

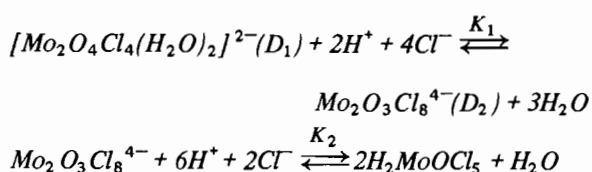
Polarographic and Spectrophotometric Studies on the Equilibration of Mo(V) Species in HCl Solutions

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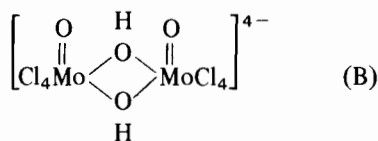
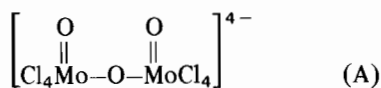
The equilibration of Mo(V) species has been investigated in 0.5–5 M HCl ($I = 5.0$). The equilibria involve the dimer(D_1)–dimer(D_2) interconversion, followed by the decomposition of D_2 to a monomeric form at greater acidities:



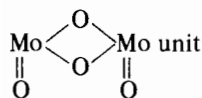
The equilibrium constants have been determined as $K_1 = 2 \pm 0.3$ and $K_2 = (1.5 \pm 0.4) \times 10^{-8}$ at 25 °C.

Introduction

A number of studies have been carried out of the behavior of Mo(V) in HCl solutions, and monomer–dimer equilibria have been proposed [1–4]. It is generally agreed that the principal species in fairly concentrated HCl ($> 8 M$) is the monomeric ion MoOCl_5^{2-} . In 5–6 M HCl, a dimer is formed for which structures A and B are suggested:

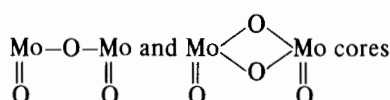


Haight favors structure A [2] while Colton and Rose favor structure B [4]. According to Colton and Rose [4], a dimer with structure A exists at lower acidities (1–3 M). On the other hand, Ardon and Pernick have postulated that a dimer with the



predominates in 1 M HCl [5].

Our recent Raman studies have shown that a monomer with the Mo=O core, and two dimers with the



are present according to the HCl concentration; all the species are chloro-complexes [6]. However, the detailed structures of the complexes have not been deduced from the Raman results.

In the present work the solution equilibria of the Mo(V)–HCl system are studied in detail, and structural features of the Mo(V) species are considered. The data were obtained by polarographic and ultraviolet (UV) spectrophotometric methods.

Experimental

UV spectra were recorded with a Hitachi Model 220-A spectrophotometer. Polarographic measurements were made with a PAR Model 174-A polarographic analyzer equipped with a Model 172-A drop-time controller and a Riken Denshi Model D-8CP X–Y recorder. The capillary had an $m^{2/3}t^{1/6}$ value of $1.765 \text{ mg}^{2/3} \text{ s}^{-1/2}$ in 1 M HCl with an open circuit. All potentials were measured against a saturated calomel electrode (SCE) with the use of a Kikusui Model 156-A digital voltmeter. Measurements were made at 25 ± 0.1 °C.

All chemicals were of analytical grade. Molybdenum(V) solutions were prepared by dissolving $(\text{NH}_4)_2\text{MoOCl}_5$ [7], and stored under nitrogen; Mo(VI) solutions were prepared from $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$; Mo(IV) solutions were prepared by heating an equimolar mixture of $(\text{NH}_4)_2\text{MoOCl}_5$ and K_3MoCl_6 (Climax Molybdenum Co.) under nitrogen at 90 °C in 3 M HCl [8].

Results

Polarographic Behavior

Figure 1 shows DC polarograms of 0.4 mM Mo(VI) in 0.1 M HCl with natural drop and forced drop

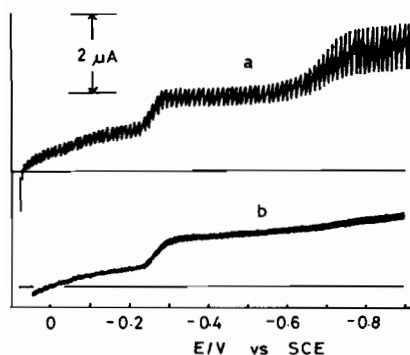


Fig. 1. DC polarograms of 0.4 mM Mo(VI) in 0.1 M HCl: a, with natural drop; b, with forced drop ($t = 0.5$ s).

($t = 0.5$ s) methods. There are no well-defined waves at more positive potentials than -0.20 V with both methods. With natural drop, two reduction waves are defined with half-wave potentials ($E_{1/2}$) of -0.27 and -0.74 V, while the latter wave is not found with a drop time of 0.5 s or for Mo(VI) concentrations $< 8 \times 10^{-5}$ M. This is analogous to the behavior observed in 0.1 M H_2SO_4 [9], which suggests that the former and latter reduction waves are ascribed to the reduction of a monomeric and a dimeric Mo(V) to Mo(III) respectively. Wittick and Rechnitz have postulated that the former wave is due to the reduction of Mo(VI) to Mo(IV), and the latter wave to the reduction of Mo(V) to Mo(III) in 0.1 M HCl [10]. According to them, the Mo(IV) species disproportionates rapidly to Mo(V) and Mo(III). However, Souchay *et al.* have prepared pure Mo(IV) which is very stable; it does not undergo disproportionation in acidic solutions [8]. In addition, Lamache-Duhameaux and Souchay have shown that no polarographic waves are ascribed to the reduction of Mo(VI) or Mo(V) to Mo(IV) [11]. A DC polarogram of Mo(IV) exhibits a reduction wave with $E_{1/2}$ of -0.48 V in 0.1 M HCl. According to Lamache-Duhameaux [12], the wave represents the reduction of Mo(IV) to Mo(III). As shown in Fig. 1, the polarographic reduction of Mo(VI) does not produce the reduction wave at -0.48 V, which indicates that no Mo(IV) species is formed at the electrode.

As the HCl concentration is increased, $E_{1/2}$'s of both waves become more positive. Simultaneously, the wave due to the reduction of the dimeric Mo(V) decreases in height, which may be due to the lower tendency of Mo(V) to dimerize at greater acidities. In trifluoromethanesulfonic acid, similar observations have been reported by Chalilpoyil and Anson [13], who have concluded that both monomeric and dimeric Mo(V) species are reduced to dimeric Mo(III), $Mo_2(III)$. It is shown that Mo(V) formed by the reduction of Mo(VI) adsorbs onto the electrode surface in acidic solutions, which may make the reduction of Mo(VI) to Mo(V) less defined [13–15].

TABLE I. Peak-potentials in Differential Pulse Polarography.^a

[HCl]/M	Mo(VI) (V vs. SCE)	Mo(V) (V vs. SCE)
0.1	-0.29 -0.75	-0.75
0.5	-0.18 -0.73	-0.73
1.0	-0.14 -0.68	-0.68
2.0	-0.10 -	-0.56

^aDrop time, 1 s; ΔE , 25 mV.

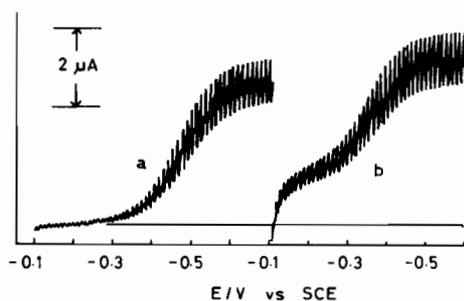


Fig. 2. DC polarograms of 1.0 mM Mo(V) in HCl. [HCl]/M: a, 2; b, 3.4.

A DC polarogram of Mo(V) in 0.1 M HCl shows a reduction wave, denoted as wave A, with $E_{1/2}$ of -0.74 V. In differential pulse polarography, as shown in Table I, the peak-potentials (E_p) of wave A are identical with those of the reduction waves of a dimeric Mo(V) to Mo(III). It is therefore reasonable to attribute wave A to the reduction of a dimeric Mo(V) to Mo(III). It is interesting to note that E_p of wave A is independent of the Mo(V) concentration in the range of 0.01–1.0 mM in 0.1 M HCl, which suggests that Mo(V) exists as a dimer even in the concentration of 0.01 mM. By the polarographic reduction of Mo(VI), as mentioned above, the monomeric Mo(V) is formed in the vicinity of the electrode. This result shows that no dimerization equilibrium is attained at the electrode surface during the drop life, which is similar to the behavior observed in 0.1–1 M H_2SO_4 [16].

Figure 2 shows DC polarograms of 1.0 mM Mo(V) in 2 and 3.4 M HCl adjusted to $I = 5.0$ with $NaClO_4$. Above 2 M HCl a new wave, denoted as wave B, appears at more positive potentials than wave A (curve b). Both waves are diffusion-controlled, which suggests that two species are present under these conditions. With an increase in the HCl concentration, the current of wave B increases at the expense of wave A (Fig. 3). The results can be interpreted in terms of the monomer–dimer interconversion [1–4]; wave B is due to the reduction of a monomeric Mo(V) to Mo(III). This is in agreement with earlier observations that the reduction potential for the monomeric Mo(V) is more positive than that for the dimeric Mo(V).

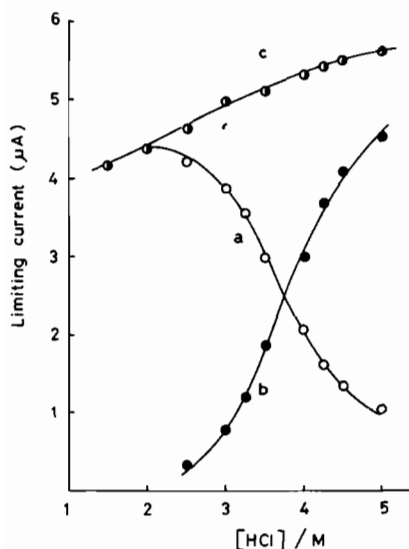


Fig. 3. Relationship between limiting currents of 1.0 mM Mo(V) and HCl concentrations. a, wave A; b, wave B; c, total wave. $I = 5.0$.

Raman measurements have shown that the following reactions occur in HCl solutions [6]:



where D_1 and D_2 are dimers with the Mo_2O_4 and Mo_2O_3 cores respectively and M represents a monomer. The equilibrium constants are given by

$$K_1 = \frac{[D_2]}{[D_1][H^+]^a[Cl^-]^b} \quad (3)$$

$$K_2 = \frac{[M]^2}{[D_2][H^+]^c[Cl^-]^d} \quad (4)$$

It is unlikely that the reduction potentials for both dimers are identical. With the reasonable assumption that only a monomer and a dimer are present under the conditions of Fig. 3, eqn. (4) can be written as

$$\log\left(\frac{[M]^2}{[D_2]}\right) = c \log[H^+] + d \log[Cl^-] + \log K_2 \quad (5)$$

Measurements to determine the stoichiometric coefficient, c were made by keeping $[Cl^-]$ at 5 M while varying $[H^+]$ from 2 to 5 M. The value of d was determined by measuring solutions in which $[H^+]$ was kept constant at 3 M while $[Cl^-]$ was varied from 1 to 5 M. The Mo(V) concentration of 1.0 mM was employed, and the ionic strength of the solutions was kept constant at 5.0 with $NaClO_4$. The results are given in Fig. 4. In Figs. 3 and 4, the limiting current of wave B (i_B) was measured at

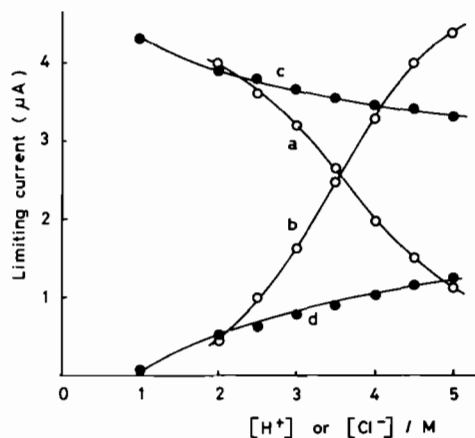


Fig. 4. Limiting currents with variation of $[H^+]$ (a, b) or $[Cl^-]$ (c, d). a, c, wave A; b, d wave B. $[Mo(V)]$; 1.0 mM, $I = 5.0$.

-0.20 V while the current of wave A (i_A) was taken as equal to the total current minus i_B .

The currents can be given by

$$i_A = 607nD_D^{1/2}m^{2/3}t^{1/6} \cdot 2[D_2] \quad (6)$$

$$i_B = 607nD_M^{1/2}m^{2/3}t^{1/6} \cdot [M] \quad (7)$$

where D_D and D_M are diffusion coefficients of the dimer and the monomer respectively.

The concentration terms are related by

$$C_t = [M] + 2[D_2] \quad (8)$$

where C_t represents the total Mo(V) concentration (1.0 mM).

On the basis of the assumption that wave A is due to the reduction of the dimer, $Mo_2(V)$ to $Mo_2(III)$, the following equation can be obtained by combining eqns. (6)–(8) and solving for i_A .

$$i_A = -D_D^{1/2}/D_M^{1/2} \cdot i_B + 2140C_tD_D^{1/2} \quad (9)$$

A discussion on the validity of this assumption is presented in a later part of this paper. By applying a least squares method to the data given in Figs. 3 and 4, the unknown values, D_D and D_M were determined to be 4.28×10^{-6} and 7.95×10^{-6} cm^2/s respectively.

The term in the left side of eqn. (5) can thus be calculated at a particular $[H^+]$ or $[Cl^-]$ value with the use of eqns. (6) and (7). A plot of $\log([M]^2/[D_2])$ against $\log[H^+]$ gave a straight line with a slope of 6.20. Similarly a plot of $\log([M]^2/[D_2])$ against $\log[Cl^-]$ was linear with a slope of 1.94. In order to confirm the results, tests of eqn. (5) were made with the data given in Fig. 3. A plot of $\log([M]^2/[D_2])$ against $\log[HCl]$ was linear with a slope of $(c + d) = 7.90$, indicating $c = 6$ and $d = 2$. From the

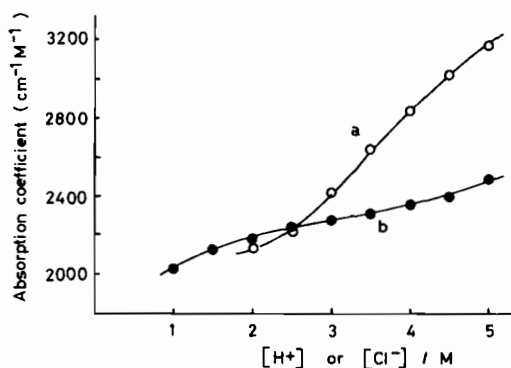


Fig. 5. ϵ_{obs} values with variation of a, $[\text{H}^+]$; b, $[\text{Cl}^-]$. $[\text{Mo(V)}]$; 1.0 mM, $I = 5.0$.

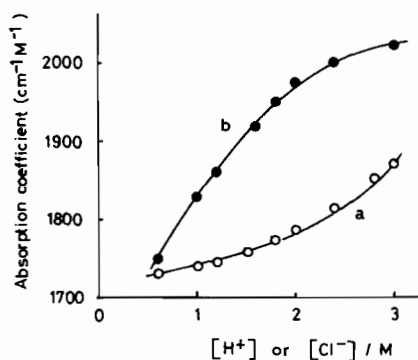


Fig. 6. ϵ_{obs} values with variation of a, $[\text{H}^+]$; b, $[\text{Cl}^-]$. $[\text{Mo(V)}]$; 1.0 mM, $I = 5.0$.

plots, the value for K_2 averaged 1.19×10^{-8} . The dimer-dimer interconversion was not detected polarographically.

Spectrophotometric Behavior

Figure 5 shows the observed ϵ values per molybdenum at 300 nm obtained under the same conditions as in Fig. 4. For the equilibrium (2), the absorbance of the solutions can be expressed as

$$\epsilon_{\text{obs}}C_t = 2\epsilon_2[D_2] + \epsilon_3[M] \quad (10)$$

where ϵ_2 and ϵ_3 are absorption coefficients per molybdenum for the dimer and the monomer respectively, and ϵ_{obs} is the observed ϵ value. By combining eqns. (8) and (10), eqn. (11) is obtained.

$$\epsilon_{\text{obs}}C_t = \epsilon_3C_t + 2(\epsilon_2 - \epsilon_3)[D_2] \quad (11)$$

Thus eqn. (4) can be written as

$$K_2 = \frac{2C_t(\epsilon_2 - \epsilon_{\text{obs}})^2}{(\epsilon_{\text{obs}} - \epsilon_3)(\epsilon_2 - \epsilon_3)[\text{H}^+]^c[\text{Cl}^-]^d} \quad (12)$$

Equation (12) is transformed into:

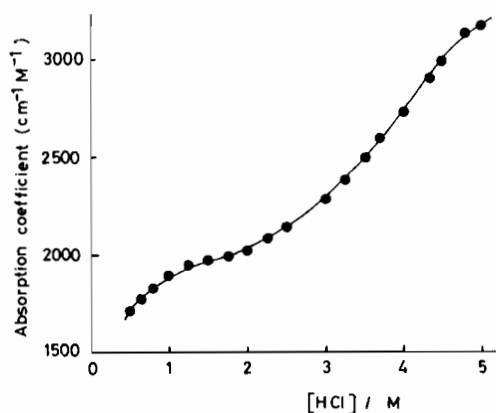


Fig. 7. ϵ_{obs} values as a function of HCl concentration. $[\text{Mo(V)}]$, 1.0 mM. The dots indicate experimental points. The solid line is calculated from the constants obtained.

$$2C_t\epsilon_2^2 + \epsilon_2(-4C_t\epsilon_{\text{obs}} + K_2\epsilon_3(\epsilon_2 - \epsilon_3)([\text{H}^+]^c[\text{Cl}^-]^d) + K_2(\epsilon_3 - \epsilon_2)(\epsilon_{\text{obs}}[\text{H}^+]^c[\text{Cl}^-]^d) = -2C_t\epsilon_{\text{obs}}^2 \quad (13)$$

where $[\text{H}^+]$, $[\text{Cl}^-]$ and ϵ_{obs} are variables.

With the known values of $c = 6$ and $d = 2$, the unknowns in eqn. (13) can be obtained by applying a least squares method to the ϵ data given in Fig. 5. The values for ϵ_2 , ϵ_3 and K_2 were found to be 1980 ± 60 , 3480 ± 60 and $(1.5 \pm 0.4) \times 10^{-8}$ respectively. The value for K_2 agrees well with that obtained polarographically, which confirms that the stoichiometry can be expressed as in eqn. (2').



In order to determine a and b in eqn. (1), ϵ values were measured where $[\text{HClO}_4]$ was varied from 0.6 to 3 M at constant $[\text{NaCl}]$ of 0.5 M, and $[\text{NaCl}]$ was varied from 0.6 to 3 M at constant $[\text{HClO}_4]$ of 0.5 M. The results are shown in Fig. 6. Making the assumption that only the two dimers exist in the solutions, it can be readily shown that

$$K_1 = \frac{(\epsilon_1 - \epsilon_{\text{obs}})}{(\epsilon_{\text{obs}} - \epsilon_2)[\text{H}^+]^a[\text{Cl}^-]^b} \quad (14)$$

If eqn. (14) is put into logarithmic form, we have the following equation:

$$\begin{aligned} \log[(\epsilon_1 - \epsilon_{\text{obs}})/(\epsilon_{\text{obs}} - \epsilon_2)] &= \\ &= a \log[\text{H}^+] + b \log[\text{Cl}^-] + \log K_1 \end{aligned} \quad (15)$$

where ϵ_1 is the absorption coefficient per molybdenum for the dimer, D_1 . Since eqn. (15) contains an unknown constant, ϵ_1 , the least-squares method was applied by substituting a provisional value for ϵ_1 . When $\epsilon_1 = 1660 \pm 30$, the ϵ_{obs} values given in Fig.

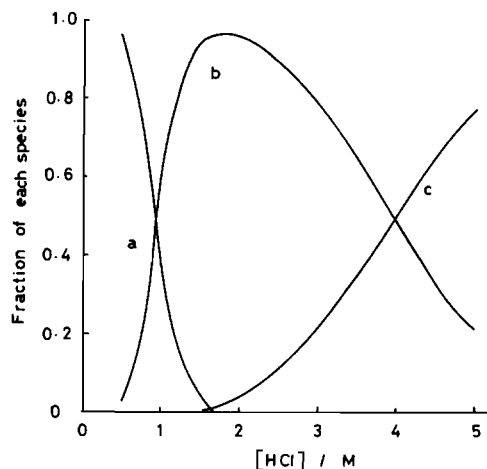


Fig. 8. Fraction of each species. a, $\text{Mo}_2\text{O}_4\text{Cl}_4(\text{H}_2\text{O})_2^{2-}$; b, $\text{Mo}_2\text{O}_3\text{Cl}_8^{4-}$; c, H_2MoOCl_5 .

6 are best fitted to eqn. (15), giving values of $a = 2.16$, $b = 3.92$ and $K_1 = 2 \pm 0.3$. From the results it follows that the stoichiometry can be expressed as



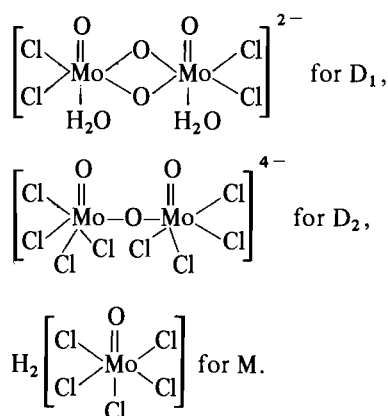
Figure 7 shows the ϵ values at 300 nm in 0.5–5 M HCl adjusted to $I = 5.0$. Using the constants obtained ($K_1 = 2$, $K_2 = 1.5 \times 10^{-8}$, $\epsilon_1 = 1660$, $\epsilon_2 = 1980$ and $\epsilon_3 = 3480$), the absorption curve was constructed and shown by the solid line. The theoretical curve fits to the experimental data, which provides strong evidence that equilibria (1') and (2') describe well the Mo(V)–HCl system in the HCl concentration range 0.5–5 M ($I = 5.0$).

The fraction α of each species was calculated using the equilibrium constants, and is shown in Fig. 8.

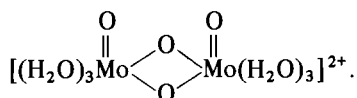
Discussion

The present results demonstrate that the equilibria in the Mo(V)–HCl system can be expressed in the most general form as in eqns. (1') and (2'). It is found that the increase in the ionic strength results in the increase of the observed ϵ value at 300 nm and a corresponding increase in the values for both equilibrium constants. In the works of ref. [1] and [3], no indifferent electrolyte was added. In the spectrophotometric work [2], Haight studied the solution equilibria of Mo(V) at the ionic strength of 6.0. As for the solution equilibria, no attempts were made to correlate the present results with the studies reported previously [1–3].

Taking our Raman results into consideration [6], the most probable structures for the three species are:



On the basis of the equilibria (1') and (2'), the monomer can be written as the undissociated form. The structures for D_2 and M are compatible with those reported by Haight [2]. According to Ardon and Pernick [5], the binuclear dipositive species exists in 1 M HCl. They have postulated the structure as



However, our Raman measurements have shown that the three Mo(V) species are chloro-complexes in HCl solutions (1 M conc.). In addition, the Raman results have excluded the possibility of the hydroxide-bridged structure postulated by Colton and Rose [4].

The value for K_2 obtained by polarography is in reasonable agreement with that obtained spectrophotometrically, which supports the assumption that D_2 is reduced not to the mixed oxidation state species such as $\text{Mo}_2(\text{III}, \text{IV})$, but to $\text{Mo}_2(\text{III})$ in HCl solutions. The results are consistent with those observed in trifluoromethanesulfonic acid by Chalilpoyil and Anson [9]. Recently, Richens and Sykes [17] and Paffett and Anson [18] have reported that trinuclear $\text{Mo}_3(\text{IV})$ ions are reduced to trinuclear $\text{Mo}_3(\text{III})$ species. It seems likely that the reduction of molybdenum species generally occurs with retention of an identical core structure.

The value for the diffusion coefficient, D_M is found to be greater than that for D_D . As shown in curve c of Fig. 3, therefore, total limiting currents increase as the HCl concentration is increased.

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