Spectrophotometric Investigation on the Equilibration of Monomeric Forms of Mo(VI) in Aqueous Sulfuric Acid

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Spectrophotometric measurements show that at Mo(VI) concentrations below 8×10^{-5} *M, only monomeric species exist in* H_2SO_4*. The change of* ϵ *value on the* H_2SO_4 *concentration is explained in terms of the presence of the monomeric Mo(VI) species* $Mo(OH)_6$, $Mo(OH)_5(H_2O)^+$ *and* $Mo(OH)_4(SO_4)_2^{2-}$*, with no evidence for the formation of a 1:1 Mo(VI)/sulfate complex. The equilibrium constant for the reaction,* $Mo(OH)_5(H_2O)^+ + 2HSO_4^- = Mo(OH)_4(SO_4)_2^{2-} + H^+$ *was found to be 3.3 ± 0.5 for* $I = 4.0$.

Introduction

The Mo(VI) species present in aqueous solutions have been the subject of a number of investigations. There is agreement that a monomeric MoO_4^{2-} ion exists in alkaline solutions [1]. On acidification of the molybdate solutions, polymerized isopolyanions are formed. The equilibria of monomer–heptamer and heptamer–octamer have been established so far [2–8]. On the other hand, less is known about the species in strongly acidic solutions.

On the basis of spectrophotometric measurements, Neumann and Cook reported that complex ions, MoO_2Cl_2 existed in HCl [9]. According to them, $MoO_2Cl_3^-$ ion is predominant in stronger HCl solutions. Kraus *et al.*, on the basis of anion-exchange work, favor the species $MoO_2Cl_4^{2-}$ [10]. Dimers such as $HMo_2O_6^+$ and $(MoO_2Cl_2)_2$ have also been postulated [11].

In 3 *M* Li(H)ClO$_4$, Ojo *et al.* studied the monomer–dimer equilibration of Mo(VI) spectrophotometrically [12]. They concluded that Mo(VI) existed as monomeric species, $HMoO_3^+$ and $H_2MoO_3^{2+}$, and dimeric species, $H_2Mo_2O_6^{2+}$ and $H_3Mo_2O_6^{3+}$, in agreement with the work by Krumenacker [13, 14]. Recently, Cruywagen *et al.* determined the protonation constant of $Mo(OH)_6$ to $Mo(OH)_5(H_2O)^+$ [15], and identified three dimeric species; $Mo_2O(OH)_9(H_2O)^+$, $Mo_2O(OH)_8(H_2O)_2^{2+}$ and $Mo_2O(OH)_7(H_2O)_3^{3+}$ in 3 *M* Na(H)ClO$_4$ [16].

In H_2SO_4, the presence of two or more species has been proposed to account for the polarographic waves [17, 18]. However, there are few studies on the nature of Mo(VI) species in H_2SO_4.

In view of the continued interest in the subject, it seems worthwhile to elucidate the Mo(VI) species present in H_2SO_4. The present paper describes the monomer–monomer equilibria in H_2SO_4 at Mo(VI) concentrations low enough to avoid dimer formation.

Experimental

Ultraviolet (UV) spectra were recorded on a Hitachi spectrophotometer, Model 220-A using appropriate quartz cells with path length from 0.01 to 5 cm. The path lengths for the smaller cells (≤0.2 cm) were determined by absorbance measurements on $Cr_2O_7^{2-}$ [19].

Sodium perchlorate was recrystallized twice from water. Other chemicals were of reagent grade and were used without further purification. Mo(VI) solutions were prepared from $Na_2MoO_4 \cdot 2H_2O$. Measurements were made at 25 °C.

Results

Figure 1 shows the absorption spectra of various concentrations of Mo(VI) in 1 *M* H_2SO_4. The spectra were recorded using appropriate quartz cells, 0.02, 0.1, 0.2 and 5 cm in length, to make $C \times l$ constant, where C is the Mo(VI) concentration and l is the path length. With an increase in the Mo(VI) concentration, the absorbance in the region 230–320 nm increased and a maximum developed around 240 nm. A wavelength of 240 nm was used for the following measurements.

Figure 2 shows the relationship between absorption coefficients, ϵ, per molybdenum and Mo(VI) concentrations in various concentrations of H_2SO_4. In 0.004–4 *M* H_2SO_4, the ϵ value at each acid concentration is practically constant for Mo(VI)

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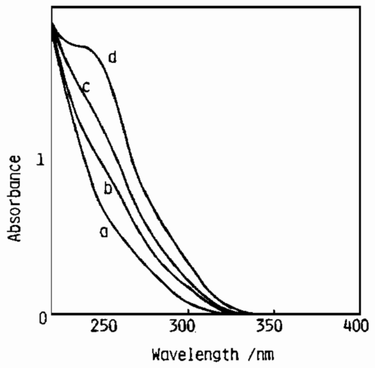

Fig. 1. UV spectra of Mo(VI) in 1 *M* H_2SO_4. a; 8×10^{-5} *M* Mo(VI), l = 5 cm. b; 2×10^{-3} *M* Mo(VI), l = 0.2 cm. c; 4×10^{-3} *M* Mo(VI), l = 0.1 cm. d; 2×10^{-2} *M* Mo(VI), l = 0.02 cm.

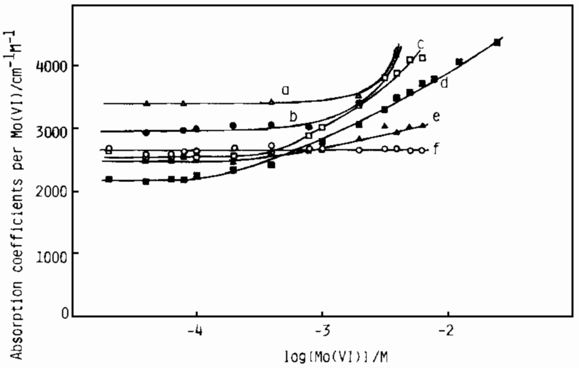

Fig. 2. Dependence of ϵ on Mo(VI) concentration. $[H_2SO_4]$/M; a, 0.02; b, 0.04; c, 0.1; d, 1.0; e, 4.0; f, 6.0.

concentrations below 8×10^{-5} *M*, and increases at higher Mo(VI) concentrations. Similar behavior has been observed in $HClO_4$ solutions and accounted for by the formation of dimeric Mo(VI) species with ϵ values greater than those of monomeric species [12–16]. In 5–8 *M* H_2SO_4, on the other hand, the ϵ value of 2640 is retained constant over the Mo(VI) concentration range studied (2×10^{-5}–2×10^{-2} *M*), which suggests that no dimerization reaction occurs under these conditions. The ϵ values at low Mo(VI) concentrations are different from each other according to the H_2SO_4 concentration, suggesting the presence of several monomeric species.

In Fig. 3, the average ϵ values for the Mo(VI) concentration range 2–8×10^{-5} *M* are plotted against the acid concentration. In a series of the experiments (curve a), no indifferent electrolyte was added so that the ionic strength I varied with the change of the H_2SO_4 concentration. Curve b was obtained for the solutions which were kept at constant ionic strength of 4.0 with $NaClO_4$ up to 4 *M* H_2SO_4, while no $NaClO_4$ was added above 4 *M* H_2SO_4. The dissociation constant, K_a for HSO_4^- (1.2×10^{-2}) was used for calculation [20]. The observed dependence of ϵ values on acid concentrations can be interpreted in terms of the presence of at least three monomeric species in these acid solutions. In the H_2SO_4 concentration range 0.01–0.2 *M*, the ϵ value decreased as the H_2SO_4 concentration was increased.

To test whether the observed phenomena were associated with the sulfate species or the acidity of the solution, the ϵ values of Mo(VI) in the concentration range 2×10^{-5}–7×10^{-5} *M* were measured in 4 *M* Na(H)ClO_4. Figure 4 shows the change in the average ϵ value at 240 nm as a function of the $HClO_4$ concentration. It was found that the ϵ value decreased with increasing the $HClO_4$ concentration.

In 3 *M* Na(H)ClO_4 for $[H^+] > 0.01$ *M*, similar behavior has been observed by Cruywagen *et al.* at wavelengths of 218, 226 and 233 nm, which is interpreted as a result of the equilibration of

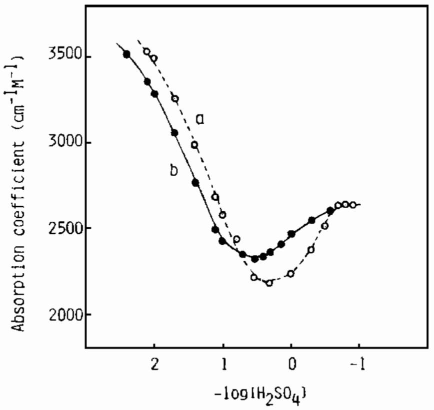

Fig. 3. Average ϵ values as a function of $-\log [H_2SO_4]$. a; No indifferent electrolyte was added. b; I = 4.0. The dots indicate experimental points. The solid line is calculated from the constants determined.

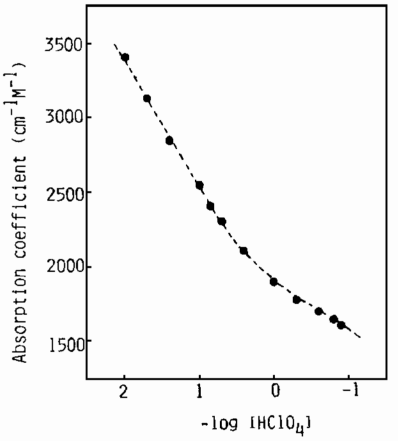

Fig. 4. Average ϵ values as a function of $-\log [HClO_4]$. I = 4.0.

$Mo(OH)_6$ with $Mo(OH)_5(H_2O)^+$ [15]. For $HClO_4$ concentrations above 3 *M*, further decrease of the ϵ value has been observed, which is ascribed to the protonation of $Mo(OH)_5(H_2O)^+$ to $Mo(OH)_4(H_2O)_2^{2+}$ [15]. This is in marked contrast to the behavior in H_2SO_4 (Fig. 3).

The protonation of monomeric $Mo(OH)_6$ to $Mo(OH)_5(H_2O)^+$ can be represented as:

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

The protonation constant, K_1 is given by

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

where ϵ_0 and ϵ_1 are the molar absorption coefficients of $Mo(OH)_6$ and $Mo(OH)_5(H_2O)^+$, respectively, and ϵ_{obs} is the observed ϵ value in each solution. All equilibria were studied solely in terms of concentrations, because of the difficulty in obtaining activity coefficients for molybdenum species and hydrogen ions.

Because there was a possibility of the overlapping of equilibria, the unknowns ϵ_0, ϵ_1 and K_1 were obtained by applying a least squares fit of data obtained in 0.01–0.4 *M* $HClO_4$ to eqn. (2). Using the dissociation constant, $K_a = 1.2 \times 10^{-2}$, the least squares treatment was applied for the ϵ values obtained in 0.01–0.08 *M* H_2SO_4 (I = 4.0). The values for ϵ_0, ϵ_1 and K_1 were found to be 3770 ± 10, 1870 ± 10 and 23 ± 1 in H_2SO_4, and to be 3830 ± 10, 1810 ± 10 and 19 ± 1 in $HClO_4$, respectively. It should be noted that the ϵ_0 and ϵ_1 values obtained in $HClO_4$ are in agreement with the corresponding values in H_2SO_4, which indicates that the protonation of $Mo(OH)_6$ to $Mo(OH)_5(H_2O)^+$ occurs in H_2SO_4. The value for K_1 is slightly higher in H_2SO_4 than in $HClO_4$. This may be primarily due to the effect of ionic strength on the dissociation of HSO_4^-. This is supported by the fact that the same curve is obtained when the ϵ values are plotted against pH adjusted with either H_2SO_4 or $HClO_4$.

We then measured ϵ values for a series of solutions containing 4×10^{-5} *M* Mo(VI), 2 *M* $HClO_4$ and different concentrations of $NaHSO_4$ (0.1–2 *M*), the ionic strength of the solutions being maintained at 4.0 with $NaClO_4$. These data show that the ϵ value increases with increasing $NaHSO_4$ concentration at constant $[H^+]$, which is explained satisfactorily in terms of the sulfate-complex formation.

The complex formation can be represented by the equation,

$$\begin{aligned} Mo(OH)_5(H_2O)^+ + nHSO_4^- &= \\ &= Mo(OH)_m(SO_4)_n^{6-m-2n} + (m + n - 5)H^+ + \\ &+ (6 - m)H_2O \end{aligned} \tag{3}$$

The equilibrium constant, K_2 can be expressed as

$$K_2 = \frac{[Mo(OH)_m(SO_4)_n^{6-m-2n}]\,[H^+]^{m+n-5}}{[Mo(OH)_5(H_2O)^+]\,[HSO_4^-]^n} \tag{4}$$

As $Mo(OH)_5(H_2O)^+$ is in equilibrium with $Mo(OH)_6$, eqn. (4) can then be written as

$$\begin{aligned} \log(\epsilon'_{obs} - \epsilon')/(\epsilon_2 - \epsilon_{obs}) &= n\log[HSO_4^-] - \\ &- (m + n - 5)\log[H^+] + \log K_2 \end{aligned} \tag{5}$$

where $\epsilon'_{obs} = \epsilon_{obs}(1/K_1[H^+] + 1)$, $\epsilon' = \epsilon_0/K_1[H^+] + \epsilon_1$, and ϵ_2 is the molar absorption coefficient of the sulfate complex. The values of $\epsilon_0 = 3770$ and $\epsilon_1 = 1870$ were used for the calculation. As mentioned before, the ϵ value was found to be constant in 5–8 *M* H_2SO_4 ($\epsilon = 2640$ cm^{-1} M^{-1}), and this value was taken as ϵ_2. As shown in Fig. 5, a plot of $\log(\epsilon'_{obs} - \epsilon')/(\epsilon_2 - \epsilon_{obs})$ *vs.* $\log[HSO_4^-]$ yielded a straight line with a slope of 1.94, indicating n = 2.

Measurements to determine $-(m + n - 5)$ were made by maintaining the $NaHSO_4$ concentration at 0.4 or 0.8 *M* while varying the $HClO_4$ concentration from 0.1 to 3.6 *M*. The ionic strength of the solutions was kept constant at 4.0 with $NaClO_4$. It was observed that the ϵ value decreased with an increase in $[H^+]$. Tests of eqn. (5) are shown by the plots in Fig. 6. Two separate plots in different concentrations of $NaHSO_4$ gave straight lines with a common slope $-(m + n - 5) = -1.0$, indicating m = 4. When this result is combined with the preceding one, we can write the complex-formation reaction as

$$Mo(OH)_5(H_2O)^+ + 2HSO_4^- = Mo(OH)_4(SO_4)_2^{2-} + H^+ \tag{6}$$

In order to get the values for ϵ_2 and K_2 and more accurate values for ϵ_0, ϵ_1 and K_1, all the observed ϵ values were treated again using the following equation.

$$\begin{aligned} &[Mo(OH)_6](\epsilon_0 - \epsilon_{obs}) + [Mo(OH)_5(H_2O)^+](\epsilon_1 - \\ &- \epsilon_{obs}) + [Mo(OH)_4(SO_4)_2^{2-}](\epsilon_2 - \epsilon_{obs}) = 0 \end{aligned} \tag{7}$$

Combining eqns. (1), (6) and (7) gives

$$\begin{aligned} \epsilon_{obs} = \epsilon_1 + \epsilon_0/K_1 1/[H^+] &- 1/K_1\epsilon_{obs}/[H^+] + \\ &+ \epsilon_2 K_2[HSO_4^-]^2/[H^+] - K_2\epsilon_{obs}[HSO_4^-]^2/[H^+] \end{aligned} \tag{8}$$

where $[H^+]$, $[HSO_4^-]$ and ϵ_{obs} are variables.
The five constants (ϵ_0, ϵ_1, ϵ_2, K_1 and K_2) in this equation can be determined by applying the least squares method to the experimental data given in Figs. 3 and 5. The results are summarized in Table I.

Discussion

The results of the present investigation show that the protonation of $Mo(OH)_6$ to $Mo(OH)_5(H_2O)^+$

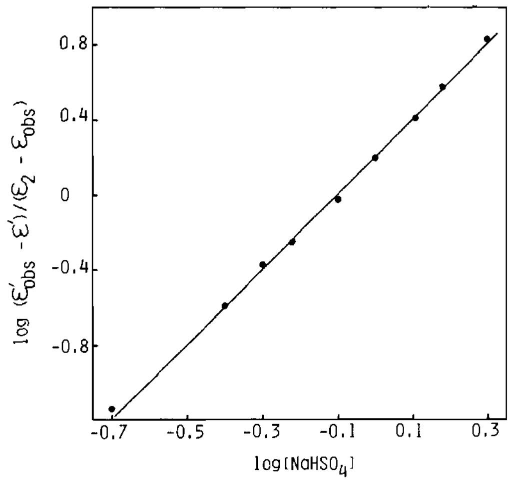

Fig. 5. A plot of $\log(\epsilon'_{obs} - \epsilon')/(\epsilon_2 - \epsilon_{obs})$ against log $[HSO_4^-]$ at I = 4.0. $[H^+]$ = 2 *M*.

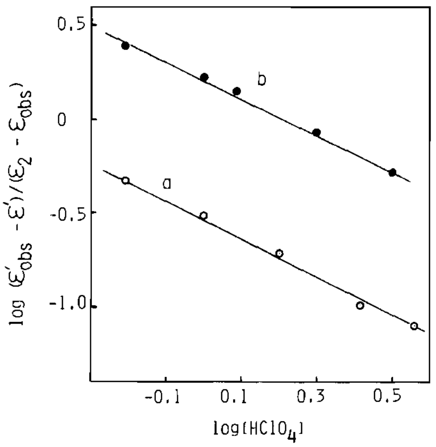

Fig. 6. Plots of $\log(\epsilon'_{obs} - \epsilon')/(\epsilon_2 - \epsilon_{obs})$ against $\log[H^+]$ at I = 4.0. $[NaHSO_4]$/*M*; a, 0.4; b, 0.8.

TABLE I. Values for ϵ_0, ϵ_1, ϵ_2, K_1 and K_2.

ϵ_0	3760 ± 30	K_1	22.4 ± 1.8
ϵ_1	1860 ± 30	K_2	3.3 ± 0.5
ϵ_2	2620 ± 30		

occurs in dilute H_2SO_4 and a sulfate complex is formed at higher H_2SO_4 concentrations. The precise formula of the sulfate complex is uncertain at present. Whereas the molybdate ion MoO_4^{2-} is tetrahedral [21], the protonated form H_2MoO_4 is known to be octahedral [5, 7, 22, 23]. On the basis of Raman measurements of Mo(VI) in strong HCl solutions, the octahedral structure with a *cis*-MoO_2 group has been postulated [24]. It seems safe to assume that the formula of the complex may be $Mo(OH)_4(SO_4)_2^{2-}$ or $MoO_2(SO_4)_2(H_2O)_2^{2-}$. It should be pointed out that the Mo(VI)-sulfate complex exists as a monomeric ion for Mo(VI) concentrations up to 2×10^{-2} *M* (Fig. 2).

Curve b of Fig. 3 shows the calculated absorption curve for I = 4.0 using the constants given in Table I. The agreement between the experimental points and the theoretical curve is excellent, indicating that the equilibria reported in this paper describe well the Mo(VI)-sulfate system.

The ϵ_2 value obtained by a least squares treatment ($\epsilon = 2620 \pm 30$ cm^{-1} M^{-1}) agrees well with the observed value ($\epsilon = 2640$ cm^{-1} M^{-1}), which suggests that no higher complexes such as a Mo(VI): sulfate ratio of 1:3 are formed in the H_2SO_4 solutions up to at least 8 M.

In the present investigation, evidence for the formation of a 1:1 Mo(VI)/sulfate complex was not obtained. On the basis of the solubility measurements of molybdic oxide, MoO_3 in H_2SO_4, Meyer and Stateczny postulated the formation of the complex formulated as MoO_2SO_4 [25]. Recently, Anany *et al.* claimed the existence of the 1:1 complex spectrophotometrically [26]. However, their conclusions are only tentative.

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