data necessary for the calculation of $\beta_{1,Mn}$ are shown in Table II. The average value obtained was 4.6 ± 0.3. We have also determined the value of $\beta_{1,Mn}$, by using cobalt(II) as an auxiliary species and the value obtained was 4.2 ± 0.3.

The value obtained for the stability constant of manganese(II) monoazide complex is in accordance to the conclusion[1,4,6] that the Irving–Williams rule[13] is obeyed in the case of the azide ligand.

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