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On the Hydrolysis of Manganese(II) in 1 *M* (Na_2,Mn)SO_4 Ionic Medium at 25°C*

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The hydrolysis of manganese(II),

$$q\,Mn^{2+} + p\,H_2O \rightleftharpoons Mn_q(OH)_p^{2q-p} + p\,H^+ \qquad (1)$$

in 1 *M* (Na_2Mn)SO_4 as self-ionic medium[1] and with the total manganese(II) concentrations, *B*, 0.1, 0.25, 0.5, and 1.0 *M* at 25°C was studied. Previous works on the above equilibrium (1) report the formation of only $MnOH^+$ complex.[2]

The stability constants for the formation of the complexes $Mn_q(OH)_p^{2p-q}$ (briefly designed as (p,q)) are given by the expression

$$\beta_{pq} = \Phi_B\, C_{pq}\, b^{-q}\, h^p \qquad (2)$$

where Φ_B represents the product of activity factors for each total concentration of manganese(II) and C_{pq}, *b*, and *h* respectively mean the equilibrium concentrations of the complexes (p,q), of Mn^{2+} and H^+.

As usual in ionic medium work, a formula like $MnOH^+$ or Mn^{2+} means the sum of all complexes containing, *i.e.*, $MnOH^+$ and various amounts of solvent species (H_2O, Na^+, SO_4^{2-}, HSO_2^-).[3] From studies on the hydrolysis of UO_2^{2+} in different ionic media, Sillén *et al.*[4] found that although there may certainly be association of anions with both UO_2^{2+} and UO_2—OH complexes, the main species are the same for all the media used.

Because the activity factors in strongly concentrated ionic media can be assumed to be constant and equal to unity by choosing proper standard states,[5] and the manganese(II) hydrolysis is very small, we can take $\Phi_B = 1$ for each experiment of constant concentration *B*. The mass balance can then be given by the equations

$$B = b + \sum_p \sum_q q\beta_{pq}\, b^q\, h^{-p} \qquad (3)$$

$$BZ = \sum_p \sum_q p\beta_{pq}\, b^q\, h^{-p} \qquad (4)$$

in which *Z* is the average number of OH^- bound or H^+ split per Mn^{2+} in equilibrium (1).

On the other hand, taking into account the HSO_4^-—SO_4^{2-} equilibrium, as we used SO_4^{2-} as counter ion, we have,

$$B = b + \sum_p \sum_q q\beta^*_{pq}\, b^q\, h^{*-p} \qquad (3a)$$

$$BZ(=h^*-H) = \sum_p \sum_q p\beta^*_{pq}\, b^q\, h^{*-p} \qquad (4a)$$

where, *H* is the total (analytical) concentration of H^+, h^* represents the sum of the free concentration of H^+ and HSO_4^-, and β^*_{pq} is an apparent stability constant. It can be shown[6,7] that h^* and β^*_{pq} are given by the expressions

$$h^* = (1+K_1(1-\Theta))\,h \qquad (5)$$

$$\beta^*_{pq} = (1+K_1(1-\Theta))^p\,\beta_{pq} \qquad (6)$$

where Θ is the average number of H^+ bound as HSO_4^- per SO_4^{2-} and K_1 is the stability constant for the HSO_4^-—SO_4^{2-} equilibrium. However, because $K_1 \simeq 2.5M^{-1}$ [6] and $\Phi \simeq 0$ for $h < 10^{-3}M$, it follows that h^* and β^*_{pq} are proportional to *h* and β_{pq}, respectively.

We measured h^* by means of the cell

$$REF // S /\ H_2,\ \text{Pt and glass electrode} \qquad (7)$$

where the reference half cell $REF = 1\,M$ Na_2SO_4/ 0.99 *M* Na_2SO_4, 0.01 *M* Ag_2SO_4/Ag, AgCl was placed in a Wilhelm bridge[8] and the solution *S* was *B M* $MnSO_4$, *H*/2 *M* H_2SO_4, $(1-B-H/2)$ *M* Na_2SO_4.

We found that at 25°C the emf of (7) follows[6,7,9] the equation

$$E = E_o + kB + jh^* + 59.15 \log h^* \qquad (8)$$

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Table I.

(p,q)	$-\log \beta^*_{pq}$					
(1,1)	10.5±0.1	10.46±0.05	10.47±0.03	10.51±0.05	10.47±0.02	10.58±0.02
(1,2)	9.9±0.1	9.87±0.05	9.82±0.06	9.92±0.05	9.91±0.02	9.94±0.02
(3,2)	25.4±0.1	25.47±0.10	25.51±0.02	25.25±0.03	25.37±0.03	25.34±0.03
$\sigma(Z)10^3$	—	0.6	0.4	0.5	0.2	0.1
B (M)	0.1-1.0	0.1-1.0	0.1	0.25	0.5	1.0

The constants E_o, k and j were determined for $h^* > 10^{-5}\,M$ when $Z=0$; Z and $-\log h^*$ were increased[10] generating OH$^-$ *in situ* by electrolysis with the following cell

$$\text{(anode)Ag}/0.1\,M\ \text{NaCl},\ 0.95\,M\ \text{Na}_2\text{SO}_4/1\,M\ \text{Na}_2\text{SO}_4//S/\text{Pt(cathode)} \qquad (9)$$

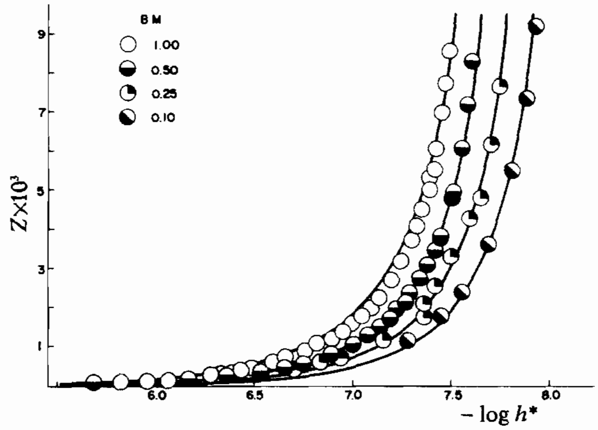

Figure 1. Z as a function of $\log h^*$. The curves are calculated with the equilibrium constants given in column 3 of Table I.

A constant current intensity of 1 mA was used.

The experimental data $Z(\log h^*)_B$, Figure 1, was treated by graphic methods[1,11] and Letagrop.[12]

Using graphic methods we obtained information on the p values from each B constant curve and on the q values from the relative positions of all $Z(\log h^*)_B$ curves assuming contancy of the activity factors. Letagrop was used then for testing the different hypotheses.

The best fit was found for the complexes (p,q) with the $\log \beta^*_{pq}$ and the standard deviations $\sigma(Z)$ values indicated in Table I. Column 2 contains the $\log \beta^*_{pq}$ values obtained from the treatment of all data sets by graphic methods and column 3 the refinements on the latter by Letagrop. Finally, columns 4, 5, 6 and 7 show the refined stability constants for $B = 0.1$, 0.25, 0.5, and 1.0 M respectively, assuming for each B constant curve the same values of (p,q) used in the previous treatment of all data sets.

Experimental work is continued.

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