

# Thermodynamic Stability of Clusters of Molybdenum Oxide

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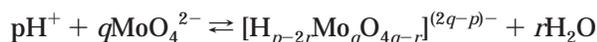
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We show that a single geometrical rule underlies the stability of “polyoxomolybdates”, the variety of clusters of molybdenum(VI) oxide in (acidified) aqueous solution that are found experimentally. We predict that upon increasing the proton or total molybdenum oxide concentration, the average size of the clusters increases. We compare our predictions with results from ultracentrifugation experiments and with data in the literature. Finally, it is shown that the formation of metal oxide clusters is thermodynamically equivalent to the formation of surfactant micelles.

## 1. Introduction

Metal oxides such as molybdenum, tungsten, vanadium, and aluminum oxide in acidified aqueous solutions spontaneously and reversibly form clusters that may contain up to 36 metal atoms. We limit ourselves to molybdenum oxides in this work, but the global behavior we predict is expected to apply to other metal oxides as well. Complexes reversibly form by consuming protons, which, following ref 1, can be written as the equilibrium



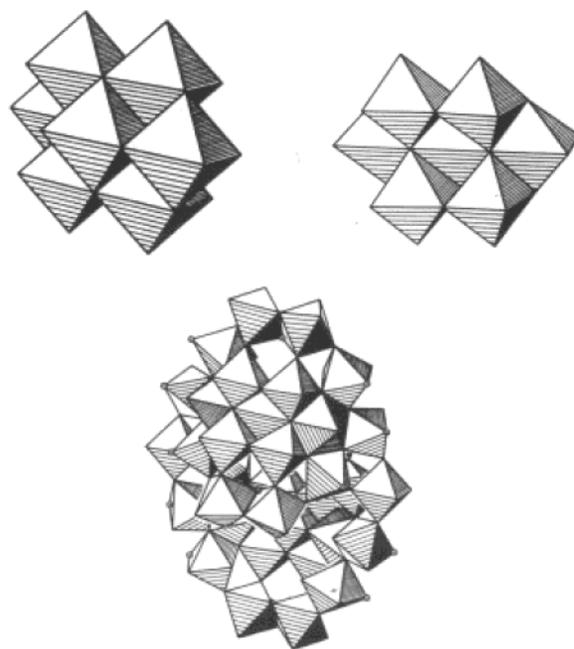
In the above equilibrium, the cluster  $[\text{H}_{p-2r}\text{Mo}_q\text{O}_{4q-r}]^{(2q-p)-}$  is characterized by the combination  $(p, q)$ : the numbers of protons and molybdenum monomers that are required to form a cluster, respectively. The value of  $r$  quantifies how many protons stick in the cluster; if no protonation occurs, it equals  $p/2$ . Most authors<sup>2</sup> agree that in the molybdenum(VI) oxide systems, clusters of sizes  $q = 7$  ( $(p, q) = (8, 7), (9, 7), (10, 7),$  or  $(11, 7)$ , depending on the degree of protonation) and 8 ( $(p, q) = (12, 8)$  or  $(13, 8)$ ), and 36 (only  $(p, q) = (64, 36)$ ) exist: not only are these species present as ions in solution, but they also form crystals. The structures of these clusters are schematically shown in Figure 1. It can be seen in this figure that clusters mainly consist of octahedrally shaped monomers that are linked at their vertexes. These links are (reversible) chemical bonds: the vertexes linked in the clusters share an oxygen atom. However, besides octahedral coordination, the  $q = 36$  cluster also contains pentagonal-bipyrimidal units where the central Mo ion is 7-fold coordinated. Bonds form between two metal oxide monomers when two protons combine with an oxygen atom at a vertex to produce water; see the above reaction and eq 1.

Strong evidence for the existence of the species depicted in Figure 1 has been obtained by comparing Raman or X-ray spectra of the solutions to those of the crystals. Other clusters, such as  $q = 12$  (with  $(p, q) = (14, 12), (15, 12),$  or  $(16, 12)$ ) and  $q = 18$  (with  $(p, q) = (32, 18)$ ), are *proposed*,

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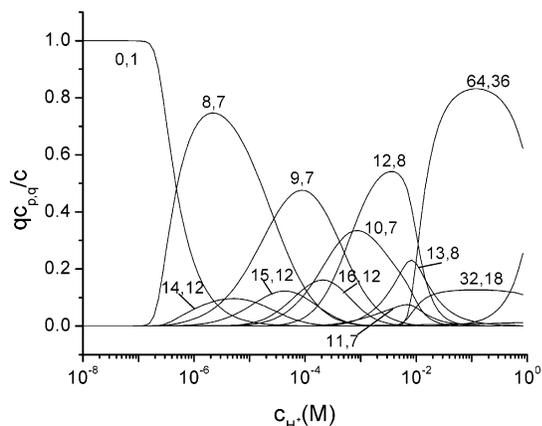
(1) Tytko, K.-H.; Glemser, O. *Adv. Inorg. Chem. Radiochem.* **1976**, *19*, 239.

(2) Tytko, K. H. *Gmelin Handbook of Inorganic Chemistry: Molybdenum*, 8th ed.; Springer: Berlin, 1987; Vol. B 3a.



**Figure 1.** Experimentally observed molybdenum oxide clusters,  $\text{Mo}_7\text{O}_{24}$  (up left),  $\text{Mo}_8\text{O}_{26}$  (up, right), and  $\text{Mo}_{36}\text{O}_{108}$  (down, middle); from ref 2. The clusters mainly consist of octahedrally shaped monomers in which the metal is located in the center of the octahedra. However, the  $\text{Mo}_{36}$  cluster also contains 7-fold coordinated units; see the text. The vertexes of the octahedra are oxygen atoms or (valence) electron pairs. Bonds between the monomers are localized at the vertexes of the metal oxide monomers: shared vertexes indicate bonds. Reprinted with permission from ref 2; copyright Springer 1987.

based on “residual differences” in potentiometric data. These Keggin type structures are expected if other ions (than Mo) are incorporated in the cluster. In tungsten oxide, it has been shown that protons appear to play the role of the central ion; see, for example, ref 1. Combination of experimental results lead to many “reaction models” in the literature.<sup>2</sup> These reaction models predict what the concentrations of clusters  $(p, q)$  are as a function of pH and total metal oxide concentration. Predictions of the most successful reaction model in terms of its ability to describe experimental data (model G\* in ref 2) are shown in Figure 2.

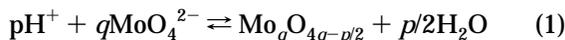


**Figure 2.** Fraction of species  $(p,q)$  as a function of proton concentration according to one of the many reaction models as summarized in ref 2: model  $G^*$ . The identities of the species  $(p,q)$  (see the text) are indicated in the figures. The total molybdate concentration is 0.1 M.

It can be seen in Figure 2 that at relatively low proton concentrations only monomers exist, but on increasing  $c_{H^+}$ , clusters with  $q = 7$  appear. These clusters disappear at the expense of even larger clusters when the proton concentration keeps increasing, and ultimately the largest polyoxomolybdate ion of  $q = 36$  is formed. Increasing the total Mo concentration at constant  $c_{H^+}$  follows the same sequence. At very low molybdate concentrations and very high proton concentrations, however, small, protonated species such as  $(p,q) = (2,1)$  and  $(5,2)$  appear. Note that for the clusters containing 8 and 12 molybdenum atoms (i.e.,  $q = 8$  and  $q = 12$ ), the “trend” that clusters become larger upon increasing proton concentration seems reversed. We will get back to this later. The many reaction models in the literature share the property that at relatively large molybdate concentrations (say  $> 0.01$  M), globally, larger clusters are encountered upon increasing proton concentration. The fractions of these clusters have maxima as a function of proton concentration. In this work, we seek to explain these properties by a global model, to be confirmed using equilibrium ultracentrifugation measurements.

## 2. Empirical Model for the Stability of Metal Oxide Clusters

**Multichemical Equilibrium.** The (reversible) clustering of molybdenum oxide can globally be written as the chemical equilibrium



where we neglect species that are protonated. These may in principle be included in our treatment. However, as stated in the Introduction, at this stage we limit ourselves to understanding the *global* behavior of the system. Thermodynamic equilibrium implies that  $\sum_i v_i \mu_i = 0$ , where  $v_i$  and  $\mu_i$  are the stoichiometric coefficients and the chemical potentials of the components  $i$ , respectively. Writing, for  $i = H^+$ ,  $MoO_4^{2-}$ , and  $Mo_qO_{4q-p/2}$ , the chemical potential as  $\mu_i \approx \mu_i^0 + kT \ln c_i$  where  $\mu_i^0$  is the standard chemical potential and  $c_i$  is the concentration of component  $i$  relative to the “standard concentration”  $c^0 = 1$  M, we get

$$c_q = K c_{H^+}^p c_1^q \quad (2a)$$

with

$$K = \exp\left(\frac{q\mu_1^0 - \mu_q^0 + p\mu_{H^+}^0 - \frac{p}{2}\mu_{H_2O}^0}{kT}\right) = e^{-\Delta G^0/RT} \quad (2b)$$

In these equations,  $K$  is the equilibrium constant. The subscripts 1 and  $q$  refer to monomers ( $MoO_4^{2-}$ ) and  $q$ -mers ( $Mo_qO_{4q-p/2}$ ) of molybdenum, respectively.  $k$  is Boltzmann’s constant,  $T$  is the absolute temperature,  $\Delta G^0$  is the (standard) molar Gibbs free energy change, and  $R$  is the gas constant. If  $K$  is known for all species of interest  $(p,q)$ , then, by eq 2a, the concentrations of  $q$ -mers (actually  $(p,q)$ -mers) can be calculated as a function of the total amount of Mo in the system (using mass conservation) and as a function of the  $H^+$  concentration. This is how Figure 2 was calculated. Here we aim to understand the occurrence of  $q$ -mers on the basis of thermodynamic concepts (but at the expense of details). Note that we presume here that certain cluster sizes appear. The question that we address is, under what conditions are these presumed cluster sizes stable? This approach is different from the approach in ref 3, where the stable cluster sizes follow from a geometrical toy model.

**Interaction Free Energy per Monomer is Approximately Constant for all Clusters.** As mentioned in the Introduction, many different polyoxometalate species, or  $q$ -mers (characterized by the combination  $(p,q)$ ), have been reported, and many different equilibrium constants have been proposed based on different sets of experiments. However, from the many sets of equilibrium constants that are reported in ref 2, it follows that all  $q$ -mers, to a good approximation, have the same free energy *per monomer*, that is,

$$\exp\left(\frac{q\mu_1^0 - \mu_q^0 + p\mu_{H^+}^0 - \frac{p}{2}\mu_{H_2O}^0}{(q-1)kT}\right) = e^{\Delta G^0/(q-1)RT} = \text{constant} \quad (3)$$

This important observation points to a single (packing) principle or rule. This is in fact the basic assumption of a recent geometrical toy model for the behavior of metal oxide clusters; see ref 3. In Table 1, we list some values of the interaction free energy per monomer using the earlier mentioned set of equilibrium constants (i.e., model  $G^*$  in ref 2), but we stress that the many values of the equilibrium constants as reported in ref 2 all point to roughly the same value of the interaction free energy per monomer. Most convincingly, the values that correspond to the species whose existence has been proved ( $q = 7, 8, 36$ ) also point to this same global value of the interaction free energy per monomer.

It is clear from Table 1 that indeed, there is no systematic variation of the interaction free energy per monomer, providing proof of the basic assumption in ref 3. It also implies that only a single geometrical rule underlies the stability of metal oxide clusters. This observation is even more interesting in the light of the fact that octahedral coordination of the Mo units in the clusters is not conserved. Note that the interaction free energy is pretty large: more than 20 times the thermal energy. The constant value of the interaction free energy per monomer implies that the number of bonds per monomer in the

**Table 1. Interaction Free Energies per Mo Atom in Several Clusters of Size  $q$  (Extracted from the Values of  $K$  in Reference 2)<sup>a</sup>**

$q$	Log $K$	$-\Delta G^\circ/(q-1)RT$	$q$	Log $K$	$-\Delta G^\circ/(q-1)RT$
7 <sup>b</sup>	52.92	22.7	18	185.13	25.1
8 <sup>b</sup>	72.59	24.7	36 <sup>b</sup>	346.5	22.8
12	109.56	22.9			

<sup>a</sup> Only nonprotonated species are listed. <sup>b</sup> The existence of these clusters has been proved.

clusters is constant. Motivated by this observation, we now define

$$\kappa = K^{1/(q-1)} = \exp\left(\frac{-\left(q\mu_1^0 - \mu_q^0 + p\mu_{\text{H}^+}^0 - \frac{p}{2}\mu_{\text{H}_2\text{O}}^0\right)}{(q-1)kT}\right) = e^{-\Delta G^\circ/(q-1)RT} \quad (3)$$

so that eq 2a can be written as

$$c_q = \kappa^{q-1} c_{\text{H}^+}^p c_1^q \quad (4)$$

The total concentration of molybdate is given by  $c = \sum_q q c_q$ . Defining  $y = \kappa c$ ,  $y_q = \kappa c_q$ , so that  $y_q = c_{\text{H}^+}^p y_1^q$ , we get

$$y = \sum_q q y_q = y_1 + \sum_q q c_{\text{H}^+}^p y_1^q \quad (5)$$

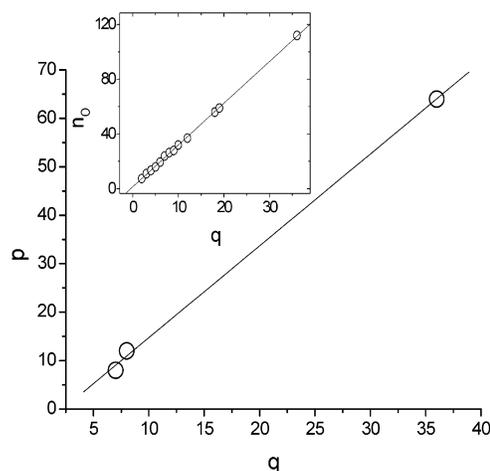
The last summation in this equation is over all clusters of size  $q > 1$ , in this case  $q = 7, 8, 12, 18$ , and  $36$ . The above equation only contains  $y_1$  as the unknown variable; the concentrations of all other species,  $y_q = c_{\text{H}^+}^p y_1^q$ , follow from  $y_1$ . We will show later that eq 5 implies that a critical concentration of monomers exists, analogous to the critical micelle concentration in surfactant systems.

**Extracting  $p(q)$  from Cluster Composition.** In the above analysis,  $p$  and  $q$  are dependent variables:  $p$  stands for the number of protons that are consumed in order to form a cluster of size  $q$ ; see the introduction and eq 1. We will write  $p(q)$  from now on, to illustrate that the variables  $(p, q)$  are dependent. In Figure 3, we plotted  $p(q)$  versus  $q$  for the only three nonprotonated species whose existence has been proved:  $(p, q) = (8, 7)$ ,  $(12, 8)$ , and  $(64, 36)$ . These numbers fall on a straight line given by

$$p(q) = 1.89q - 4.24 \quad (6)$$

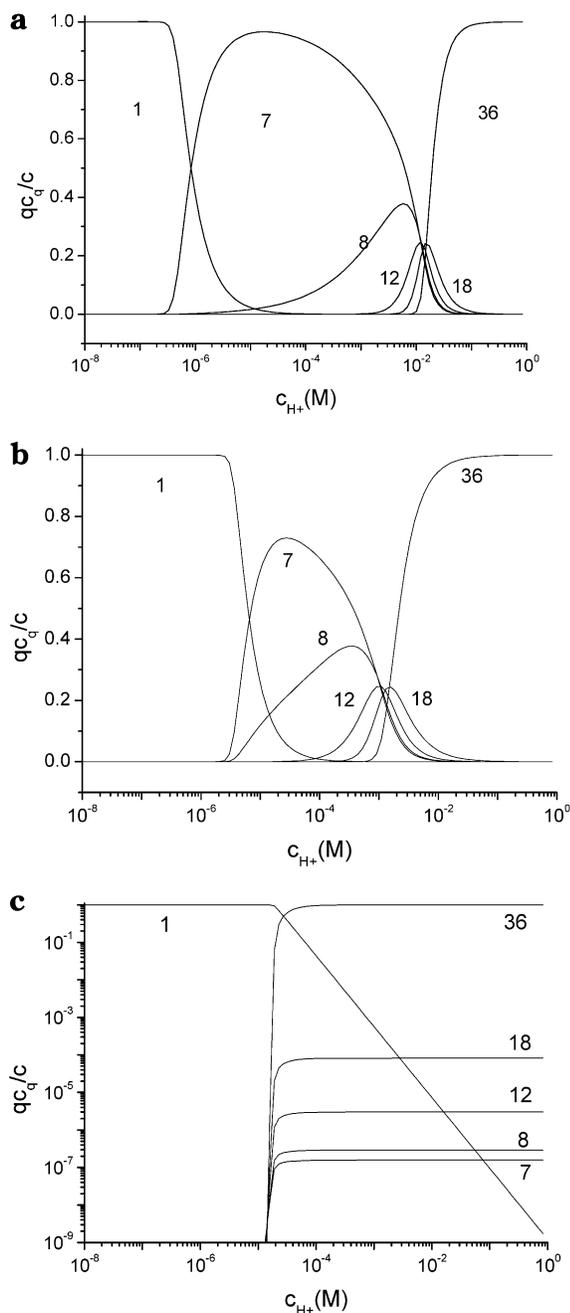
The function  $p(q)$  can also be extracted from the chemical compositions of the many nonprotonated clusters as proposed (but not proved) by many sources in ref 2: from eq 1, it follows that  $p(q)$  is given by the number of oxygen atoms in a cluster,  $n_o$ , via  $p = 8q - 2n_o$ . In the inset in Figure 3, we plotted  $n_o$  versus  $q$  of all the polyoxomolybdate species that were listed in ref 2; we extract  $p(q)$  and find, to a good approximation, again a linear relation given by  $p(q) = 1.89q - 2.73$ . It turns out that this function leads to qualitatively similar behavior as compared to eq 6; see Figure 4. However, since eq 6 is based on experimentally proved species, this is what we will use in our further calculations.

**Comparison with Current Models.** In Figure 4a, we plotted the fraction of molybdate in clusters of size  $q$ ,  $qc_d/c$ , as a function of  $c_{\text{H}^+}$ , for the same (total) molybdenum concentrations (0.1 M) as in Figure 2. These curves were calculated by numerically solving eq 5 and using eq 6. In Figure 4b, as a comparison, we used  $p(q) = 1.89q - 2.73$  instead of eq 6, as obtained from the inset of Figure 3, based on an extensive list of polyoxomolybdate species. The different functions of  $p(q)$  only lead to quantitative



**Figure 3.** Plot of  $p(q)$  versus  $q$ , where  $p$  is the number of protons and  $q$  is the number of monomers that are consumed upon formation of a cluster. We plotted the only three nonprotonated species whose existence has been proved (see description in the text). These numbers fall on a straight line given by  $p(q) = 1.89q - 4.24$ . Inset: We plot  $n_o$  versus  $q$  ( $n_o$  is the number of oxygen atoms in a cluster) of all the polyoxomolybdate species that have ever been reported, extract  $p(q)$ , and find, to a good approximation, a linear relation given by  $p(q) = 1.89q - 2.73$  (for further explanation see the text).

and no qualitative differences. As can be seen in Figure 4a,b, our model predicts that upon increasing the proton concentration, larger and larger species appear at the expense of smaller ones. Although this is globally in agreement with experiments, for  $q = 8$  and  $q = 12$  the trend is reversed compared to Figure 2: we predict that  $q = 12$  appears at higher  $c_{\text{H}^+}$  than  $q = 8$ , while according to the latest reaction model, it is the other way around. As mentioned in the Introduction, however, the species  $q = 12$  and  $q = 18$  have never been observed directly. In particular, the proposal that  $q = 12$  exists is motivated by the tungsten oxide system. Indeed, strong evidence of tungsten oxide clusters containing 12 monomers has been presented; see ref 1. More relevant, the number of protons that the  $q = 12$  molybdenum species consume upon formation out of monomers seems inconsistent with the proposed equilibrium constants. Let us motivate this statement. The proposed  $q = 12$  molybdenum species with values of  $p$  between 14 and 16 (corresponding to  $\text{Mo}_{12}\text{O}_{40}(\text{OH})_2^{10-}$ ,  $\text{HMo}_{12}\text{O}_{40}(\text{OH})_2^{9-}$ , and  $\text{H}_2\text{Mo}_{12}\text{O}_{40}(\text{OH})_2^{8-}$ ) consume significantly fewer protons ( $p/2$ ) upon formation compared to the other species: it can easily be verified that these values are between 2.4 and 4.4 smaller than expected from the behavior of the species whose existence has been proved, given by eq 6. At the same time, its proposed equilibrium constant (shown for (15,12), but the ones for (14,12) and (16,12) are not much different) points to an average interaction free energy that is comparable to that of the other species. However, if fewer protons are consumed, fewer bonds will be formed and thus a smaller absolute value of the interaction free energy per monomer is expected. This is clearly not the case, as can be seen in Table 1. So, unless  $q = 12$  is stabilized by a mechanism that is completely different from that of the other species, we believe that the species (14,12), (15,12), and (16,12) do not exist; that is, their equilibrium constants are much smaller than those reported in ref 2 (and shown in Table 1), so that they are not going to appear in appreciable amounts. We do not rule out that species with  $q = 12$  appear, but then the corresponding  $p$  value of the unprotonated species is predicted to be around  $p(q=12)$



**Figure 4.** (a) Fraction of species of size  $q$  (indicated in the figure) as a function of the proton concentration. These fractions  $qc_q/c$  were calculated by numerically solving eq 5 with a total concentration of monomers  $c = 0.1$  M,  $1/\kappa = 5.43 \times 10^{-11}$ , and  $p(q) = 1.89q - 4.24$  (eq 6) for nonprotonated species whose existence has been proved (see Figure 3). As can be seen for  $q = 8$  and  $q = 12$ , the trend is reversed compared to Figure 2. (b) As in panel a, but now for  $p(q) = 1.89q - 2.73$ , following from an extensive list of polyoxomolybdate species that have ever been proposed; see Figure 3, inset. (c) Fraction of species ( $p, q$ ) as a function of proton concentration using  $p(q) = 1.89q$ , a total concentration of monomers  $c = 0.1$  M, and  $1/\kappa = 7.5 \times 10^{-11}$ . It may seem that the species  $q > 1$  reach a constant value while  $q = 1$  keeps decreasing, thereby violating mass conservation. In fact, all cluster concentrations  $q > 1$  keep increasing with  $c_{H^+}$ .

$\approx 1.89q - 4.24 \approx 18$ , as has implicitly been assumed in calculating Figure 4a.

The same qualitative trend as in Figure 4 is observed if  $c_{H^+}$  is kept constant, and the total molybdenum concentration is increased (not shown). As illustrated in Figure 4c, this behavior depends on the detailed form of

the function  $p(q)$ . In this figure, we used  $p(q) = 1.89q$ , and clearly cluster fractions with  $q > 1$  continuously increase with proton concentration without reaching maxima. We systematically checked the influence of the function  $p(q)$  on the qualitative behavior of the cluster fractions as functions of proton and total molybdenum concentration. We conclude that functions of the form  $p(q) = aq - b$ , with  $a, b > 0$ , lead to qualitatively similar behavior as in Figure 4a,b. This illustrates that not only the interaction energies are important (these determine if “magic numbers” such as  $q = 7, 8, 12, \dots$  are to appear at all) but also the stoichiometry of the equilibrium qualitatively influences the behavior of the systems.

From Figure 4a,b, we conclude that our model globally captures the behavior of the molybdate system. However, there is an important detail concerning the appearance of the species with  $q = 8$  and  $q = 12$ : our model and the reaction model in ref 2 contradict. In the next section, we will use equilibrium ultracentrifugation measurements as an attempt to settle this issue but also to independently study and check the evolution of average cluster sizes with proton concentration.

### 3. Experimental Section: Equilibrium Ultracentrifugation (UC)

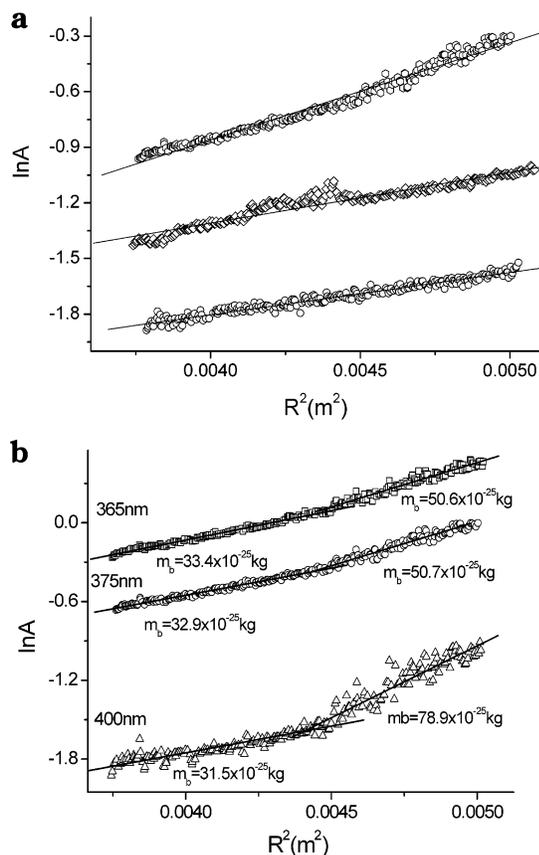
**Sample Preparation.** Molybdenum(VI) oxide solutions were prepared at different pHs (adjusted by  $HClO_4$  and  $NaOH$ ) and at constant ionic strength of  $3 M^2$  by adding  $NaClO_4$ . The total molybdate concentration in solution was  $0.1$  M.

**Determination and Calculation of Cluster Buoyant Masses.** The buoyant masses of the clusters were determined from the measured optical absorption profiles (at several wavelengths) using analytical ultracentrifugation (Beckman XL-1). If clusters do not interact, each equilibrium concentration profile (in our case established after 1–2 weeks) is an exponential function of its buoyant mass, that is,

$$c(r) = c(r_0) \exp\left(\frac{m_b \omega^2 (r^2 - r_0^2)}{2kT}\right) \quad (7)$$

where  $c(r)$  is the concentration as a function of radial position  $r$ ,  $r_0$  is a reference radial position,  $m_b$  is the buoyant mass of a single species, and  $\omega$  is the rotational velocity. We expect that several different complexes are present, with sizes depending on the pH. Concentration profiles as eq 7 in principle follow from the optical absorption profiles. Different clusters may absorb at different wavelengths; for this reason, the optical absorption profiles at several different wavelengths were measured. These wavelengths were chosen on the basis of the optical absorption spectra of the samples.

The buoyant mass of a cluster follows from  $m_b = m(1 - \rho_w/\rho_c)$ , where  $m$  and  $\rho_c$  are the mass and mass density of a cluster, and  $\rho_w$  is the mass density of the aqueous solution. The mass densities of the clusters were calculated from the atomic radii, assuming close packing of the atoms in a cluster. This leads to, for example,  $\rho_c = 7.2$  g/cm<sup>3</sup> for  $Mo_{36}O_{112}^{8-}$ . To check this method of calculating mass densities, we compared the mass density as calculated above to the one reported for the crystalline form of  $Mo_{36}O_{112}(H_2O)_{16}^{8-}$ . The latter equals  $2.77$  g/cm<sup>3</sup><sup>2,4</sup> (note that the large fraction of water in the clusters significantly reduces their mass density), while by our method, we find



**Figure 5.** (a) Representative equilibrium optical absorption profiles of systems with different pH values and constant total molybdate concentration (0.1 M Mo), in an ultracentrifuge ( $\omega = 10^4$  rpm), plotted as  $\ln A$  versus  $r^2$  (see eq 7 and the discussion in the Experimental Section). The buoyant masses,  $m_b$ , of the clusters that follow from the slopes of the curves are  $m_b = 17.0 \times 10^{-25}$  kg (pH = 6, 360 nm,  $\circ$ ),  $m_b = 20.4 \times 10^{-25}$  kg (pH = 4, 380 nm,  $\square$ ), and  $m_b = 39.2 \times 10^{-25}$  kg (pH = 2, 375 nm,  $\circ$ ). (b) As in panel a, but only for the system at pH = 2, observed at different wavelengths, indicated in the figure. The curves clearly consist of two linear parts. The buoyant masses,  $m_b$ , of the particles that follow from the slopes of the curves are indicated in the figure. The curves are noisy due to very small absorption at the observed wavelength. However, the buoyant masses calculated from the largest slopes indicate the presence of clusters with  $q = 64$ ; for more details see the Experimental Section.

a value of  $3.55 \text{ g/cm}^3$  for  $\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{16}^{8-}$ . This is an acceptable difference, in particular considering the fact that throughout the crystals of  $\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{16}^{8-}$ , atoms are not close-packed. Note that even though the error that we make in calculating  $\rho_c$  is significant, the error it causes in  $m_b$  is still small as long as  $\rho_w/\rho_c \ll 1$ , which is the case here. Thus we estimate the error we make in calculating the buoyant masses to be less than 10%.

**Experimental Results.** It can immediately be seen in Figure 5a, where we plotted (the logarithm of) the absorption profile, that clusters become larger, on average, upon decreasing the pH. At the smallest investigated pH value of 2, two linear parts of the profiles can be distinguished, as shown in Figure 5b. We believe that these two parts indicate the presence of two significantly different cluster sizes. The buoyant masses extracted from the absorption profiles slightly depend on the wavelength at which they were measured. In Table 2, we summarize the results. Table 2a contains the calculated values of an extensive list of complexes at the pHs where they are expected, based on ref 2. Table 2b lists the experimentally observed buoyant masses, at different pHs and wave-

**Table 2**(a) Proposed Clusters and Their Calculated Buoyant Masses ( $m_b$ ) at Several pH Values

pH	( $p, q$ )	complexes	$m_b (\times 10^{-25})$ kg (calculated)
6	(8,7)	$\text{Mo}_7\text{O}_{24}^{6-}$	14.9
6	(8,7)	$\text{Mo}_7\text{O}_{20}(\text{OH})_8^{6-}$	16.6
6	(9,7)	$\text{HMo}_7\text{O}_{24}^{5-}$	15.0
6	(14,12)	$\text{Mo}_{12}\text{O}_{40}(\text{OH})_2^{10-}$	26.0
4	(8,7)	$\text{Mo}_7\text{O}_{24}^{6-}$	14.9
4	(8,7)	$\text{Mo}_7\text{O}_{20}(\text{OH})_8^{6-}$	16.6
4	(9,7)	$\text{HMo}_7\text{O}_{24}^{5-}$	15.0
4	(10,7)	$\text{H}_2\text{Mo}_7\text{O}_{24}^{4-}$	15.0
4	(12,8)	$\text{Mo}_8\text{O}_{26}^{4-}$	16.8
4	(15,12)	$\text{HMo}_{12}\text{O}_{40}(\text{OH})_2^{9-}$	26.0
4	(16,12)	$\text{H}_2\text{Mo}_{12}\text{O}_{40}(\text{OH})_2^{8-}$	26.0
2	(10,7)	$\text{H}_2\text{Mo}_7\text{O}_{24}^{4-}$	15.0
2	(12,8)	$\text{Mo}_8\text{O}_{26}^{4-}$	16.9
2	(11,7)	$\text{H}_3\text{Mo}_7\text{O}_{24}^{3-}$	15.0
2	(13,8)	$\text{HMo}_8\text{O}_{26}^{3-}$	16.9
2	(32,18)	$\text{Mo}_{18}\text{O}_{56}^{4-}$	37.5
2	(32,18)	$\text{Mo}_{18}\text{O}_{56}(\text{H}_2\text{O})_{10}^{4-}$	31.9
2	(32,18)	$\text{Mo}_{18}\text{O}_{54}(\text{OH})_4(\text{H}_2\text{O})_8^{4-}$	33.8
2	(64,36)	$\text{Mo}_{36}\text{O}_{112}^{8-}$	75.0
2	(64,36)	$\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{16}^{8-}$	66.1
1	(2,1)		
1	(5,2)		
1	(32,18)	$\text{Mo}_{18}\text{O}_{56}^{4-}$	37.5
1	(32,18)	$\text{Mo}_{18}\text{O}_{56}(\text{H}_2\text{O})_{10}^{4-}$	31.9
1	(32,18)	$\text{Mo}_{18}\text{O}_{54}(\text{OH})_4(\text{H}_2\text{O})_8^{4-}$	33.8
1	(64,36)	$\text{Mo}_{36}\text{O}_{112}^{8-}$	75.0
1	(64,36)	$\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{16}^{8-}$	66.1

(b) Buoyant Masses ( $m_b$ ) at Different pH Values, Observed at Different Wavelengths  $\lambda$ 

pH	$m_b (\times 10^{-25})$ kg (UC)	$\lambda$ (nm)	pH	$m_b (\times 10^{-25})$ kg (UC)	$\lambda$ (nm)
6	15.0	345	2	42.2	365
6	15.5	350	2	32.0	370
6	17.0	360	2	39.2	375
6	18.0	370	2	41.0	400
4	19.3	360	2	(33.4)	365
4	19.4	365	2	(32.9)	375
4	19.7	370	2	(31.5)	400
4	20.4	380	2	(50.6)	365
4	21.1	390	2	(78.9)	400

lengths. The values between brackets were extracted from profiles corresponding to (at least) two differently sized clusters, shown in detail in Figure 5b.

As far as we are aware, only the cluster with  $q = 36$  has been observed by UC measurements.<sup>4</sup> Comparing sections a and b of Table 2 verifies the presence of  $q = 7$  and  $q = 8$  at pH = 6 and pH = 4, as well as  $q = 18$  and  $q = 36$  at pH = 2. The value of  $m_b \approx 50 \times 10^{-25}$  kg, as extracted from the steepest part of absorption profiles (not the average) shown in Figure 5b, does not correspond to any of the proposed clusters in Table 2a. Probably this value does not correspond to a single species but arises because of the presence of both  $q = 18$  and  $q = 36$  clusters. Indeed, the profile at larger wavelength clearly points to  $q = 18$  and  $q = 36$  being present. It is expected that the largest cluster absorbs at larger wavelength than the smallest cluster, and therefore the profile at larger wavelength is more sensitive to  $q = 36$ .

The value of  $m_b$  that we find that is the closest to a cluster with  $q = 12$  is  $21 \times 10^{-25}$  kg at pH = 4. However, this value is still closer to a cluster with  $q = 8$ ; see Table 2a. There is no indication that the sedimentation profiles at pH = 4 consist of two parts, as in Figure 5b. Therefore, it is not plausible that the value of  $m_b \approx 21 \times 10^{-25}$  kg is effectively an average between clusters of different sizes, although it cannot be ruled out at this point. From the

data presented here, we are led to believe that  $q = 12$  does not show up in detectable concentrations in the samples that we studied. However,  $q = 18$  has, to our knowledge, never been observed before; it has been proposed by symmetry considerations.<sup>2</sup> We find strong indications that this cluster with  $q = 18$  is indeed stable at pH = 2. It clearly follows from Table 2b that clusters become larger on average upon decreasing the pH, as predicted.

#### 4. Connection with Micelle Formation

If  $c_{H^+}$  is set to unity and if only a single species with  $q > 1$  is present, then eq 5 reduces to the well-known equation by Debye<sup>5</sup> that describes micelle formation:  $y = y_1 + qy_1^q$ . In that case,  $y_1$  corresponds to surfactant monomers, and  $y_q = y_1^q$  to micelles of size  $q$ ; a typical value of  $q$  would be 80 in micelles.<sup>6</sup> Regarding the total surfactant concentration  $y$  as the variable,  $y_1 = y$  as long as  $y < 1$  and  $q \gg 1$ . In other words, as long as the total concentration of surfactants is small, only monomers appear. As soon as  $y$  becomes of order unity, however, the second term takes over:  $y_1$  becomes unity and almost constant while the concentration of monomers in the form of clusters,  $qy_q = qy_1^q$ , increases linearly with  $y$ . At the crossover, from the definition  $y = \kappa c$  and  $y_q = \kappa c_q$  it is easy to see that the real concentration of monomers  $c_1 = 1/\kappa$ . This well-known quantity is the *critical micelle concentration*.

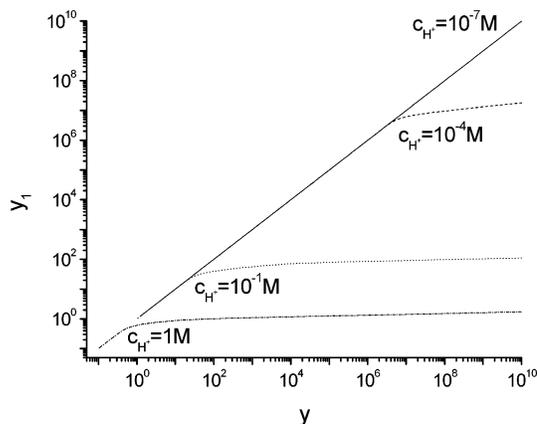
In the case of cluster formation in metal oxides, the situation is a little more complicated but not fundamentally different from the situation described above. First of all, if  $c_{H^+} = 1$ , the limiting concentration of cluster monomers is indeed  $y_1 \approx 1$  or  $c_1 \approx 1/\kappa$ . This is shown in Figure 6 where we plotted the monomer concentration  $y_1$  versus  $y$ . Since  $q$  is not very much larger than unity (the smallest value that we have is  $q = 7$ ), the crossover from  $y_1 = y$  to  $y_1 \approx 1$  that we observe is not as sharp as it is for micelles where  $q \gg 1$ . At other proton concentrations, the critical value of  $y$  above which clusters start forming depends on the proton concentration and on the value of  $q$  corresponding to the cluster first formed,  $q$ . We propose to term this value of  $y_1$  the "critical cluster concentration". Indeed, the value of the critical cluster concentration follows from  $y_1 \approx y_q = c_{H^+}^{p(q)} y_1^q$  and is given by

$$y_1^* = c_{H^+}^{-p(q)/(q-1)} \quad (8a)$$

or in terms of the real monomer concentration

$$c_1^* = \kappa^{-1} c_{H^+}^{-p(q)/(q-1)} \quad (8b)$$

where the star indicates the value of the critical cluster concentration. It can be verified from Figure 6 that indeed,



**Figure 6.** Concentration of free monomers  $y_1$ , as a function of the total monomer concentration,  $y$ , at several values of the proton concentration indicated in the figure. Curves are plots of the function  $y = \sum q y_q$  (eq 5). The crossovers from  $y_1$  rising linearly with  $y$  to almost constant values indicate cluster formation analogous to the formation of micelles in surfactant solutions (see explanation in the text).

these values of  $y_1^*$  or  $c_1^*$  as a function of proton concentration are well described by eq 8.

#### 5. Concluding Remarks

We have shown that the conditions under which clusters of molybdenum oxide are stable follow from two basic assumptions: (1) the average interaction free energy per monomer in a cluster is constant and independent of cluster size  $q$ , and (2) the relation between the number of protons required to form a cluster of size  $q$ ,  $p(q)$ , is a function of  $q$  of the form  $p(q) = aq - b$ , with  $a, b > 0$ . Using these considerations as input in a phenomenological model, we predict, among other things, that clusters of increasing size appear upon increasing the proton concentration. This is globally in agreement with experiments, but in current reaction models<sup>2</sup> the situation for clusters containing 8 and 12 Mo atoms is reversed with respect to our predictions. Using ultracentrifugation measurements, we found no indications that clusters with 12 Mo atoms exist at all, which resolves the controversy. We do find indications for the presence of another species not seen before: clusters containing 18 Mo atoms.

Finally, we showed that globally, molybdenum(VI) oxide clusters behave as micelles. However, the critical cluster concentration sensitively depends on proton concentration and is given by eq 8. Our next goal is to generalize the concepts provided in this work to the beautiful, highly symmetrical clusters with reduced centers (Mo(V)) containing up to 176 monomers or the ones found in the presence of acetate and sulfate ions that may contain as many as 132 and 368 monomers, respectively; see, for example, refs 7 and 8.

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(5) Debye, P. J. W. *Ann. N.Y. Acad. Sci.* **1949**, *51*, 575.  
 (6) Israelachvili, J. *Intermolecular & Surface Forces*, 2nd ed.; Academic Press: San Diego, 1992.

(7) Müller, A.; Krickemeyer, E.; Dillinger, S.; Bogge, H.; Proust, A.; Plass, W.; Rohlfing, R. *Naturwissenschaften* **1993**, *80*, 560.  
 (8) Müller, A.; Kögerler, P.; Bögge, H. *Struct. Bonding* **2000**, *96*, 203.