Complex Formation between Molybdate and Alizarin Red S

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The complex formation between molybdate and Alizarin Red S (ARS) has been studied by spectrophotometry and pH titration. Results by the former method confirm that the composition of the complexes formed corresponds to a ratio of 1:1 for molybdate to ARS and that the complexes are stable between pH 2 to 6. Those by the latter are summarized by the following stability constants at 25 °C and an ionic strength of 0.1: $MoO_4^{2-}+ars^{3-}+2H^+=MoO_3ars^{3-}+H_2O$, $\log(\beta_1/mol^{-3}\,L^3)=20.18\pm0.01$; $MoO_4^{2-}+ars^{3-}+3H^+=MoO_3(Hars)^{2-}+H_2O$, $\log(\beta_2/mol^{-4}\,L^4)=24.93\pm0.04$ (the completely deprotonated species of ARS is denoted by ars^{3-}, and the concentration of H_2O is not included in the definition of stability constants). Protonation constants of MoO_4^{2-} and ars^{3-} were also determined under the same conditions.

Nearly three decades ago, Nazarchuk[1)] observed the formation of a complex between molybdate and Alizarin Red S (9,10-dihydro-3,4-dihydroxy-9,10-dioxo-2-anthracenesulfonic acid monosodium salt, abbreviated to ARS) at pH 2—5, and used for colorimetric determinations of molybdenum. He considered that the composition of the complex was 1:1. However, Dey *et al.*,[2)] Ishibashi *et al.*,[3)] and Csanyi[4)] reported it as 1:2. Krizan and Nozaki[5)] wrote it as 1:1. Although these authors all have used spectrophotometry and conditions employed for the measurements are not so different each other (except Krizan and Nozaki who used 1:1 ethanol–water mixture as solvent), their conclusions are not in harmony. The present investigation aimed at determining the composition of the complex and its stability constant. We have used pH titration in conjunction with a spectrophotometric method, and found the formation of, instead of one, two complexes, one protonated and another unprotonated both with the composition corresponding to a ratio of 1:1 for molybdate to ARS.

Experimental

All chemicals used were of guaranteed reagent grade. Solutions were prepared with usual precautions, and the ionic strength was controlled to 0.1 with sodium nitrate. Sodium molybdate was used as a source of the molybdate ion.

Absorption spectra were recorded with a HITACHI UV-VIS spectrophotometer Model 200-10 and 10-mm quartz cells. A glass electrode (TOA HGS-2005) and a reference electrode (TOA HS-205S) were used with a TOA pH-meter Model HM-20E for pH titrations, and nitrogen was bubbled through the solution to exclude carbon dioxide. All measurements were made at 25.0 °C.

The refinement of equilibrium constants was carried out by a SHARP personal computer PC-3200.

Results and Discussion

Determination of the Composition of the Complex by Spectrophotometry. Figure 1 shows absorption spectra of ARS and its mixture with sodium molybdate at pH 4.00. An absorption maximum of ARS at 420 nm shifts to longer wavelengths on the complex formation with molybdate which is transparent in the visible region. A continuous variation curve at this pH and 475 nm indicates that the composition of the complex or complexes formed was 1:1, though it has a slight distortion (Fig. 2). The same conclusion was drawn from measurements at other pH's. The pH dependence of the ordinate of the continuous variation curve at the 1:1 composition is given by curve 1 in Fig. 3. The curve illustrates that the complex or complexes formed in a range of pH 2—6, and that they became unstable at outside of these limits. These facts are in accord with results reported by previous authors.[1—5)]

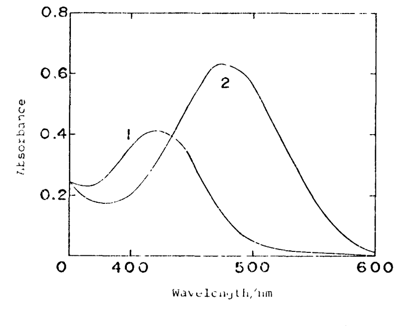


Fig. 1. Absorption spectra of ARS in the absence and presence of sodium molybdate. Concentration of ARS, 8.0×10^{-5} mol/L; pH 4.00. Concentration of sodium molybdate: curve 1, 0 mol/L; curve 2, 17.6×10^{-5} mol/L.

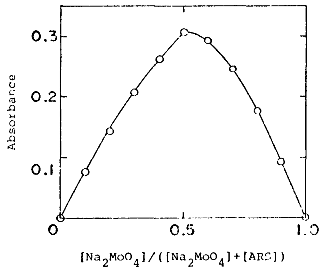


Fig. 2. Continuous variation curve for sodium molybdate and ARS mixture at 475 nm. Total concentration, 1.00×10^{-4} mol/L; pH 4.00.

Determination of Protonation Constants of MoO_4^{2-} by pH Titration. Measurements were carried out by titrating dilute mixtures of sodium molybdate and nitric acid with a sodium hydroxide solution. The protonation of MoO_4^{2-} proceeds through following two steps:

$$H^+ + MoO_4^{2-} = HMoO_4^- \quad K_1^M = \frac{[HMoO_4^-]}{[H^+][MoO_4^{2-}]}, \quad (1)$$

TABLE 1. PROTONATION CONSTANTS OF MoO_4^{2-} AND ars^{3-}, AND STABILITY CONSTANTS OF THEIR COMPLEXES IN 0.1 mol L^{-1} $NaNO_3$ SOLUTION AT 25 °C

Protonation constant					
$\log \frac{K_1^M}{\text{mol}^{-1}\,\text{L}}$	3.77±0.02	$\log \frac{K_2^M}{\text{mol}^{-1}\,\text{L}}$	2.35±0.16	$\log \frac{K_{78}^M}{\text{mol}^{-14}\,\text{L}^{14}}$	53.00±0.05
$\log \frac{K_1^L}{\text{mol}^{-1}\,\text{L}}$	10.34±0.02	$\log \frac{K_2^L}{\text{mol}^{-1}\,\text{L}}$	5.66±0.01	$\log \frac{K_3^L}{\text{mol}^{-1}\,\text{L}}$	2.12±0.07
Stability constant					
$\log \frac{\beta_1}{\text{mol}^{-3}\,\text{L}^3}$	20.18±0.01	$\log \frac{\beta_2}{\text{mol}^{-4}\,\text{L}^4}$	24.93±0.04		

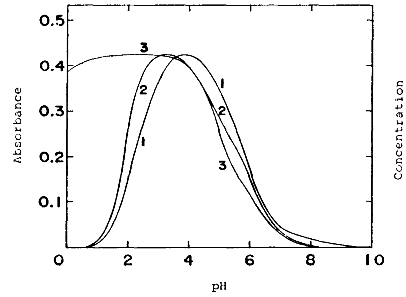


Fig. 3. pH dependence of the absorbance of the continuous variation curve for sodium molybdate and ARS mixture at the 1 : 1 composition. Wavelength, 475 nm; concentration of sodium molybdate, 8.0×10^{-5} mol/L; concentration of ARS, 8.0×10^{-5} mol/L. Curve 1, observed pH dependence of the absorbance; curve 2, $[MoO_3ars^{3-}]+[MoO_3(Hars)^{2-}]$; curve 3, $[MoO_3ars^{3-}]+[MoO_2ars^{-}]$. The concentration curves were drawn on arbitrary scales to make their highest points on equal level with the highest point of the absorbance curve.

and

$$H^+ + HMoO_4^- = H_2MoO_4 \quad K_2^M = \frac{[H_2MoO_4]}{[H^+][HMoO_4^-]}, \tag{2}$$

where [X] is the concentration of species X in mol/L. Besides, molybdate ion in acidified solutions is known to produce many kinds of isopolyanions.[6] Under the experimental conditions adopted in this study, an assumption of the formation of heptamolybdate ion, $Mo_7O_{24}^{6-}$, is sufficient to explain titration curves.

$$8H^+ + 7MoO_4^{2-} = Mo_7O_{24}^{6-} + 4H_2O$$

$$K_{78}^M = \frac{[Mo_7O_{24}^{6-}]}{[H^+]^8[MoO_4^{2-}]^7}. \tag{3}$$

Protonation constants were calculated by the method for two-pK systems by Briggs and Stuehr[7] with some modifications for the formation of heptamolybdate ion. Instead of Eq. 9 in their paper, the computation was carried out by using the equation

$$\frac{(1+K_1^M[H^+]+7K_{78}^M[H^+]^8[MoO_4^{2-}]^6)(V+R-\Delta V)}{2+K_1^M[H^+]+6K_{78}^M[H^+]^8[MoO_4^{2-}]^6} = -\frac{K_1^M[H^+]^2(V+R-\Delta V)}{2+K_1^M[H^+]+6K_{78}^M[H^+]^8[MoO_4^{2-}]^6}K_2^M + V_e, \tag{4}$$

where

$$R = ([H^+]-[OH^-])V_t/C_B, \tag{5}$$

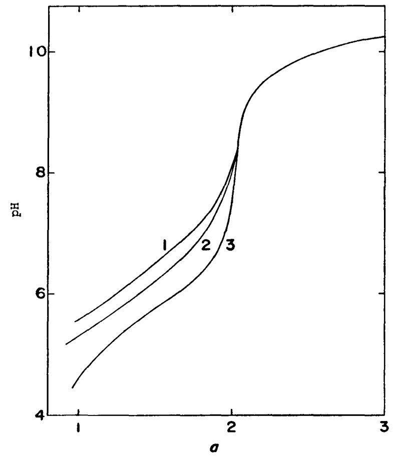


Fig. 4. Titration curves of ARS in the absence and presence of sodium molybdate. Concentration of ARS, 4.90×10^{-4} mol/L. Concentration of sodium molybdate: curve 1, 5.33×10^{-4} mol/L; curve 2, 2.67×10^{-4} mol/L; curve 3, 0 mol/L. The abscissa a is the ratio of the volume of sodium hydroxide solution added to the theoretical volume of the base per proton required to neutralize the acid H_3ars.

and C_B is the concentration of sodium hydroxide in the titrating solution, V is the volume of the base added, V_t is the total volume of the solution titrated, V_e is the theoretical volume of the base per proton required to neutralize the acid H_2MoO_4, and ΔV is the volume of the base neutralized by any strong acid present in the solution at the beginning of the titration. Protonation constants obtained are given in Table 1.

Determination of Protonation Constants of ARS by pH Titration. Curve 3 in Fig. 4 is a titration curve of ARS in the absence of the molybdate. The protonation of ARS consists of following three steps:

$$H^+ + ars^{3-} = Hars^{2-} \quad K_1^L = \frac{[Hars^{2-}]}{[H^+][ars^{3-}]}, \tag{6}$$

$$H^+ + Hars^{2-} = H_2ars^- \quad K_2^L = \frac{[H_2ars^-]}{[H^+][Hars^{2-}]}, \tag{7}$$

and

$$H^+ + H_2ars^- = H_3ars \quad K_3^L = \frac{[H_3ars]}{[H^+][H_2ars^-]}. \tag{8}$$

In the above, ars^{3-} represents the completely deprotonated species of ARS with three negative charges.

Protonation constants were calculated by the method for three-pK systems.[7] The constants obtained are shown in Table 1.

Identification of the Complex Species Formed and Determination of Their Stability Constants by pH Titration. Figure 4 shows titration curves of ARS in the presence and absence of the molybdate. Titration curves in the presence of the molybdate lie above the curve in the absence of the molybdate in the lower pH range and coincide with it in the upper range. Titration curves of this kind represent the formation of the ester between participating species, *i.e.* molybdate and ARS. The corresponding formation reaction of the complex consumes protons and thereby increases pH of the solution.

Conditions of the 1:1 composition and of the instability in acid solutions limit possible complex species to ones whose formation reactions are given by

$$\mathrm{MoO_4^{2-} + ars^{3-} + }m\mathrm{H^+ = MoO_{4-}}_{n}\mathrm{(H}_{m-2n}\mathrm{ars)^{(5-}}^{m)-} + n\mathrm{H_2O}, \tag{9}$$

where $5>m\geqslant 2n>0$. This restriction leaves only three candidate complexes to be considered: $\mathrm{MoO_3ars^{3-}}$, $\mathrm{MoO_3(Hars)^{2-}}$, and $\mathrm{MoO_2ars^-}$. Formation reactions of these complexes are

$$\mathrm{MoO_4^{2-} + ars^{3-} + 2H^+ = MoO_3ars^{3-} + H_2O}, \tag{10}$$

$$\mathrm{MoO_4^{2-} + ars^{3-} + 3H^+ = MoO_3(Hars)^{2-} + H_2O}, \tag{11}$$

and

$$\mathrm{MoO_4^{2-} + ars^{3-} + 4H^+ = MoO_2ars^- + 2H_2O}. \tag{12}$$

Stability constants are defined as follows:

$$\beta_1 = \frac{[\mathrm{MoO_3ars^{3-}}]}{[\mathrm{MoO_4^{2-}}][\mathrm{ars^{3-}}][\mathrm{H^+}]^2}, \tag{13}$$

$$\beta_2 = \frac{[\mathrm{MoO_3(Hars)^{2-}}]}{[\mathrm{MoO_4^{2-}}][\mathrm{ars^{3-}}][\mathrm{H^+}]^3}, \tag{14}$$

and

$$\beta_3 = \frac{[\mathrm{MoO_2ars^-}]}{[\mathrm{MoO_4^{2-}}][\mathrm{ars^{3-}}][\mathrm{H^+}]^4}. \tag{15}$$

As shown in Fig. 4, the titration of ARS in the presence of the molybdate was carried out at above pH 5, where the atomic ratio of molybdenum of the heptamolybdate to the total molybdenum was below 10^{-5}. Hence the concentration of heptamolybdate ions is ignored in the following derivation of equations.

Total concentrations of the molybdate, ARS, and dissociable hydrogen ions are respectively given as follows:

$$M_\mathrm{t} = [\mathrm{MoO_4^{2-}}] + [\mathrm{HMoO_4^-}] + [\mathrm{H_2MoO_4}] + [\mathrm{MoO_3ars^{3-}}] + [\mathrm{MoO_3(Hars)^{2-}}] + [\mathrm{MoO_2ars^-}], \tag{16}$$

$$L_\mathrm{t} = [\mathrm{ars^{3-}}] + [\mathrm{Hars^{2-}}] + [\mathrm{H_2ars^-}] + [\mathrm{H_3ars}] + [\mathrm{MoO_3ars^{3-}}] + [\mathrm{MoO_3(Hars)^{2-}}] + [\mathrm{MoO_2ars^-}], \tag{17}$$

and

$$H_\mathrm{t} = [\mathrm{H^+}] - [\mathrm{OH^-}] + [\mathrm{HMoO_4^-}] + 2[\mathrm{H_2MoO_4}] + [\mathrm{Hars^{2-}}] + 2[\mathrm{H_2ars^-}] + 3[\mathrm{H_3ars}] + 2[\mathrm{MoO_3ars^{3-}}] + 3[\mathrm{MoO_3(Hars)^{2-}}] + 4[\mathrm{MoO_2ars^-}]. \tag{18}$$

Combination of these equations and equilibrium constants results Eqs. 19 and 20:

$$f_1f_5[\mathrm{MoO_4^{2-}}]^2 + (f_2f_3-f_1f_4-f_5f_6)[\mathrm{MoO_4^{2-}}] + (f_4f_6-f_3f_7) = 0, \tag{19}$$

and

$$(L_\mathrm{t}-F[\mathrm{MoO_4^{2-}}])\beta_3[\mathrm{H^+}]^4 + \{(L_\mathrm{t}-F[\mathrm{MoO_4^{2-}}])\beta_2-K_1^\mathrm{L}K_2^\mathrm{L}K_3^\mathrm{L}F\}[\mathrm{H^+}]^3 + \{(L_\mathrm{t}-F[\mathrm{MoO_4^{2-}}])\beta_1-K_1^\mathrm{L}K_2^\mathrm{L}F\}[\mathrm{H^+}]^2 - K_1^\mathrm{L}F[\mathrm{H^+}] - F = 0, \tag{20}$$

where

$$f_1 = 1 + K_1^\mathrm{M}[\mathrm{H^+}] + K_1^\mathrm{M}K_2^\mathrm{M}[\mathrm{H^+}]^2, \tag{21}$$

$$f_2 = 4 + 3K_1^\mathrm{M}[\mathrm{H^+}] + 2K_1^\mathrm{M}K_2^\mathrm{M}[\mathrm{H^+}]^2, \tag{22}$$

$$f_3 = 1 + K_1^\mathrm{L}[\mathrm{H^+}] + K_1^\mathrm{L}K_2^\mathrm{L}[\mathrm{H^+}]^2 + K_1^\mathrm{L}K_2^\mathrm{L}K_3^\mathrm{L}[\mathrm{H^+}]^3, \tag{23}$$

$$f_4 = K_1^\mathrm{L}[\mathrm{H^+}] + 2K_1^\mathrm{L}K_2^\mathrm{L}[\mathrm{H^+}]^2 + 3K_1^\mathrm{L}K_2^\mathrm{L}K_3^\mathrm{L}[\mathrm{H^+}]^3, \tag{24}$$

$$f_5 = 2\beta_1[\mathrm{H^+}]^2 + \beta_2[\mathrm{H^+}]^3, \tag{25}$$

$$f_6 = M_\mathrm{t} - L_\mathrm{t}, \tag{26}$$

$$f_7 = 4M_\mathrm{t} - H_\mathrm{t} + [\mathrm{H^+}] - [\mathrm{OH^-}], \tag{27}$$

and

$$F = M_\mathrm{t}/[\mathrm{MoO_4^{2-}}] - f_1. \tag{28}$$

The procedure for obtaining a set of the best values of stability constants involves the following steps:

(1) Estimate β_1, β_2, and β_3.

(2) Calculate f_i's for data points in the appropriate pH region using the estimates of stability constants and the values of other equilibrium constants.

(3) Solve Eq. 19 for $[\mathrm{MoO_4^{2-}}]$, and calculate F.

(4) Solve Eq. 20 for $[\mathrm{H^+}]$.

(5) Convert $[\mathrm{H^+}]$ to pH, and find the standard error of estimate from the experimental and calculated pH values.

(6) Vary β_3 by small amounts, and repeat steps 4—5 until a minimum in the standard error of estimate is obtained.

(7) Repeat steps 2—6 using new estimates of β_2 until the smallest standard error of estimate is found.

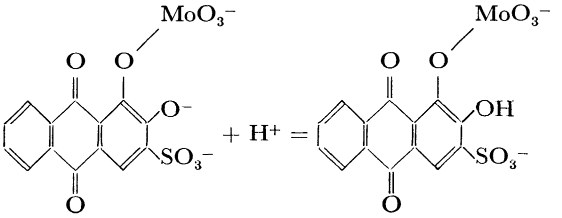
(8) Repeat steps 2—7 using new estimates of β_1 until the lowest standard error of estimate of pH is gotten. A set of values of β_1, β_2, and β_3 which yields the lowest standard error of estimate is chosen as the most probable set of values.

Although it is possible to compute the three stability constants with the above method by adopting the three-complex-species (*i.e.* $\mathrm{MoO_3ars^{3-}}$–$\mathrm{MoO_3(Hars)^{2-}}$–$\mathrm{MoO_2ars^-}$) model, this is not the best way to explain titration curves. This unnecessarily increases the number of new species, which must be a minimum indispensable.

Three one-complex-species models were tried at first. However they failed to reproduce titration curves. Two of two-complex-species models were equally successful to reproduce the curves. These are the $\mathrm{MoO_3ars^{3-}}$–$\mathrm{MoO_3(Hars)^{2-}}$ and $\mathrm{MoO_3ars^{3-}}$–$\mathrm{MoO_2ars^-}$ models. The concentrations of respective complex species were calculated as functions of pH by using resulted values of stability constants, and examined whether they were in accord with observed results illustrated by curve 1 in Fig. 3 or not. Curves 2 and 3 in this figure are, respectively, the sum of concentrations of $\mathrm{MoO_3ars^{3-}}$ and $\mathrm{MoO_3(Hars)^{2-}}$, and the sum of concentrations of MoO_3ars^{3-} and MoO_2ars^-. If the difference of molar absorption coefficient between different species is taken into account, the discrepancy between curve 1 (absorbance) and curve 2 (sum of the concentrations) is explicable, but the one between curve 1 and curve 3 (sum of the concentrations) is not. Hence, the MoO_3ars^{3-}–$MoO_3(Hars)^{2-}$ model is acceptable, but the MoO_3ars^{3-}–MoO_2ars^- model is not.

Values of stability constants of MoO_3ars^{3-} and $MoO_3(Hars)^{2-}$ in Table 1 are ones based on the MoO_3ars^{3-}–$MoO_3(Hars)^{2-}$ model. Dey *et al.* reported two values of 9.5[2b)] and 9.2[2c)] for logarithm of the stability constant of the 1:2 complex at pH 3.5. Csanyi gave a value of 7.7 for the same constant at pH 3.8.[4)] Krizan and Nozaki reported a value of 5.4 for the logarithmic constant of the 1:1 complex at pH 5.[5)] These are all apparent constants, however. Hence it is not profitable to compare these with the values in Table 1.

It seems natural that the ester formation takes place at a site where the protonation occurs most easily in free ars^{3-}. Yampol'skii *et al.*[8)] stated that the protonation in ars^{3-} occurs at the anionic 1-O at first. Therefore the MoO_3 group is concented to ARS through the 1-O in MoO_3ars^{3-}. The protonation of this complex is given by



(29)

and the protonation constant was calculated to be $10^{4.75}$ mol^{-1} L from values shown in Table 1. This value is about an eighth of K_2^L, the corresponding protonation constant of uncomplexes $Hars^{2-}$. The decrease of the protonation constant is a reflection of the difficulty of proton's arriving at the anionic 2-O due to the overcrowding around the O-atom by complexation with the MoO_3 group at the 1-O.

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