Spectrophotometric Studies on the Monomer–Monomer Equilibration of Mo(VI) in Hydrochloric Acid Solutions

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The equilibration of monomeric forms of Mo(VI) in the HCl concentration range 0.02–6 M *has been investigated spectrophotometrically. The equilibria occurring in hydrochloric acid solutions involve a protonation step of* $Mo(OH)_6$ *to* $Mo(OH)_5(H_2O)^+$*, followed by a two-step complex formation. The first-step complex formation reaction, showing a first-order dependence on* $[H^+]$ *and a second-order dependence on* $[Cl^-]$*, is represented by the equation:*

$$Mo(OH)_5(H_2O)^+ + H^+ + 2Cl^- = Mo(OH)_4Cl_2 + 2H_2O$$

At higher HCl concentrations, the second-step reaction shows a first-order dependence on either $[H^+]$ *or* $[Cl^-]$*:*

$$Mo(OH)_4Cl_2 + H^+ + Cl^- = Mo(OH)_3Cl_3 + H_2O$$

The values of the equilibrium constants were determined at ionic strength $I = 4.0$*.*

Introduction

A number of attempts to identify the Mo(VI) species existing in hydrochloric acid have been reported. Methods employed in these studies were mainly ultraviolet (UV) spectrophotometry [1], ion-exchange [2, 3], solvent extraction [4, 5] and Raman spectroscopy [6, 7]. According to Kraus *et al.*, neutral and anionic species are present above 4 *M* HCl; the charge of the anionic species was not established. Aveston *et al.* concluded that MoO_2Cl_2 exists in 3.6–9.6 *M* HCl. Neumann and Cook claim that MoO_2Cl_2 predominates in this acidity range and a 1:3 Mo(VI)/Cl species becomes important at greater acidities. Nelidow and Diamond report that the Mo(VI) species extracted by ethers are MoO_2Cl_2, $MoO_2Cl_3^-$ and $MoO_2Cl_4^{2-}$, but Zharovskii claims that $HMoO_2Cl_3$ is also extracted.

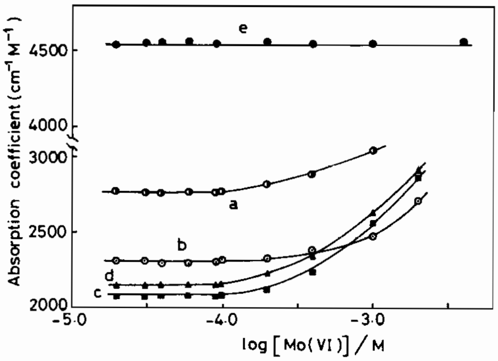

Fig. 1. Dependence of ϵ on Mo(VI) concentration. [HCl] /*M*; a, 0.1; b, 0.4; c, 1.0; d, 2.0; e, 6.0.

Generally acceptable conclusions do not seem to have been achieved, due to a lack of precise knowledge of the species present. It therefore seems desirable to investigate the equilibria between monomeric Mo(VI) species present in hydrochloric acid, with a view to determining the stoichiometry and the equilibrium constants.

Experimental

UV spectra were measured on a Hitachi spectrophotometer, Model 220-A. All reagents were of analytical reagent grade; Mo(VI) solutions were prepared from $Na_2MoO_4 \cdot 2H_2O$. Sodium perchlorate was recrystallized twice from water.

Results

Determination of the Stoichiometry and Preliminary Constants

Figure 1 shows the relationship between the molar absorption coefficient ϵ at 240 nm and the Mo(VI)

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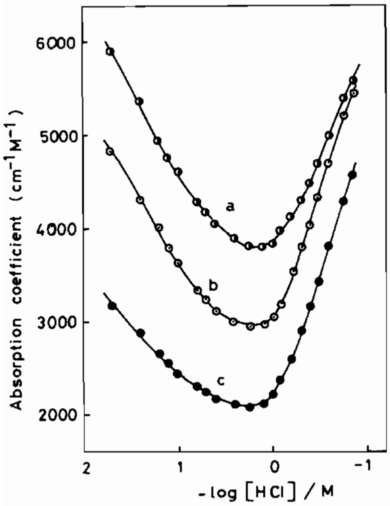

Fig. 2. Average ϵ values as a function of $-\log[HCl]$. Wavelengths/nm; a, 220; b, 230; c, 240. The dots indicate experimental points. The solid lines are calculated from the constants in Table IV.

concentration in various concentrations of HCl. The ϵ value increases at Mo(VI) concentrations greater than 1×10^{-4} *M*, suggesting the formation of dimeric species which have greater ϵ values than the values of the monomeric species [8–11]. On the other hand, the ϵ value remains constant for Mo(VI) concentrations below 8×10^{-5} *M*, which indicates that no dimer formation occurs under these conditions.

Figure 2 shows the average ϵ values for the Mo(VI) concentration range 2–8×10^{-5} *M* in 0.02–4 *M* HCl adjusted to $I = 4.0$ with sodium perchlorate; no indifferent electrolyte was added to the solutions of 5 and 6 *M* HCl. A discussion on the effect of the ionic strength is presented in a later part of this paper. The ϵ data at 220 and 230 nm are also included in the Figure. In the HCl concentration range 0.02–0.4 *M*, the ϵ value decreased with an increase in the HCl concentration. This behavior, which is quite analogous to that observed in perchloric acid [8] and sulfuric acid [10], has been explained by the protonation of $Mo(OH)_6$ to $Mo(OH)_5(H_2O)^+$.

The protonation reaction is represented by the equation

$$Mo(OH)_6 + H^+ = Mo(OH)_5(H_2O)^+ \tag{1}$$

It can be readily shown that

$$K_1 = \frac{(\epsilon_0 - \epsilon_{obs})}{(\epsilon_{obs} - \epsilon_1)[H^+]} \tag{2}$$

where K_1 is the protonation constant, ϵ_{obs} is the observed ϵ value, and ϵ_0 and $\epsilon_1$are the molar absorption coefficients of $Mo(OH)_6$ and $Mo(OH)_5(H_2O)^+$,

TABLE I. Values for K_1, ϵ_0 and ϵ_1 at 240 nm.

	in HCl	in $HClO_4$[a]	in H_2SO_4[a]
ϵ_0	3790 ± 20	3830 ± 10	3760 ± 30
ϵ_1	1840 ± 20	1810 ± 10	1860 ± 30
K_1	20 ± 2	19.1 ± 1	22.4 ± 1.8

[a] Ref. 10.

respectively. The three unknowns, ϵ_0, ϵ_1 and K_1 were determined from the ϵ_{obs} values at 240 nm in the HCl concentration range 0.02–0.2 *M* by solving eqn. 2 through a least squares procedure, and were compared with the values obtained in $HClO_4$ and H_2SO_4 solutions [10]. The results are given in Table I. As can be seen, the ϵ_0 and ϵ_1 values are in agreement with the ϵ_0 and ϵ_1 values obtained in $HClO_4$ and H_2SO_4, which indicates that the protonation of $Mo(OH)_6$ to $Mo(OH)_5(H_2O)^+$ occurs in dilute HCl solutions.

Above 0.4 *M* HCl, the observed ϵ value increased with an increase in the HCl concentration, which was similar to the behavior observed in H_2SO_4 solutions [10]. This result suggests that the complex formation between Mo(VI) and Cl^- occurs under these conditions.

The complex formation reaction can be written as

$$Mo(OH)_5(H_2O)^+ + aH^+ + bCl^- =$$

$$= Mo(OH)_{5-a}Cl_b^{a-b+1} + (a+1)H_2O \tag{3}$$

The equilibrium constant, K_2 is given by

$$K_2 = \frac{[Mo(OH)_{5-a}Cl_b^{a-b+1}]}{[Mo(OH)_5(H_2O)^+][H^+]^a[Cl^-]^b} \tag{4}$$

Combining eqns. 1 and 4 gives the expression:

$$\log(\epsilon' - \epsilon'_{obs})/(\epsilon_{obs} - \epsilon_2) =$$

$$= a\log[H^+] + b\log[Cl^-] + \log K_2 \tag{5}$$

where $\epsilon' = \epsilon_0/K_1[H^+] + \epsilon_1$, $\epsilon'_{obs} = \epsilon_{obs}(1/K_1[H^+] + 1)$ and ϵ_2 is the molar absorption coefficient of complex (I); ϵ' is the absorption coefficient of $Mo(OH)_5(H_2O)^+$ corrected for the contribution of $Mo(OH)_6$ at the equilibrium concentration.

To determine a, ϵ values were measured for the solutions containing 4×10^{-5} *M* Mo(VI), 1 *M* NaCl and different concentrations of $HClO_4$ (0.4–2 *M*). Measurements to determine b were made by keeping the $HClO_4$ concentration at 1 *M* while varying the NaCl concentration from 0.4 to 2 *M*. The ionic

TABLE II. ϵ_{obs} Values at 240 nm.

I	HCl (M)	NaCl (M)	ϵ_{obs} ($cm^{-1}\ M^{-1}$)	HCl (M)	$HClO_4$ (M)	ϵ_{obs} ($cm^{-1}\ M^{-1}$)
4	2	0	2880	2	0	2880
4	2	0.5	2940	2	0.5	2920
4	2	1.0	3110	2	1.0	3060
4	2	1.5	3140	2	1.5	3180
4	2	2.0	3190	2	2.0	3310

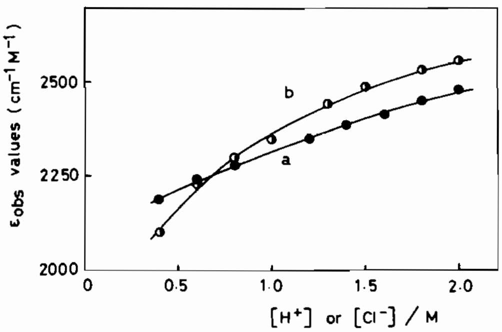

Fig. 3. ϵ_{obs} values with variation of a, $[H^+]$; b, $[Cl^-]$. [Mo(VI)]/M; 4 × 10^{-5}, I = 4.0.

TABLE III. Effect of Ionic Strength on ϵ_{obs} Values at 240 nm.

HCl (M)	$NaClO_4$ (M)	ϵ_{obs} ($cm^{-1}\ M^{-1}$)	HCl (M)	ϵ_{obs} ($cm^{-1}\ M^{-1}$)
4	0	3730	4	3730
4	1	3880	5	4190
4	2	3970	6	4550

strength of the solutions was maintained at 4.0 with $NaClO_4$. The results are given in Fig. 3. Eqn. 5 contains ϵ_2 as an unknown parameter. The least squares treatment was therefore used by substituting a provisional value for ϵ_2 in eqn. 5.

With the change of the provisional value, the treatment was repeated until the best fit of the data to eqn. 5 was obtained. When ϵ_2 = 2800 ± 100 cm^{-1} M^{-1}, the experimental data given in Fig. 3 are best fitted to eqn. 5, giving approximate values of a = 1.1_8, b = 1.9_1 and K_2 = 0.7. This means that we can write the complex formation reaction as

$$Mo(OH)_5(H_2O)^+ + H^+ + 2Cl^- =$$

$$= Mo(OH)_4Cl_2 + 2H_2O \qquad (6)$$

Since the observed ϵ values beyond 2 M HCl are greater than the ϵ_2 value, a further equilibrium

$$Mo(OH)_4Cl_2 + cH^+ + dCl^- =$$

$$= Mo(OH)_{4-c}Cl_{d+2}^{c-d} + cH_2O \qquad (7)$$

must be taken into account in addition to the equilibrium 6. Using eqns. 1 and 6 it can be shown that

$$K_3 = \frac{(\epsilon' - \epsilon'_{obs})}{(\epsilon_{obs} - \epsilon_3)[H^+]^c[Cl^-]^d} \qquad (8)$$

where $\epsilon' = \epsilon_0/K_1K_2[H^+]^2[Cl^-]^2 + \epsilon_1/K_2[H^+][Cl^-]^2 + \epsilon_2$, $\epsilon'_{obs} = \epsilon_{obs}(1/K_1K_2[H^+]^2[Cl^-]^2 + 1/K_2[H^+][Cl^-]^2 + 1)$ and ϵ_3 is the molar absorption coefficient of complex (II).

In order to determine c and d in eqn. 8, measurements were made where the $HClO_4$ concentration was varied from 0 to 2 M at constant [HCl] of 2 M and the NaCl concentration was varied from 0 to 2 M at constant [HCl] of 2 M. The results are given in Table II. The least squares treatment was made by using the known values, K_1 = 20, K_2 = 0.7, ϵ_0 = 3790, ϵ_1 = 1840, ϵ_2 = 2800 and provisional ϵ_3 values for the logarithmic form of eqn. 8. When ϵ_3 = 5600 ± 300, the results of c = 1.5_4 and d = 1.2_1 were obtained.

The data in the HCl concentration range 2–6 M given in Fig. 2 were treated by the same least squares method as mentioned above. Before treating eqn. 8, the effect of ionic strength on the observed ϵ value was investigated. As shown in Table III, the ϵ_{obs} value in 4 M HCl increased with an increase in the ionic strength of the solution from 4.0 to 6.0; no experiments were possible above 3 M $NaClO_4$ due to the appearance of crystalline sodium chloride. The ϵ value of 3880 cm^{-1} M^{-1} at 4 M HCl and I = 5.0 agrees with the value at 4.30 M HCl (I = 4.30) in the ϵ *vs.* [HCl] curve. Similarly the ϵ value of 3970 cm^{-1} M^{-1} at 4 M HCl and I = 6.0 is equal to the value at 4.48 M HCl (I = 4.48). The results mean that the increase of I from 4.0 to 5.0 corresponds to the increase by 0.30 M of the HCl concentration, and the increase of I from 4.0 to 6.0, to the increase by 0.48 M. We can therefore regard the ϵ_{obs} values

TABLE IV. Final Values for ϵ Values of Individual Species and Equilibrium Constants.

λ (nm)	ϵ_0	ϵ_1	ϵ_2	ϵ_3	K_1	K_2	K_3
220	6980 ± 40	3550 ± 40	4300 ± 40	6280 ± 40	20.8 ± 2	0.30 ± 0.03	0.034 ± 0.005
230	5790 ± 50	2670 ± 50	3910 ± 50	6250 ± 50	19.8 ± 2	0.26 ± 0.03	0.042 ± 0.005
240	3760 ± 50	1890 ± 50	2940 ± 50	5440 ± 50	20.2 ± 2	0.32 ± 0.03	0.033 ± 0.005
Average					20.3 ± 2	0.29 ± 0.03	0.036 ± 0.005

in 5 *M* HCl (I = 5.0) and 6 *M* HCl (I = 6.0) as the values in 5.54 *M* and 6.95 *M* HCl (I = 4.0), respectively. In Fig. 2, the ϵ values in 5 and 6 *M* HCl are plotted against the reduced [HCl] values for I = 4.0. In this case we obtained the value of (c + d) = 2.1_7 when ϵ_3 = 5500 ± 200 cm^{-1} M^{-1}. On the basis of these results, we can estimate the value of c = d = 1. The formation of complex (II) can then be represented by

$$Mo(OH)_4Cl_2 + H^+ + Cl^- = Mo(OH)_3Cl_3 + H_2O \quad (9)$$

Refinement of the ϵ Values and Equilibrium Constants

Having established the equilibria involved in the Mo(VI)–HCl system, refined values for the ϵ values and equilibrium constants were calculated according to the equation,

$$[Mo(OH)_6](\epsilon_0 - \epsilon_{obs}) + [Mo(OH)_5(H_2O)^+](\epsilon_1 - \epsilon_{obs})$$
$$+ [Mo(OH)_4Cl_2](\epsilon_2 - \epsilon_{obs}) +$$
$$+ [Mo(OH)_3Cl_3](\epsilon_3 - \epsilon_{obs}) = 0 \quad (10)$$

Combination of eqns. 1, 6 and 9 gives the expression $\epsilon_1 + \epsilon_0/K_1 \cdot 1/[H^+] - 1/K_1 \cdot \epsilon_{obs}/[H^+] + K_2\epsilon_2 \cdot [H^+] \cdot [Cl^-]^2 - K_2 \cdot \epsilon_{obs}[H^+][Cl^-]^2 + K_2K_3\epsilon_3 \cdot [H^+]^2[Cl^-]^3 - K_2K_3 \cdot \epsilon_{obs}[H^+]^2[Cl^-]^3 = \epsilon_{obs}$ where $[H^+]$, $[Cl^-]$ and ϵ_{obs} are variables.

The unknown constants, ϵ_0, ϵ_1, ϵ_2, ϵ_3, K_1, K_2 and K_3 can be determined by applying a least squares method to the experimental data given in Table II and Figs. 2 and 3. The results are summarized in Table IV, which also includes the results obtained by the data at wavelengths of 220 and 230 nm.

Using the constants (average values for the equilibrium constants) given in Table IV, the absorption curves at wavelengths of 220, 230 and 240 nm were calculated and are shown by the solid lines in Fig. 2. The excellent fit of the theoretical curves to the experimental points shows that the equilibria (1), (6) and (9) give a satisfactory description of the Mo(VI)–HCl system over the HCl concentration range 0.02–6 *M*.

Discussion

In the present investigation, the equilibria in the Mo(VI)–HCl system were established in the HCl concentration range 0.02–4 *M* adjusted to I = 4.0; in this acidity range, the protonation of $Mo(OH)_6$ to $Mo(OH)_5(H_2O)^+$ occurs, followed by a two-step complex formation reaction. The fraction, α of each species was calculated using the average equilibrium constants given in Table IV and shown in Fig. 4. It was found that the equilibria depended on the ionic strength of the solution (Table III). No evidence for the formation of a 1:1 Mo(VI)/Cl complex was obtained.

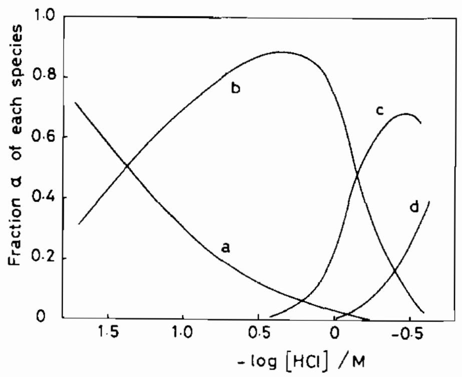

Fig. 4. Fraction α of each species. a, $Mo(OH)_6$; b, $Mo(OH)_5(H_2O)^+$; c, $Mo(OH)_4Cl_2$; d, $Mo(OH)_3Cl_3$.

There seems to be general agreement that Mo(VI) has tetrahedral coordination in MoO_4^{2-} [12, 13], but the coordination is octahedral in the protonated form, H_2MoO_4 [14, 15]. On this basis the formulae of the Mo(VI)–Cl complexes were written tentatively as $Mo(OH)_4Cl_2$ and $Mo(OH)_3Cl_3$. On the basis of Raman spectroscopy, however, the octahedral Mo(VI)–Cl complex with a *cis*-MoO_2 group has been postulated [7]. If we follow the postulation, we can write complex (I) as $MoO_2Cl_2(H_2O)_2$, and complex (II) as $HMoO_2Cl_3H_2O$ or $MoO(OH)Cl_3 \cdot H_2O$.

To determine the precise formulae and geometries of the complexes, Raman measurements of Mo(VI) in various concentrations of HCl are being undertaken in this laboratory.

There is some doubt whether $MoO_2Cl_3^-$ or $MoO_2Cl_4^{2-}$ is the predominant species in concentrated HCl solutions. In order to explain the anion-exchange behavior of Mo(VI) in hydrochloric acid, the formation of a complex $MoO_2Cl_4^{2-}$ has been postulated at greater acidities [2, 4]. Neumann and Cook [1] isolated the complex containing Mo(VI) and Cl in the ratio of 1:4. However, due to the limit of the ionic strength in this experiment, no attempts were made to obtain information on the 1:4 Mo(VI)/Cl complex.

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