

A Spectro-photometric Study of Aqueous Molybdate Solutions

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In a recent review¹ of the polymolybdates, the author discussed a theory concerning the ionic conditions present in aqueous solutions. That discussion was based on experimental evidence of different kinds, but especially on diffusion measurements and conductometry. The results were not quite conclusive, however, and the present investigation has been carried out in order to give a more definite confirmation of the theory developed.

Spectro-photometric methods have earlier been used to study the stepwise formation of mononuclear weak complexes. This problem has been attacked very successfully by Scandinavian chemists (J. Bjerrum², Olerup³, Fro-naeus⁴), who have worked out mathematically clear and experimentally suitable methods. The polynuclear complexes are too complicated, however, to permit such a stringent treatment. But if only strong complexes are considered, the following simplified method can be used.

MODE OF CALCULATION

Earlier spectro-photometric works on molybdate solutions have been carried out by Jander⁵ and Carpéni⁶, who measured extinction curves for different acidities and found that the curves are shifted towards longer wave lengths on acidification. Fig. 1 showing the curves of molybdate solutions with pH 0 and 14, has been given by Carpéni⁶. An absorption edge occurs towards shorter wave lengths where, consequently, no measurements can be made. On the horizontal parts of the curves ($\lambda > 3400 \text{ \AA}$), however, the assumption of a constant molar extinction coefficient will still be correct.

This affords a possibility of measuring the effect of the addition of mineral acids to molybdate solutions on their light absorption properties. It is still

better, however, to calculate the effect of a given consumption of H^+ ions by the molybdate solutions as will be discussed here.

The following notation is used:

Extinction coefficient ϵ , defined by $\epsilon \cdot l = {}^{10}\log \frac{I}{I_0}$

Concentration of added, strong monobasic acid S .

Concentration of remaining H^+ ions h .

The extinction for $S = 0$ ($\epsilon_{\text{MgO}_4^{2-}}$) ϵ'

$\Delta \epsilon = \epsilon - \epsilon'$ the increase of ϵ caused by the H^+ consumption $S - h$.

$\frac{\Delta \epsilon}{S - h}$ is then the effect on the extinction of one mole of consumed H^+ .

Plotting $\frac{\Delta \epsilon}{S - h} = f(S - h)$ vs. $S - h$ more or less complicated curves are obtained:

If one type of ions is predominant at the first stages of acidification, the curve will start as a straight horizontal line. If, then, a second type of ion were formed with no interference between the two ionic species, the curve would continue as a new straight line. There is always an overlap, however, which will give rise to S-shaped curves instead of straight lines. The greater the difference in the $S - h$ values at which complexes are formed, the straighter the lines will appear. In the polymolybdate case the interference is sufficiently small to permit a consideration of the curves as almost straight lines.

As to the magnitude of ϵ , Jander⁵ claimed that a larger value of ϵ (at a given concentration) indicates a larger complex. This assumption seems rather reasonable for this type of complexes, but it is of course only a hypothesis.

EXPERIMENTAL METHODS

Extinction measurements. A Beckmann Spectro-photometer Model DU, with an hydrogen lamp and 10 mm quartz cells, was used for the optical measurements. As no thermostat device was available, there was always a continuous rise with time in the temperature of the cell compartment, and therefore the investigations were carried out $\frac{1}{2}$ – $1\frac{1}{2}$ hour after the lamp had been started, when the corresponding rise of the ϵ values was never more than 2%. For one series of solutions the values obtained with the hydrogen lamp were compared with those obtained with a tungsten lamp and a blue filter, and they were found to be identical within the limit of experimental error. This was governed in most cases by the temperature drift error but greater errors appear, certainly at very high and very low extinction values which are undoubtedly very inaccurate.

In the wave length region used (3500–3900 Å) only the molybdate ions contribute to the extinction; the exclusion of the effect of H^+ , Na^+ and Cl^- ions is very important (cf. the conductometry).

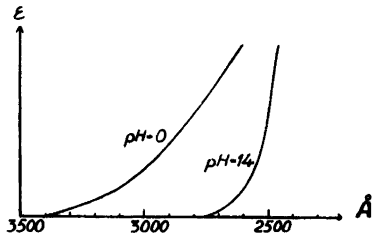
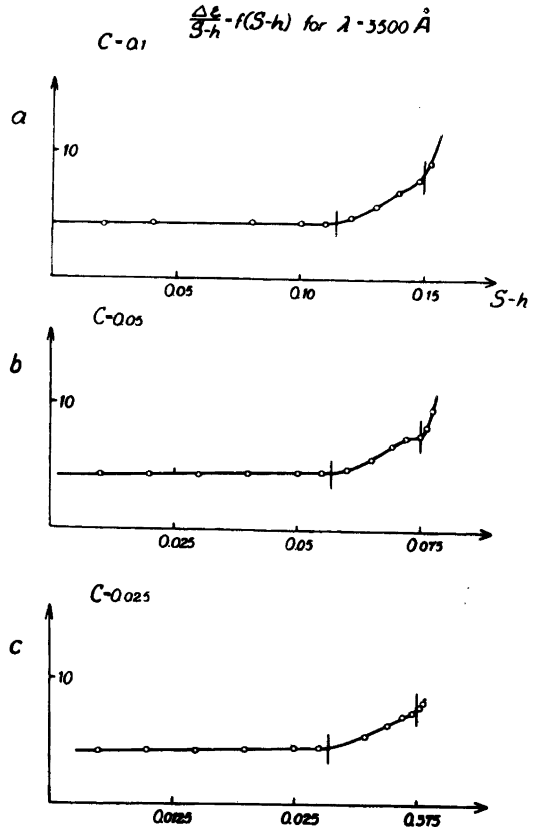


Fig. 1. The extinction curves of molybdate solutions with pH 0 and 14.

Fig. 2. $\frac{\Delta \epsilon}{S-h} = f(S-h)$ for $\lambda = 3500$ Å at different concentrations

- a) $C = 0.100$
- b) $C = 0.050$
- c) $C = 0.025$



Concentration of remaining H^+ ions. The measurement of h can only be carried out with a large salt excess giving ionic strengths to the molybdate solutions almost identical with those of the acids used for comparison. All solutions were therefore 2-molar in NaCl.

These measurements were carried out on a battery-supplied tube potentiometer (Ermi, Stockholm, described by Blomgren ⁷) with a glass electrode and a saturated calomel electrode. The *emf* values of HCl solutions with different concentrations were measured simultaneously with the molybdate solutions. It was then possible to deduce the h values consistent with a measured *emf* for the molybdate solutions from the *emf* values obtained with the standard HCl solutions. As the performance of the glass electrode was not quite constant the *emf* values in each series (*v. infra*) of molybdates and standard HCl solutions were measured in a sequence determined by their magnitudes. (This was made possible by a preliminary pH measurement of the molybdate solutions.) The *emf* values were measured with an accuracy of at least 2 mV, which corresponds to a largest error in h of 5%. Standard solutions of HCl more dilute than 0.001-molar can not be used because of their low buffering capacity.

The best accuracy would have been obtained if all measurements had been made at the same constant temperature, but there are indications, that this is not necessary for our

purpose. Potentiometric measurements at 20° C and 25° C give the same values of h , and the variation of ε due to the temperature differences does not exceed 2 %.

Procedure. Varying amounts of HCl and H₂O were added to a number of molybdate solutions so that solutions with identical total concentrations (C) of Na₂MoO₄ were obtained. (They were also 2-molar in NaCl.) The only varying factor in each series was thus S (HCl added). h and ε were then measured for the different solutions and the function $\frac{\Delta \varepsilon}{S - h} = f(S - h)$ was calculated. This procedure was repeated for different concentrations of Na₂MoO₄. It was found that no appreciable contraction took place during the preparations.

In one series HClO₄ was used instead of HCl with the same result.

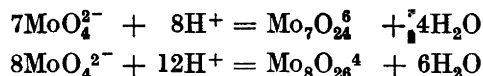
Concentration $C > 0.4$ lead to formation of solid polymolybdates, and for $C < 0.01$ the inaccuracy of $S - h$ increases rapidly. The concentration range investigated was therefore $0.01 < C < 0.4$.

RESULTS

The experimental data are given in Table 1. In Fig. 2 the function $\frac{\Delta \varepsilon}{S - h} = f(S - h)$ is shown for some series.

Three curves (Fig. 2) all show one straight practically horizontal line, continued by another slightly S-shaped line. They show also a third part after a second break.

The two breaks indicate the existence of the ions Mo₇O₂₄⁶⁻ and Mo₈O₂₆⁴⁻ in the solutions according to the equations:



as is shown by the agreement of the experimental with the calculated discontinuities (*cf.* Fig. 2) at $\frac{S-h}{C} = \frac{8}{7}$ and $\frac{S-h}{C} = \frac{12}{8}$. (The existence of Mo₇O₂₄⁶⁻ and Mo₈O₂₆⁴⁻ has also been discussed in ref. 1.)

The slight S-shape can easily be interpreted as due to a formation of small amounts of Mo₈O₂₆⁴⁻ before all MoO₄²⁻ ions are transformed into Mo₇O₂₄⁶⁻. This explanation is also supported by the very small but clear positive inclination of the initial lines (Table 2).

The third kind of ion formed after Mo₈O₂₆⁴⁻ may be still larger than Mo₈O₂₆⁴⁻ (as assumed in ref. 1) and it is even formed for MoO₄²⁻ concentrations as low as 0.005-molar (as indicated by a continued rise in ε on addition of sufficient HCl; the values are not given in Table 1).

Table 1. Results of the spectro-photometric measurements (Each series gives the mean values of two measured series).

S	$S - h$	ϵ_{3500}	ϵ_{3600}	ϵ_{3700}	ϵ_{3800}	ϵ_{3900}
$C = 0.4$						
0.000	0.000	0.011	0.010	0.009	0.009	0.008
0.400	0.400	1.756	0.516	0.162	0.053	0.021
0.440	0.440	2.004	0.611	0.188	0.061	0.023
0.480	0.480	—	0.766	0.277	0.108	0.048
0.520	0.520	—	1.227	0.476	0.197	0.092
0.560	0.559	—	1.870	0.763	0.323	0.147
0.600	0.596	—	—	1.004	0.455	0.217
0.640	0.619	—	—	1.686	0.699	0.300
$C = 0.2$						
0.000	0.000	0.008	0.007	0.007	0.007	0.007
0.040	0.040	0.177	0.053	0.018	—	—
0.200	0.200	0.912	0.263	0.081	0.028	0.012
0.220	0.220	1.014	0.294	0.092	0.033	0.014
0.240	0.240	1.336	0.396	0.148	0.061	0.029
0.260	0.260	—	0.574	0.232	0.102	0.050
0.280	0.279	—	0.832	0.335	0.145	0.069
0.300	0.296	—	1.003	0.410	0.179	0.086
0.320	0.310	—	1.669	0.633	0.261	0.114
0.340	0.322	—	—	1.051	0.409	0.153
0.360	0.332	—	—	1.334	0.465	0.173
$C = 0.1$						
0.000	0.000	0.007	0.006	0.006	0.006	0.006
0.020	0.020	0.090	0.030	0.014	—	—
0.040	0.040	0.180	0.055	0.021	0.010	—
0.080	0.080	0.368	0.108	0.036	0.014	0.008
0.100	0.100	0.449	0.135	0.044	0.017	0.009
0.110	0.110	0.509	0.155	0.051	0.020	0.011
0.120	0.120	0.598	0.216	0.087	0.040	0.023
0.130	0.130	0.775	0.300	0.129	0.062	0.036
0.140	0.139	0.992	0.393	0.166	0.079	0.044
0.150	0.148	1.190	0.460	0.195	0.091	0.046
0.160	0.152	1.437	0.575	0.239	0.108	0.056
0.170	0.157	—	0.883	0.348	0.143	0.062
0.180	0.162	—	1.258	0.485	0.193	0.083
0.190	0.166	—	1.613	0.612	0.231	0.094
0.200	0.169	—	—	0.685	0.258	0.102

S	$S - h$	ϵ_{3500}	ϵ_{3600}	ϵ_{3700}	ϵ_{3800}	ϵ_{3900}
$C = 0.05$						
0.000	0.000	0.006	0.006	0.006	0.005	
0.010	0.010	0.046	0.018	—	—	
0.020	0.020	0.095	0.031	0.013	—	
0.030	0.030	0.136	0.042	0.017	0.008	
0.040	0.040	0.185	0.056	0.021	0.010	
0.050	0.050	0.235	0.072	0.026	0.011	
0.055	0.055	0.256	0.081	0.029	0.012	
0.060	0.060	0.295	0.102	0.041	0.019	
0.065	0.065	0.378	0.145	0.063	0.029	
0.070	0.069	0.477	0.183	0.078	0.037	
0.075	0.072	0.543	0.209	0.086	0.040	
0.080	0.075	0.581	0.225	0.094	0.043	
0.085	0.076	0.628	0.243	0.100	0.046	
0.090	0.077	0.754	0.296	0.122	0.053	
$C = 0.025$						
	0.0000	0.0000	0.005	0.004	0.003	
	0.0050	0.0050	0.026	0.010	0.004	
	0.0100	0.0100	0.049	0.017	0.007	
	0.0150	0.0150	0.070	0.025	0.010	
	0.0200	0.0200	0.093	0.030	0.011	
	0.0250	0.0250	0.116	0.036	0.013	
	0.0275	0.0275	0.127	0.040	0.016	
	0.0300	0.0299	0.144	0.050	0.020	
	0.0325	0.0323	0.183	0.072	0.026	
	0.0350	0.0344	0.227	0.093	0.039	
	0.0375	0.0361	0.261	0.104	0.045	
	0.0400	0.0369	0.279	0.111	0.048	
	0.0425	0.0372	0.288	0.114	0.050	
	0.0450	0.03755	0.299	0.119	0.051	
	0.0475	0.03765	0.304	0.122	0.053	
$C = 0.01$						
	0.0000	0.0000	0.009	0.009	0.008	
	0.0020	0.0020	0.017	0.011	0.009	
	0.0040	0.0040	0.026	0.013	0.009	
	0.0060	0.0060	0.034	0.016	0.010	
	0.0080	0.0080	0.043	0.019	0.011	
	0.0100	0.0100	0.053	0.022	0.012	
	0.0110	0.0110	0.058	0.025	0.013	
	0.0120	0.0119	0.065	0.028	0.015	
	0.0130	0.0128	0.080	0.035	0.020	
	0.0140	0.0136	0.094	0.043	0.024	
	0.0150	0.0142	0.106	0.047	0.026	
	0.0160	0.0147	0.113	0.051	0.028	
	0.0170	0.0150	0.119	0.053	0.029	
	0.0180	0.01505	0.123	0.054	0.030	
	0.0190	0.0151	0.125	0.057	—	

Table 2. $f(S - h)$ for $\lambda = 3600 \text{ \AA}$.

$\frac{S - h}{C}$	Concentrations			
	0.025	0.05	0.1	0.2
0.200	1.2	1.2	1.2	1.2
1.000	1.3	1.3	1.3	1.3

One further fact may be noted in this connection; the $\text{Mo}_8\text{O}_{26}^{4-}$ break is obtained at $\frac{S - h}{C} = 1.5$, where $\frac{S}{C} \geq 1.5$ and not at $\frac{S}{C} = 1.5$. This shift is not so evident in conductometric measurements because it is then compensated by rapid increase of the amount of unconsumed H^+ ions already for $\frac{S}{C} < 1.5$. A rounded break near the correct position is therefore obtained (cf. ref. 1).

In the previous discussion of the ionic conditions, one question was left unanswered, *viz.* whether there is a dissociation of the $\text{Mo}_8\text{O}_{26}^{4-}$ ions to $\text{Mo}_4\text{O}_{13}^{2-}$ ions in dilute solutions.

The discussion of this question may be preceded by a study of the identity of the $\text{Mo}_7\text{O}_{24}^{6-}$ ions at different concentrations. For comparison, the values of $f(S - h)$ for $\frac{S - h}{C} = 1.0$ are given in Table 3. Evidently there is a complete constancy of $f(S - h)$ within the limits of experimental error in the concentration range 0.01–0.4.

A similar discussion of $\text{Mo}_8\text{O}_{26}^{4-}$ is more difficult because of the increasing inaccuracy of $S - h$ in that region. In Table 4 a comparison is made between $f(S - h)$ values for $\frac{S - h}{C} = 1.5$ interpolated for different concentrations from the measurements. It is evident that the results are not so conclusive in

Table 3. $f(S - h)$ for $\frac{S - h}{C} = 1.000$.

$\lambda \text{ \AA}$	Concentrations					
	0.01	0.025	0.05	0.1	0.2	0.4
3500	4.4	4.5	4.6	4.4	4.5	4.4
3600	—	1.3	1.3	1.3	1.3	1.3
3700	—	—	—	0.37	0.37	0.38

Table 4. $f(S - h)$ for $\frac{S - h}{C} = 1.500$.

$\lambda \text{ \AA}$	Concentrations					
	0.010	0.025	0.05	0.1	0.2	0.4
3600	2.9	3.0	3.1	3.2	3.5	—
3700	1.3	1.3	1.2	1.3	1.4	1.7
3800	—	—	0.52	0.58	0.60	0.76
3900	—	—	—	0.27	0.28	0.36

this case. The occurrence of larger values at higher concentrations can be explained by two different assumptions: (i) that there is a dissociation of $\text{Mo}_8\text{O}_{26}^{4-}$ on dilution, or (ii) that complexes larger than $\text{Mo}_8\text{O}_{26}^{4-}$ are formed already before the $\text{Mo}_8\text{O}_{26}^{4-}$ break at high concentrations.

The problem must be considered more critically before any final decision is made. It has been concluded that $\text{Mo}_8\text{O}_{26}^{4-}$ ions are present in concentrated solutions (*cf.* ref. 1). A dissociation $\text{Mo}_8\text{O}_{26}^{4-} \rightarrow 2\text{Mo}_4\text{O}_{13}^{2-}$ could be reconciled with the experimental data only if the degree of dissociation were constant for $C \leq 0.1$ (*cf.* Table 4), and as dissociation increases with dilution, this is only possible if there is a complete dissociation into $\text{Mo}_4\text{O}_{13}^{2-}$ ions in this concentration range. This assumption can be disproved by reference to the results of Jander's diffusion measurements. These show definitely that acidification of 0.1-molar Na_2MoO_4 solutions leads to the formation of complexes with increasing molecular weights⁵. Thus the ions existing at the concentrations $C \leq 0.1$ cannot be $\text{Mo}_4\text{O}_{13}^{2-}$.

The only alternative is that $\text{Mo}_8\text{O}_{26}^{4-}$ ions are formed after the $\text{Mo}_7\text{O}_{24}^{6-}$ break. The slight S-shape of the curves is then explained by the formation of small amounts of $\text{Mo}_8\text{O}_{26}^{4-}$ together with $\text{Mo}_7\text{O}_{24}^{6-}$ before the break. At higher concentrations ($C > 0.1$) larger ions are formed together with $\text{Mo}_8\text{O}_{26}^{4-}$ before the $\text{Mo}_8\text{O}_{26}^{4-}$ break. This formation has not yet started at the acidification stage $\frac{S - h}{C} = 1.25$ (Table 5) where $f(S - h)$ has a constant value independent of the concentrations.

This theory is in agreement with Dumanski's theories⁸ about the formation of colloidal ions in molybdate solutions as well as with Jander's results⁵.

Table 5. $f(S - h)$ for $\frac{S - h}{C} = 1.250$.

3600 \AA	Concentrations					
	0.01	0.025	0.05	0.1	0.2	0.4
	1.9	1.9	2.0	2.0	1.9	2.0

Table 6. Spectro-photometric measurements of salt free solutions.

<i>S</i>	ϵ_{3500}	ϵ_{3600}	ϵ_{3700}	<i>S</i>	3500	ϵ_{3600}
<i>C</i> = 0.1			<i>C</i> = 0.025			
0.000	0.008	0.008	0.008	0.0000	0.007	0.007
0.020	0.099	0.035	0.015	0.0050	0.027	0.013
0.040	0.184	0.060	0.023	0.0100	0.048	0.021
0.060	0.277	0.088	0.032	0.0150	0.073	0.029
0.080	0.357	0.123	0.044	0.0200	0.100	0.039
0.100	0.467	0.158	0.057	0.0250	0.134	0.053
0.110	0.516	0.179	0.068	0.0275	0.152	0.063
<i>C</i> = 0.05			<i>C</i> = 0.01			
0.000	0.007	0.007	0.007	0.0000	0.007	
0.010	0.049	0.019	0.009	0.0020	0.013	
0.020	0.093	0.033	0.014	0.0040	0.024	
0.030	0.137	0.048	0.018	0.0060	0.037	
0.040	0.183	0.065	0.027	0.0080	0.047	
0.050	0.236	0.087	0.035	0.0100	0.062	
0.055	0.265	0.100	0.041	0.0110	0.066	

COMPLEMENTARY INVESTIGATION OF SALT-FREE SOLUTIONS

The method of measuring h and thus $S - h$, can not be applied to solutions which do not contain a salt excess, but as long as the h values are very small compared with S ($S - h \sim S$) the same procedure can be used. This is true for $\frac{S}{C}$ values below 1.1 and therefore such solutions have been investigated.

The results are given in Table 6 and Fig. 3. (It may be noted that the molar extinction coefficient of $\text{Mo}_7\text{O}_{24}^{6-}$ is almost independent of the large difference in ionic strength.)

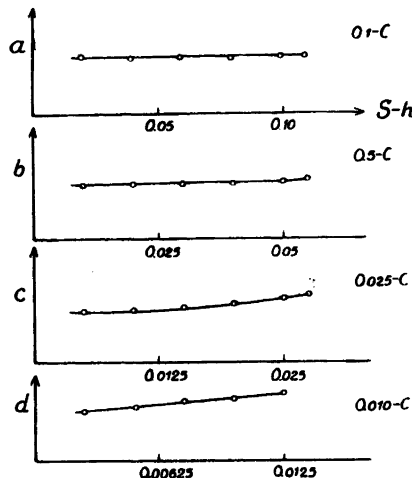
From Fig. 3 it is easily seen that for low concentrations ($C < 0.05$) there is an increasing formation of $\text{Mo}_8\text{O}_{26}^{4-}$ together with $\text{Mo}_7\text{O}_{24}^{6-}$ in the early stages of the acidification (an increasing positiv inclination of the line).

A comprehensive description of the reactions which take place on acidification of molybdate solutions of different concentrations and ionic strengths has thus been obtained. It remains to determine the nature of the large ions formed on strong acidification. Probably a structure determination of an „octo” or „decamolybdate” would provide the answer.

It can not be neglected that also other polymolybdate ions may exist in very small amounts or under special conditions.

Fig. 3. $\frac{\Delta \varepsilon}{S} = f(S)$ for $\lambda = 3500 \text{ \AA}$
at different concentrations.

- a) $C = 0.100$
b) $C = 0.050$
c) $C = 0.025$
d) $C = 0.010$



SUMMARY

A spectro-photometric method has been devised for studying the formation of polymolybdate ions. The measurements give strong evidence to the assumption that the reactions taking place upon acidification are $\text{MoO}_4^{2-} \rightarrow \text{Mo}_7\text{O}_{24}^{6-} \rightarrow \text{Mo}_8\text{O}_{26}^{4-} \rightarrow$ larger complexes.

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REFERENCES

1. Lindqvist, I. *Nova Acta Reg. Soc. Sci. Ups.* IV, 15, no. 1.
2. Bjerrum, J. *Metal ammine formation in aqueous solution*. Dissertation, Köpenhamn (1941).
3. Olerup, H. *Järnkloridernas komplexitet i 2-molar överklorosyra*. Dissertation, Lund (1944).
4. Fronaeus, S. *Komplexsystem hos koppar*. Dissertation, Lund (1948).
5. Jander, G., Jahr, K. F., and Heukeshoven, W. *Z. anorg. Chem.* 194 (1930) 383.
6. Carpéni, G. *Bull. Soc. Chim.* [5] 14 (1947) 490.
7. Blomgren, E. *Transactions, instruments and measurements conference*. Stockholm (1949).
8. Dumanski, A. *et coll. Koll. Z.* 38 (1926) 208.
9. Doucet, Y. Thèse, Paris (1942).
10. Byé, J. Thèse, Paris (1945).

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