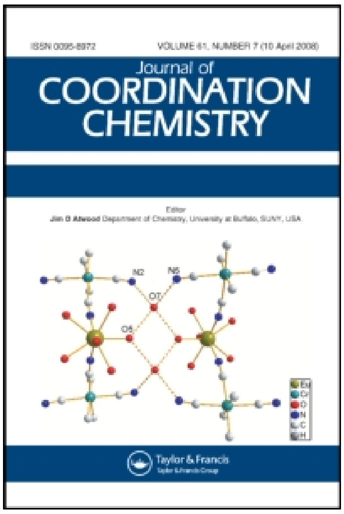

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POTENTIOMETRIC STUDY OF THE AZIDE COMPLEXES OF MANGANESE(II)

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INTRODUCTION

The manganese(II) azide system has been previously studied spectrophotometrically.[1] In that study, which was performed at ionic strength 1.0 M and at 25.0°C, only the first stability constant has been determined. In this paper we report the study of the manganese(II) azide system potentiometrically by the use of glass electrode measurements of solutions containing manganese(II) and azide-hydrazoic acid buffer. This study was performed at ionic strength 1.0 and at 25.0°C.

On the other hand the value of β_1 for iron(II) monoazide complex was determined by interpolation of the plot log β_1 vs atomic number for the first transition series.

EXPERIMENTAL

The preparation, purification and standardization of stock solutions of manganese(II) perchlorate, sodium azide and sodium perchlorate were performed as described previously.[1] The type of cell, the potentiometer and the electrodes used in the e.m.f. measurements were also described previously.[2]

The average ligand number, $\bar{n}$, for the formation of manganese(II) azide complexes is calculated by the equation:

$$\bar{n} = \frac{C_L - C_H + h - [L]}{C_M}$$

The values of the stability constants, β_j of manganese(II) azide complexes were calculated by the method of Fronaeus.[3] The value of the association constant of hydrazoic acid at ionic strength 1.0 M and at 25.0°C necessary to our calculations was obtained from literature.[4]

RESULTS AND DISCUSSION

The plot $\bar{n}/[L]$ vs $[L]$ is shown in Figure 1. The experimental data of the various titrations are given in the legend of this figure. The fact that the curves are the same for different values of C_M lead us to conclude on the non formation of polynuclear species. In the range of ligand concentration studied the experimental data are compatible with the formation of the species MnN_3^+ and $Mn(N_3)_2$. The values of the stability constants obtained by the method of Fronaeus[3] are: $\beta_1 = 4.3 \pm 0.4$ and $\beta_2 = 1.9 \pm 0.6$. This value of β_1 agrees fairly well with the value obtained spectrophotometrically, 4.6 ± 0.3.[1] The values of β_1 and β_2 that are obtained by the use of the method of Fronaeus as a polynomial function in $\bar{a}$[1 3] agrees with the above values. With the objective to check the above conclusions we have used the projection-strip method[5,6] and the values obtained are $\beta_1 = 4.4 \pm 0.5$ and $\beta_2 = 2.5 \pm 0.8$. By considering the values of β_1 for the first transition series various authors[7,8,9] have observed that the Irving Williams rule is obeyed in the case of azide ligand. A plot of the logarithm of the stoichiometric stability constants β_1, obtained at ionic strength 1.0 M and at 25°C, for the first transition series in function of the atomic number is shown in Figure 2. The values whose logarithms are used in this figure are 4.3 (this paper) and 4.6[1] for Mn; 5.3[7] and 5.8[2] for Co(II); 6.9[7] and 7.4[4] for Ni(II); $1.08 . 10^2$ [10] for Cu(II) and 5.73[11] for zinc(II) monoazide complex. As can be seen in Figure 2 it is possible to obtain by interpolation the value of the stoichiometric stability constant at ionic strength 1.0 M for the iron(II) monoazide complex. The value obtained in this manner is 4.9.

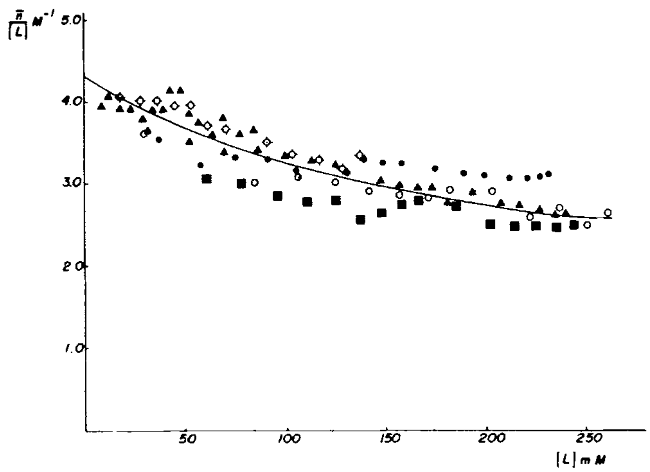

FIGURE 1 Plot $\bar{n}/[L]$ vs. $[L]$ for the manganese(II) azide system. ▲ – C_M = 53.55 mM, C_H = 14.65 to 13.59 mM, C_L = 29.52 to 113.9 mM. ▵ – C_M = 107.1 mM, C_H = 25.10 mM, C_L = 36.78 to 279.2 mM. ■ – C_M = 53.55 mM, C_H = 50.12 mM, C_L = 120.4 to 327.1 mM. ● – C_M = 70.03 mM, C_H = 50.12 mM, C_L = 96.53 to 333.0 mM. ⊙ – C_M = 32.32 mM, C_H = 50.12 mM, C_L = 83.30 to 333.0 mM. ◇ – C_M = 32.32 mM, C_H = 14.71 to 13.37, C_L = 34.87 to 166.6 mM.

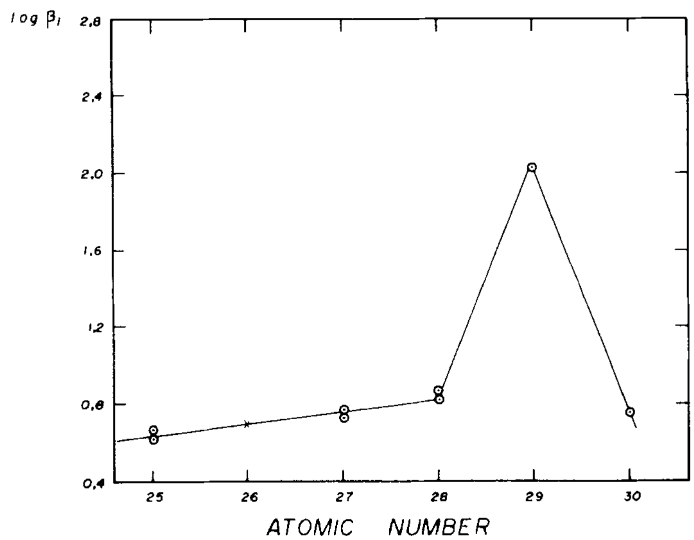

FIGURE 2 Plot of log β_1 for the first transition series in the case of the azide ligand. ⊙ – Experimental values of β_1; X-value of β_1 for iron(II) monoazide complex obtained by interpolation.

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