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Hydrolysis of Molybdenum(VI). Ultracentrifugation, Acidity Measurements, and Raman Spectra of Polymolybdates[1]

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The aggregates formed on acidification of alkali molybdate solutions have been studied by equilibrium ultracentrifugation by potentiometric acidity measurements, and by Raman spectroscopy. Equilibrium ultracentrifugation indicates that polymerization increases sharply between $p = 0$ and $p = 1$, and that species having average degrees of polymerization of 6–9 occur in the range $p = 1$–1.5, where p is the average number of protons bound per molybdenum. Higher molecular weights are found for $p > 1.5$; with excess acid, molecular weights decrease, but some polymerization appears to persist even in 3 *M* excess HCl. Acidity measurements up to $p = 1.5$ can be explained equally well by schemes involving monomer–heptamer, monomer–octamer, or monomer–heptamer–octamer equilibria. Comparison of the Raman spectra of solutions and of solids, whose aggregation is known from X-ray evidence, indicates that the paramolybdate ($Mo_7O_{24}^{6-}$) ion exists in solution at p *ca.* 1.14, and that octamolybdates ($Mo_8O_{26}^{4-}$) occur in solutions of p about 1.5. There is no evidence for the presence of important amounts of species having degrees of polymerization intermediate between monomers and heptamers under the conditions studied. Although there is some indication of counterion (Na^+ or Li^+) binding by the polymolybdates, the evidence is inconclusive. Volumes and refractive index increments of hydrolyzed molybdate solutes are reported.

Although it is generally accepted that isopolyanions are formed when acid is added to an alkali molybdate (*e.g.*, Na_2MoO_4) solution, little is known with certainty about the nature of the species formed. Since the pioneer work of Jander some 30 years ago, in which ions containing 3, 6, 12, and 24 molybdenum atoms were postulated (in a later publication[4f] this scheme was somewhat modified), at least 30 papers on the subject have been published. Methods which have been used include dialysis and diffusion,[4] conductometric titrations,[5] pH titrations,[6] light scattering,[7] cryoscopy,[8] ion exchange,[9] and ultraviolet spectrophotometry.[10]

Lindqvist[11] has reviewed the work up to 1950 and concluded, mainly from the cryoscopic evidence of Byé[5d] and analogy with solid compounds, that the ions previously shown by X-ray diffraction to be present in the crystalline ammonium molybdates $Mo_7O_{24}^{6-}$ and $Mo_8O_{26}^{4-}$ are also formed in solution.

$$7MoO_4^{2-} + 8H^+ \rightleftharpoons Mo_7O_{24}^{6-} + 4H_2O$$
$$8MoO_4^{2-} + 12H^+ \rightleftharpoons Mo_8O_{26}^{4-} + 6H_2O$$

In subsequent spectrophotometric studies Lindqvist[10a] and later Daniele[10c] obtained additional evidence for the above scheme, which is also in accord with the light scattering work of Tyree, *et al.*[7a,b] Recently Sasaki, Lindqvist, and Sillén,[6e] in a preliminary report of acidity measurements, using the precise potentiometric techniques developed by Sillén, found a very good fit with a scheme in which $Mo_7O_{24}^{6-}$ is the first polymeric species formed on acidification of molybdate solutions; they propose, however, more highly protonated heptamers at increased acidities in place of the octamer listed by Lindqvist.[10] The two monomeric species $HMoO_4^-$ and H_2MoO_4 were proposed to be present in significant amounts in dilute solutions.

However, at a time when some measure of agreement between various workers, at least with respect to the first polymeric hydrolysis product formed on acidification of MoO_4^{2-}, had been attained, Cooper and Salmon,[9a] using an anion-exchange resin to measure the average charge per molybdenum of the species adsorbed as a function of pH of the external solution, suggested that the initial hydrolysis product is a tetra-

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mer $Mo_4O_{13}^{2-}$, which on further protonation condenses to $H_2Mo_{10}O_{32}^{2-}$. They specifically exclude both $Mo_7O_{24}^{6-}$ and $Mo_8O_{26}^{4-}$. Heitner-Wirguin and Cohen,[9b] using a similar method, also favor $Mo_4O_{13}^{2-}$.

In this brief discussion, we have by no means given an exhaustive survey of the work reported on this system, nor have we even mentioned many of the species which have been proposed at one time or another. Inspection of the abstracts of the I.U.P.A.C. Seventh International Conference on Coordination Chemistry (Stockholm, 1962) makes it evident that agreement has not yet been achieved; why such extensive work has not led to generally acceptable conclusions is an interesting question. Much of the conflict existing in the literature stems from over-ambitious attempts to interpret "breaks" in pH and conductometric titration curves. For example, to distinguish between two species which have been frequently proposed, $H_7Mo_6O_{24}^{5-}$ and $Mo_7O_{24}^{6-}$ (or its equivalent for present purposes, $H_8(MoO_4)_7^{6-}$, which differs only in that the formula includes four waters), with 1.167 and 1.143 protons per molybdenum atom, respectively, it is necessary to locate such breaks with a precision of better than 1%. This is virtually impossible with the molybdate system owing to the broadening of the inflection points, arising from the coexistence of several molybdate species at a given acidity and total molybdate concentration. Moreover, even if the breaks were sufficiently defined, such methods would merely yield a value for the average number of protons bound per molybdenum atom and would give no direct information on the number of molybdenum atoms in the complex. Thus many of the data which have been taken to indicate a tetrameric species could equally well be interpreted on the basis of some multiple of this unit, *e.g.*, $Mo_8O_{26}^{4-}$ (or $H_{12}(MoO_4^{4-})_8$).

With respect to other methods, Sasaki[12] has pointed out the possibility of interference by strongly absorbing silicomolybdate ions in spectrophotometry, and a few measurements of ours confirm this. Tobias[13] has discussed difficulties in estimation of degrees of polymerization, at least of highly aggregated solutes, by cryoscopy. Baker and Pope[14] demonstrated that diffusion coefficients of two heteropoly acids having quite different molecular weights are identical. It seems probable, therefore, that some of the techniques employed in the past have not been as definitive as had been hoped by their users.

In view of the continued widespread interest in the subject, it seemed worthwhile to examine molybdate solutions of various degrees of neutralization by equilibrium ultracentrifugation. The results of this study, which was commenced independently at the National Chemical Laboratory, Teddington, and at this laboratory, soon enabled many of the proposed schemes to be rejected, but did not allow a definitive choice among other possibilities. These measurements were therefore supplemented by acidity measurements and Raman spectroscopy in hope of a more decisive selection.

Experimental

(1) **Centrifugation.**—Details of centrifugation technique and of the computational procedure used in the interpretation of results have been presented elsewhere.[15] Approximations involved in the treatment of data for a solute analogous to the present one (in that it was polydisperse, charged, and that its various species had different refractive index increments and volumes) also have been discussed earlier.[16] Centrifugations were carried out using a Spinco Model E ultracentrifuge and, except for the solutions containing excess acid, 12-mm. interference cells were used. The temperature was 25° and speeds varied between 16,200 and 23,150 r.p.m. Interference optics was used. In a few runs in excess acid, sedimentation was followed by schlieren optics with 30-mm. cells. The latter were interpreted in an approximate manner outlined elsewhere[17]; they were carried out at 33,450 r.p.m. and at approximately 30°.

(2) **Density and Refractive Index Measurements.**—Densities were measured with a *ca.* 24-ml. pycnometer and refractive index increments with a Brice-Phoenix differential refractometer. The refractive index of one of the solutions was checked with a 12-mm. synthetic boundary cell and gave a value within 0.3% of that measured with the refractometer.

(3) **Acidity Measurements.**—The e.m.f. of the cell

$$\text{glass electrode} \,\|\, (Na^+ (1\ M), H^+)((H_pMoO_4^{(2-p)-}), Cl^-) \mid NaCl\ (1\ M), AgCl(s);\ Ag(s)$$

was measured by means of a vibrating reed electrometer.[18] The symbol **p** refers to the average number of protons bound per Mo(VI); it is obtained from the stoichiometric ratio of acid to molybdate, with a correction for free acid where necessary ($p < 1.3$). For the few measurements in 3 *M* NaCl and 3 and 1 *M* LiCl supporting electrolyte, the composition of the silver–silver chloride half-cell was changed accordingly. The electrode system, which was described previously,[16] was standardized every hour with a solution of 0.001 *M* HCl in 0.999 *M* NaCl and the acidity of the molybdate solutions taken as

$$\log c_H = \log (c_H)_{std} + (E_{Mo(VI)\ soln} - E_{std})/59.16 \quad (1)$$

where *E* is the potential in millivolts. The response of the glass electrode was checked using a series of HCl–NaCl mixtures 1 *M* in total chloride and was found to approach closely the theoretical value of 59.16 for acid concentrations below 0.005 *M*. Junction potentials arising from the change in acidity between the standard and the molybdate solutions should be negligible. An attempt was made in preliminary experiments to estimate the junction potential contributed by the molybdate species by making measurements both with and without a junction, but in the more acid solutions a blue color at the Ag–AgCl electrode indicated reduction of the molybdate to molybdenum blue, and only the measurements with a junction are reported here. The precision of the measurements was better than 0.1 mv., but uncertainties arising from junction potential, activity coefficient variations, etc., make the values of log c_H considerably less accurate than the precision would imply.

The most concentrated (0.08 *M*) molybdenum solutions were prepared by weight from analyzed stock solutions, and the more dilute solutions were prepared by volume dilution with calibrated burets. Solutions were aged for 2 weeks before the acidities were measured.

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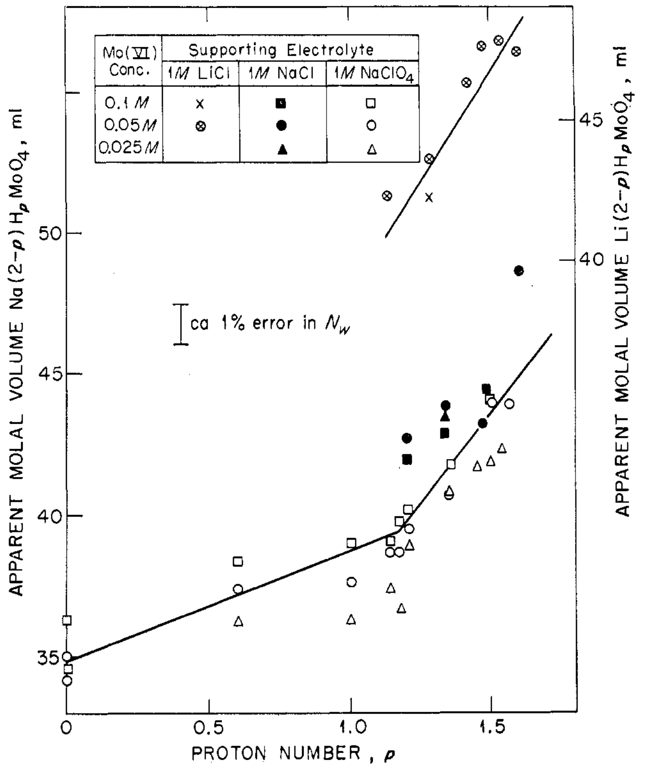

Fig. 1.—Apparent molal volume of hydrolyzed sodium and lithium molybdates.

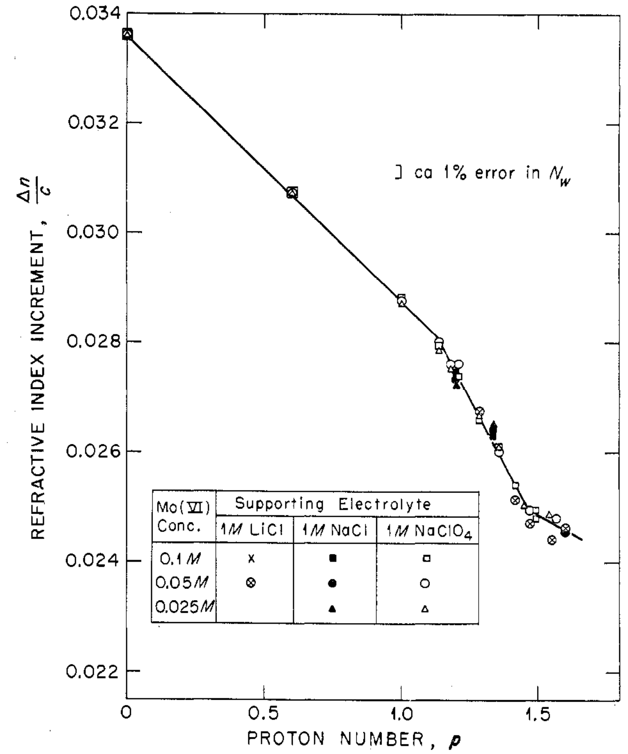

Fig. 2.—Refractive index increments at 546 mμ of hydrolyzed sodium and lithium molybdates, (Na or Li)$_{2-p}$H$_p$MoO$_4$.

(4) **Raman Spectra.**—Raman spectra were obtained with a Cary Model 81 spectrophotometer. The 4358 Å. mercury line was isolated with a filter solution of Cyasorb U.V.-24 and ethyl violet in *n*-propyl alcohol solution. The cell used for the crystalline spectra was developed by Keller.[19] Standard Cary 19-mm. cells were used for the solutions.

(5) **Materials.**—Sodium molybdate, ammonium paramolybdate, sodium chloride, and lithium chloride were of reagent grade (Baker Analyzed reagent) and were used without further purification. Lithium hydroxide was prepared by dissolving the metal in water in an atmosphere of N_2. Sodium perchlorate was prepared by neutralizing sodium hydroxide with perchloric acid to pH 4, removing CO_2 with a stream of nitrogen, and then neutralizing further to pH 7. A slight precipitate formed on standing; this was filtered off, the solution reacidified to pH 4 under nitrogen, and then brought back to pH 7 with NaOH prepared by dilution of a saturated solution with carbonate-free water. Molybdic acid, *ca.* 0.3 *M*, was prepared by cation exchange from sodium molybdate solution with a column of Dowex 50W-X12 in the H^+ form.

Sodium molybdate was analyzed by precipitation as $PbMoO_4$ and the total cation content checked by ion exchange using Dowex 1-X8 in the hydroxide form and titrating the effluent with acid. Molybdic acid and ammonium molybdate solutions were evaporated to dryness at 110°. The molybdenum was determined as MoO_3 by ignition to constant weight at 400°, and molybdic acid by titration with sodium hydroxide solutions to pH 9. Hydrochloric acid was standardized against sodium hydroxide, which in turn had been titrated against potassium acid phthalate. Supporting electrolyte stock solutions were analyzed by evaporation of samples to dryness, followed by drying to constant weight at 110° for $NaClO_4$ and 300° for NaCl.

In measurements of Raman spectra of crystals, Fisher reagent grade ammonium paramolybdate (Batch 700719) was used without further treatment. The solid was analyzed for Mo and for NH_3, the latter by displacement as gas by base, recapture in a known amount of acid, and titration of the excess acid. Water was estimated by difference, both for the para- and octamolybdate; p is given by 2 − (moles of ammonium/mole of Mo(VI)).

Anal. Calcd. for $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$: MoO_3, 81.52; $(NH_4)_2O$, 12.62; H_2O, 5.86; p, 1.143. Found: MoO_3, 81.55; $(NH_4)_2O$, 12.60; H_2O, 5.85; p, 1.144.

Ammonium octamolybdate (or tetramolybdate, as it is sometimes called) was prepared by adding the calculated amount of molybdic acid to ammonium paramolybdate, followed by crystallization. The analysis favored a formula with four, rather than five, waters per unit.

Anal. Calcd. for $(NH_4)_4Mo_8O_{26}\cdot 5H_2O$: MoO_3, 85.57; $(NH_4)_2O$, 7.74; H_2O, 6.69; p, 1.500. Calcd. for $(NH_4)_4Mo_8O_{26}\cdot 4H_2O$: MoO_3, 86.73; $(NH_4)_2O$, 7.85; H_2O, 5.42; p, 1.500. Found: MoO_3, 86.73; $(NH_4)_2O$, 7.94; H_2O, 5.33; p, 1.493.

Solutions for Raman measurements were prepared by mixing LiOH and molybdic acid solutions in proper proportions and were concentrated by evaporation.

Results

(1) **Apparent Molal Volumes and Refractive Index Increments.**—Partial molal volumes of the solute of interest and of the supporting electrolytes are necessary for interpretation of ultracentrifugation results. In addition, the relation between the refractive index of the solution and the concentration of each solute is needed to obtain concentration distributions from interference patterns.

The apparent molal volumes and refractive index increments of the molybdate species in sodium chloride, sodium perchlorate, and lithium chloride supporting electrolytes are shown as functions of p in Fig. 1 and 2, respectively. These are presented for components $Na_{2-p}H_pMoO_4$ or $Li_{2-p}H_pMoO_4$. Solutions having a p of about 1.6 correspond to a solution of molybdic acid in the appropriate supporting electrolyte, *i.e.*, about 0.4 mole of H^+ is ionized from 1 mole of H_2MoO_4

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[19] O. L. Keller, Jr., and R. H. Busey, to be published.

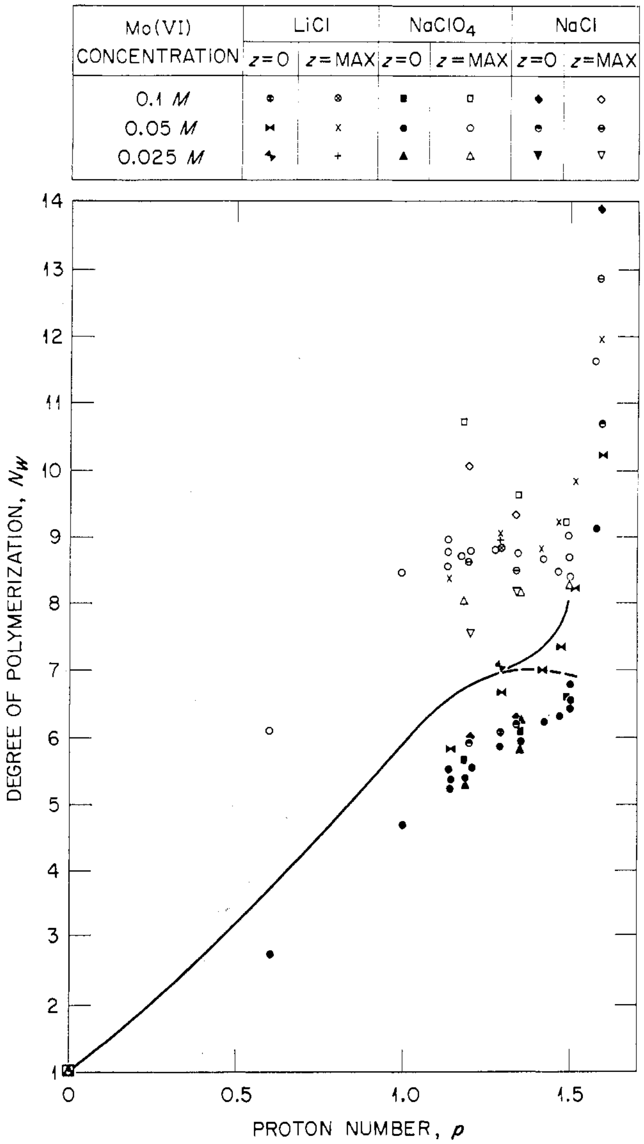

Fig. 3.—Weight average degree of polymerization of Mo(VI) as a function of average number of protons bound per Mo atom: solid line computed for scheme H, Table III; broken line, scheme C.

under these conditions. The apparent molal volumes of the hydrolyzed molybdates were calculated by the equation

$$\phi_{\mathrm{Mo(VI)}} = \frac{1000 - V_{\mathrm{H_2O}} - c_{\mathrm{MX}}\phi_{\mathrm{MX}} - c_{\mathrm{HX}}\phi_{\mathrm{HX}}}{c_{\mathrm{Mo(VI)}}} \qquad (2)$$

where $V_{\mathrm{H_2O}}$ is the volume of pure water in 1 l. of solution; c_{MX} and c_{HX} are the concentration of salt and free acid in moles/l.; and ϕ_{HX} and ϕ_{MX} are their apparent molal volumes, in a three-component solution of the same molality of salt and acid as the molybdate solution. The apparent and partial molal volumes of NaCl,[20] HCl,[20] $NaClO_4$,[21] $HClO_4$,[21] and LiCl[22] were computed from density data in the literature.

In computation of N_w, the weight average degree of polymerization of the Mo(IV) solute, we have used for partial molal volumes values of apparent volumes given by the lines in Fig. 1, which are weighted to favor the more precise values at higher concentrations. The concentration dependence of $\phi_{\mathrm{Mo(VI)}}$ appears significant; it would lead to values for the partial molal volumes roughly 1 ml. greater than the apparent values, but precision does not warrant this adjustment. The error in N_w involved in these approximations is probably less than 1%, unimportant in comparison with some other uncertainties.

Literature values were used for the refractive index gradients for the supporting electrolytes NaCl,[23] $NaClO_4$,[24] and LiCl,[24] both in interpretation of centrifugations and in correcting for the small differences in supporting electrolyte concentration in the two compartments of the refractometer during measurement of increments of the molybdate solutes. The refractive index increments of the molybdate species showed no significant concentration dependence and mean values of $\Delta n/c$, weighted toward the higher concentrations, were used in the centrifugation computations; these values are indicated by the lines in Fig. 2. The uncertainty in N_w stemming from the scatter of refractive index increments is about the same as that from molal volumes.

There is a rather abrupt change in slope at **p** *ca.* 1.15, both of $\Delta n/c$ *vs.* **p** and ϕ *vs.* **p** plots, which is consistent with the formation of an initial hydrolysis product containing eight bound protons per seven molybdenum atoms. A second, less marked change in the $\Delta n/c$ graph occurs in the region of **p** = 1.5. These inflections are consistent with the conclusions we shall draw, although, as we pointed out in the introduction, a definite choice between species having similar values of **p** is difficult from such evidence.

From measurements of the density of a solution of sodium molybdate in 8 *M* HCl, the volume of the assumed species MoO_2Cl_2 was estimated to be 50 cc. This value is quite approximate, but should be adequate for present purposes.

(2) **Ultracentrifugation Results.** (a) **From p = 0 to 1.6.**—The sedimentation of an ionized solute, even in the presence of a large excess of slightly sedimenting supporting electrolyte, depends markedly on its charge as well as on its molecular weight. Part of the charge effect is concentration dependent, and with a monodisperse solute it is possible by varying the ratio of solute concentration to that of the supporting electrolyte to find the value of the charge, *z*, for which the calculated degree of polymerization *N* is independent of concentration. Results previously obtained for unhydrolyzed sodium molybdate[15] indicated that, as expected, the molybdate species is monodisperse, monomeric, and has a charge corresponding to complete dissociation of the salt. The various assumptions made, of which that regarding the constancy of activity coefficients is probably most important, resulted in an error of only about 5%.

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(21) H. E. Wirth and F. N. Collier, *ibid.*, **72**, 5292 (1950).
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(23) A. Kruis, *Z. physik. Chem.*, **B34**, 13 (1936).
(24) H. Kohner, *ibid.*, **B1**, 427 (1928).

With polydisperse solutes having a constant z' (charge per monomer unit) and the same refractive index increment and volume per monomer unit for all species, the centrifuge equations yield a weight average degree of polymerization. In most of the solutions dealt with here, these quantities are different for the different species, and some approximation is therefore introduced in using values which are averages for all species in the solution. A more serious limitation arises from the fact that the weight average degree of polymerization of a polydisperse solute of the type being considered, in which the various species are in equilibrium with each other, will increase with increasing concentration, acidity being constant. For this reason, the comparison is made here between solutions of different Mo(VI) concentration, but having the same value of $\mathbf{p}$. Solutions compared in this way usually will have more similar ratios of the amounts of various species (*i.e.*, more nearly the same value of N_w) than solutions compared at constant pH, although it is not safe to assume *a priori* that the ratios are completely constant even in the former case. It is therefore difficult to make an estimate of z' from the concentration dependence of sedimentation. For this reason, we presented here values of N_w computed for zero charge and for maximum average charge ($z' = 2 - \mathbf{p}$), corresponding to complete dissociation of Na^+ or Li^+. The actual values will lie between these limits, since the other approximations should be less important, at least in the range of most of our results ($\mathbf{p} = 1$–1.5).

Equilibrium ultracentrifugations were carried out for over 25 molybdate solutions with $\mathbf{p}$ ranging from 0 to 1.6 and Mo(VI) concentration between 0.025 and 0.1 *M*. The supporting electrolyte was NaCl, $NaClO_4$, or LiCl, and was at a concentration of 1 *M* in each instance. The values of N_w, computed for maximum and zero charge, are shown as a function of $\mathbf{p}$ in Fig. 3. All solutions between $\mathbf{p} = 0$ and *ca.* 1.35 appeared polydisperse by the criterion that plots of $\ln n^*$ *vs.* x^2 were concave upward (n^* is the difference in refractive index between solution and background and x is the radius); the polydispersity reached a maximum at $\mathbf{p} = 0.6$. At $\mathbf{p}$ *ca.* 1.35, the solutes by this test appeared to be monodisperse; in NaCl and $NaClO_4$, the graphs were linear, and in LiCl, concave downward, as expected for a charged solute. As $\mathbf{p}$ is further increased to 1.5, the plots again indicate polydispersity, and beyond 1.5, polydispersity and molecular weight increase sharply. In some cases also, difficulty in attaining centrifugation equilibrium above $\mathbf{p} = 1.5$ indicated that polymerization reactions were continuing.

The centrifuge results clearly indicate that aggregates of an average degree of polymerization greater than 6 and less than 9 are present in the range $\mathbf{p} = 1.2$–1.5 and that higher species are present above 1.5. (It is of interest to remember that $\mathbf{p}$ of molybdic acid in these media is about 1.6, although since free acid is too high for accurate measurement in such solutions, the exact value is somewhat uncertain.) Hydrolysis schemes[6d,9b] involving species no higher than tetramers are therefore excluded, and a mixture of tetramers and decamers[9a] seems unlikely. Schemes involving hexamers[4c,f,5b] are possible, but those involving heptamers, octamers, or mixtures of heptamers and octamers[6e,j,10a,c] are more plausible; definite choice between them cannot be made from the ultracentrifugation results alone.

(b) **Mo(VI) in Excess Acid.**—Since the $\mathbf{p}$ of molybdic acid at concentrations in the range centrifuged and in 1 *M* NaCl is *ca.* 1.6, in order to make measurements at higher degrees of protonation (including the region of cationic species past the isoelectric point), it is necessary to add excess acid. In such cases, however, the free acid is too high for accurate measurement, and one no longer knows what the value of $\mathbf{p}$ is. Conclusions drawn from centrifugation are therefore less certain here than those for low acidity. It is possible, however, to gain a useful idea of the extent of aggregation and its dependence on acidity.

We report (Table I) some measurements carried out with schlieren optics of Mo(VI) solutions in excess HCl. The value of $\mathbf{p}$ being unknown, interpretation is based on the assumed species MoO_2Cl_2. If H_2MoO_4 had been assumed instead, the reported degrees of polymerization would have been about 20% higher, or for $HMoO_3Cl$, which Raman spectra do not exclude (see below), about 10% higher. The actual situation should lie between these extremes, and should of course move toward one of the species containing chlorine with increasing acidity. The computations were made for zero charge. Neglect of charge makes values of N_w lower; with polydisperse systems, this will be somewhat balanced[17] by the fact that schlieren optics give a so-called *Z*-average molecular weight, which is greater than the weight average.

TABLE I

POLYMERIZATION OF Mo(VI) IN ACID SOLUTIONS

Mo(VI), moles/l.	HCl,[a] moles/l.	NaCl,[a] moles/l.	Apparent deg. of polymn.[b]
0.051	5.8	0.1	0.9
0.100	2.6	0.2	1.7
0.025	2.9	0.05	1.5
0.050	0.8	0.1	2.8[c]

[a] Stoichiometry on basis of MoO_2Cl_2. [b] Computed for zero charge, MoO_2Cl_2 monomer unit. [c] Not at equilibrium.

In 0.8 *M* HCl (a solution 0.05 *M* in Na_2MoO_4 dissolved in 1 *M* HCl), chemical equilibrium was not attained; the sedimentation pattern was moving in the direction of increasing molecular weight when the experiment was terminated. The distribution was clearly polydisperse. Equilibrium was apparently attained in 2.6–2.9 *M* excess acid, and the solute was still somewhat polymerized. Only in *ca.* 6 *M* HCl was there no indication of aggregation; in this region, activity coefficient variations can be expected to be such as to make the values somewhat suspect.

A similar trend was found in centrifugations in 1 and 3 *M* $HClO_4$, but degrees of polymerization are not reported, because the uncertainty of the values arising from lack of knowledge of **p** is much greater in perchlorate than in chloride solutions.

(3) **Acidity Measurements. 1 *M* NaCl.**—The results of the potentiometric titrations of Sasaki, *et al.*,[6e] in which a series of heptamolybdates was proposed, have unfortunately not yet been published in sufficient detail to permit the testing of alternative hypotheses which might also be consistent with our centrifugation results. Moreover, these titrations were made in 3 *M* $NaClO_4$ medium, which is not particularly convenient for ultracentrifugations. In view of possible sodium binding that could conceivably stabilize complexes unimportant in 1 *M* Na^+ solutions, comparison between results for the two media might be misleading. We have therefore carried out a somewhat less extensive series of acidity measurements or "point titrations" on acidified Na_2MoO_4 solutions in 1 *M* Na(Cl). A few measurements for Mo(VI) = 0.08 and 0.005 *M* were also made in 3 *M* NaCl, 3 *M* LiCl, and 1 *M* LiCl. The results in 1 *M* NaCl are given in Table II, and all the points for $0 < \mathbf{p} < 1.5$ are plotted as **p** *vs.* log c_H, where c_H is the hydrogen ion concentration, in Fig. 4. As the centrifugation results indicated the presence of highly complex species for $\mathbf{p} > 1.5$, no attempt was made to fit our limited data in this region. Below $\mathbf{p} = 1.5$, species containing 6–9 molybdenum atoms appear to be most probable from ultracentrifugation.

TABLE II

ACIDITY DATA FOR Mo(VI) IN 1 *M* NaCl

Mo(VI) = 0.080 *M*.—p, −log c_H: 0, 7.235; 0.0493, 6.000; 0.0988, 6.001; 0.2022, 5.916; 0.3990, 5.790; 0.5973, 5.653; 0.7995, 5.471; 0.9944, 5.194; 1.102, 4.929; 1.202, 4.534; 1.294, 3.982; 1.397, 3.323; 1.475, 2.692; 1.530, 2.154; 1.548, 1.909; 1.574, 1.748; 1.672, 1.573

Mo(VI) = 0.020 *M*.—p, −log c_H: 0, 6.753; 0.0492, 5.596; 0.0987, 5.540; 0.2020, 5.461; 0.3988, 5.336; 0.5970, 5.208; 0.7990, 5.037; 0.9937, 4.800; 1.101, 4.601; 1.200, 4.314; 1.289, 3.912; 1.381, 3.355; 1.444, 2.941; 1.492, 2.599; 1.496, 2.386; 1.511, 2.240; 1.536, 2.027

Mo(VI) = 0.0050 *M*.—p, −log c_H: 0, 6.368; 0.0480, 5.189; 0.0973, 5.113; 0.2003, 5.023; 0.3965, 4.907; 0.5940, 4.786; 0.7949, 4.642; 0.9874, 4.447; 1.092, 4.293; 1.186, 4.096; 1.267, 3.855; 1.343, 3.524; 1.394, 3.269; 1.432, 3.060; 1.454, 2.907; 1.467, 2.781; 1.498, 2.595

Mo(VI) = 0.00125 *M*.—p, −log c_H: 0.0005, 6.182; 0.0414, 5.034; 0.0854, 4.776; 0.1838, 4.639; 0.3645, 4.514; 0.5557, 4.404; 0.7580, 4.284; 0.9370, 4.144; 1.030, 4.049; 1.112, 3.951; 1.181, 3.847; 1.241, 3.721; 1.301, 3.603; 1.355, 3.483; 1.376, 3.388; 1.396, 3.299; 1.437, 3.148

Formation quotients

$$k_{p,q} = \frac{[H_p(MoO_4)_q{}^{(2q-p)-}]}{[MoO_4{}^{2-}]^q[H^+]^p} \qquad (3)$$

for various schemes with $q = 6$, 7, 8, or 9 and p/q between 1 and 1.5 were calculated and refined using the OR-GLS Fortran least-squares program[25] to give the least-square deviations in **p** from our experimental points. The formation quotients and their standard error, together with the corresponding standard deviations in **p**, σ_p (the italicized *p* refers to hydrogens

TABLE III

TEST BY FIT TO ACIDITY DATA OF HYDROLYSIS SCHEMES INVOLVING SPECIES $H_p(MoO_4)_q{}^{(2q-p)-}$

Values of log $k_{p,q}$ given with their standard error just below

Scheme	p, q																		σ_p
	1,1	2,1	6,6	7,6	8 6	9,6	8,7	9,7	10,7	11,7	9,8	10,8	11,8	12,8	10,9	11,9	12,9	13,9	
A	3.79	*a*					53.09							7.59					
	0.16						0.07							0.12					0.050
B	3.23	7.04	39.49	45.61	49.85	53.11													
	0.18	0.12	0.15	0.03	0.03	0.07													0.0139
C	3.55	7.20					52.81	57.39	61.02	63.40									
	0.04	0.04					0.01	0.02	0.03	0.05									0.0069
D	3.69	7.29									59.92	64.85	68.75	71.75					
	0.03	0.04									0.03	0.03	0.03	0.05					0.0085
E	3.77	7.38													66.99	72.23	76.35	79.83	
	0.05	0.06													0.07	0.06	0.07	0.11	0.165
F	3.41						52.83	57.43	61.04					71.99					
	0.11						0.03	0.04	0.08					0.08					0.146
G		7.19					52.83	57.44	60.73					71.56					
		0.06					0.03	0.03	0.09					0.09					0.0124
H	3.53	7.26					52.80	57.42	60.84					71.56					
	0.05	0.03					0.02	0.02	0.05					0.06					0.0078

[a] With H_2MoO_4 included, matrix had zero diagonal element. Values listed computed with (2,1) species omitted.

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(25) W. R. Busing and H. A. Levy, ORNL-TM-271.

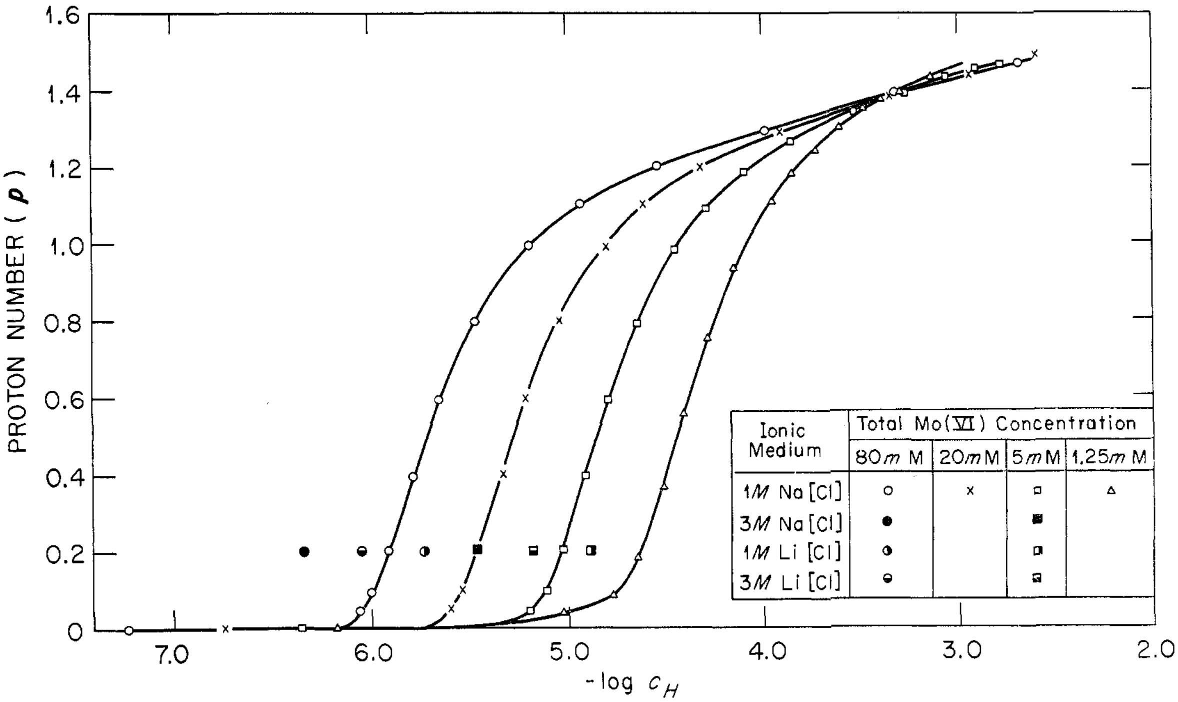

Fig. 4.—Hydrolysis of Mo(VI). Curves computed with constants obtained by least-squares fit of all data points in 1 *M* NaCl below $\mathbf{p} = 1.5$ for scheme H, Table III.

bound by a postulated definite species, rather than the average number of protons bound per Mo(VI), **p**), are shown in Table III.

An attempt (scheme A) was made to fit the data up to $\mathbf{p} = 1.5$ with only two polymeric species, in addition to $HMoO_4^-$ and H_2MoO_4; the latter are needed in order to fit the data for low values of **p** in the case of the lowest Mo(VI) concentration. A molybdate with p/q *ca.* 1.5, *e.g.*, $Mo_8O_{26}^{4-}$ (or its equivalent in eq. 3, (H_{12}-$(MoO_4)_8^{4-}$)), must be included to fit the experimental data in the region of $\mathbf{p} = 1.5$. Also, from the spacing of the curves with Mo(VI) concentration for constant values of **p** below about 0.8, it was concluded that $Mo_7O_{24}^{6-}$ (or $H_8(MoO_4)_7^{6-}$) would give the best fit for low values of **p**. However, the least-square fit obtained with the use of only these two polymeric species, a scheme originally proposed by Lindqvist,[10a] was unacceptable.

As one would expect, agreement with the experimental data improves as more polymeric species are included. The scheme of Sasaki, *et al.*[6e] (scheme C), in which several heptamers of various degrees of protonation are proposed, gives a satisfactory fit. However, as good agreement for practical purposes is obtained by postulating a series of octamers (scheme D) or a mixture of heptamers and octamers (scheme H). Plots of the deviations between observed **p** and values computed from these schemes are shown in Fig. 5. Choice between them does not seem warranted from the acidity measurements alone. This finding is of interest in view of the emphasis sometimes given this technique.[26]

Schemes involving the same number of species with only hexamers (B) or nonamers (E) give appreciably less successful agreement. Elimination of either of the monomeric species from the successful schemes, particularly H_2MoO_4, also leads to greater deviations (F and G). It is possible, however, that different combinations of the species listed would give as good fit as the successful schemes.

It could be, of course, that more precise and extensive data than we present would make a choice between the schemes in Fig. 5 possible. To state that such a choice is physically meaningful, however, rather than simply curve fitting, one has to take the position that inherent uncertainties of the method—variation of activity coefficient ratios over the experimental conditions, junction potentials, and differences between free and stoichiometric counterion concentration stemming from complexing by the polymeric species—are small compared to the scatter of data. Such a proposition is not, to us, self-evident.

Another implication of Table III is worth mentioning, since it does not seem to be universally recognized, although the point would appear to be obvious. For schemes C and D, involving series of heptamers and octamers, respectively, all the values of log $k_{p,q}$ have low standard error. Since these schemes cannot be simultaneously correct, it is clear that the fact that a formation quotient appears well determined on a statistical basis is no assurance that the corresponding species actually exists in the solution.

Comparison of our data with those of Sasaki shows that although the shape and spacing of the titration curves is similar, our curves are shifted in the direction of increasing acidity by as much as 0.7 log c_H unit. This results in a reduction of the apparent value of log $k_{8,7}$ from the value 57.76 given by Sasaki for 3 *M* $NaClO_4$ to 52.81, which we compute from our results in

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[26] See, *e.g.*, L. G. Sillén, *Quart. Rev.* (London), **13**, 146 (1959); H. S. Dunsmore, S. Hietanen, and L. G. Sillén, *Acta Chem. Scand.*, **17**, 2644 (1963).

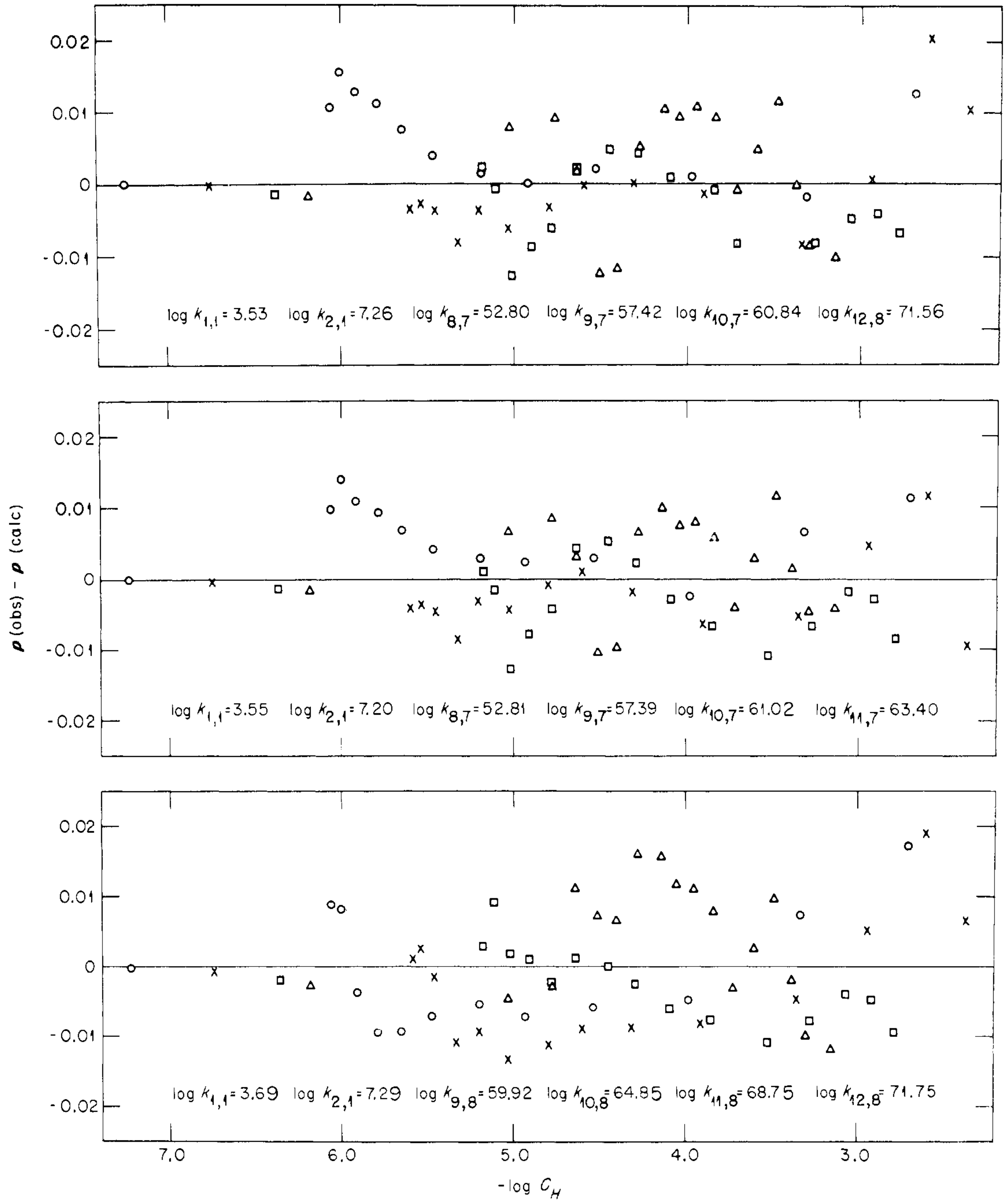

Fig. 5.—Tests of various hydrolysis schemes for Mo(VI) in NaCl. Deviation of observed proton number, p (obsd.), from values computed with constants obtained from least-squares fit, p (calcd.), of all points below p = 1.5. Symbols represent total molarity of Mo(VI) as: ○ = 0.08; × = 0.02; □ = 0.005; △ = 0.00125. All solutions 1 *M* in total sodium.

1 *M* Na(Cl) on the basis of the same scheme. The formal stepwise quotients for the more highly protonated heptamers given by Sasaki are, however, about the same as we obtain.

(4) **Counterion Binding.**—With aggregates which in the absence of counterion binding carry such high charges as these, complexing of Na^+ or Li^+ would not be surprising. In an analogous case involving a cationic polymer,[15] for example, to explain centrifugation results as a function of concentration, it was necessary to postulate two of the weakly complexing perchlorate ions were held per Bi(III) hexamer. Some of the results obtained in this study appear at first glance to indicate considerable counterion binding, and a review of the evidence is in order.

(a) **Ultracentrifugation Results.**—It was mentioned in section 2 that the ln n^* *vs.* x^2 plots indicated that Mo(VI) solute is monodisperse for **p** *ca.* 1.35. Although our conclusion will be that under these conditions, all the Mo(VI) is not found in a single species, but rather is distributed in species of not very different molecular weights, monodispersity seems closely enough approached to make an attempt to estimate charge worthwhile. Graphs of N_w computed as a function of assumed charge are presented in Fig. 6. The results for NaCl and $NaClO_4$ media are similar, with the curves approaching one another for N_w about 7 and z' about 0.3. At face value, this would indicate considerable binding, since the maximum charge here is *ca.* 0.65. The value of N_w at $z' = 0.3$ is also within the uncertainty of the value which is predicted by our conclusions. The experiments in LiCl are not strictly comparable, since the value of **p** is 1.29, but on this basis, the lithium polymers appear to be completely dissociated, with the curves converging for maximum z' and N_w slightly less than 9.

Inferences concerning ion binding, however, are not convincing. The gradients of activity coefficients of the Mo(VI) species might very well be somewhat different for solutions of different concentration in a given supporting electrolyte, and the dependence of this gradient on Mo(VI) concentration is likely to vary between LiCl and NaCl solutions. Slight variations could shift the N_w *vs.* z' curves computed from the equilibrium distribution up or down relative to one another slightly, but affect the z' of intersection drastically. The fact that the value of N_w in LiCl media obtained in this way is different from that in NaCl and $NaClO_4$ suggests that an effect of this sort is contributing to the results, since other results in this study indicate that the polymolybdate species are not different for the different counterions involved (see section 5).

(b) **Variations of Acidity with Medium.**—The shift in pH for solutions of a given **p** and Mo(VI) concentration between 1 and 3 *M* Na^+ is superficially an even more striking indication of counterion complexing. For a more quantitative discussion, it is useful to use a formation constant defined by the equation

$$k_{n,p,q} = \frac{[Na_nH_{(p-2w)}(MoO_{(4-(w/q))})_q{}^{(2q-n-p)-}]}{[MoO_4{}^{2-}]^q[H^+]^p[Na^+]^n}\, a_{H_2O}{}^w\Gamma \quad (3a)$$

where Γ is the appropriate activity coefficient ratio for the solute components, a_{H_2O} is the activity of water, and w is the number of moles of water produced in the reaction of protons and molybdate ions to produce the (n, p, q) species. In the comparison of results for different media, the number of moles of water included in the polymeric species may no longer be a matter of indifference. In solutions of the acidity and Mo(VI) concentration compared here (Fig. 4), our conclusion will be that most of the Mo(VI) is present as the species $MoO_4{}^{2-}$ and as a ($p = 8$, $q = 7$) species, probably $Mo_7O_{24}{}^{6-}$, *i.e.*, w of eq. 3a is 4. If n, the number of sodiums bound by the species, is taken to be single valued, and with the most naïve assumption, that Γ is the same in the two media, the observed shift in acidity at a given **p** should be

$$\Delta \log c_H = -(n/p)\,\Delta \log c_{Na} + (w/p)\,\Delta \log a_{H_2O} \quad (4)$$

with the approximation that the ratio of concentrations of Mo(VI) species is constant for a given **p**. A fairly reliable estimate of $\Delta \log a_{H_2O}$ may be obtained from literature values[27] for the supporting electrolyte in question, since the Mo(VI) present probably affects a_{H_2O} relatively little. The effect of the second term on the right of eq. 4, with w/p taken to be 4/8 (probably an upper limit), was equivalent at most to 0.02 in $\Delta \log c_H$, and in the ensuing discussion we shall ignore this correction.

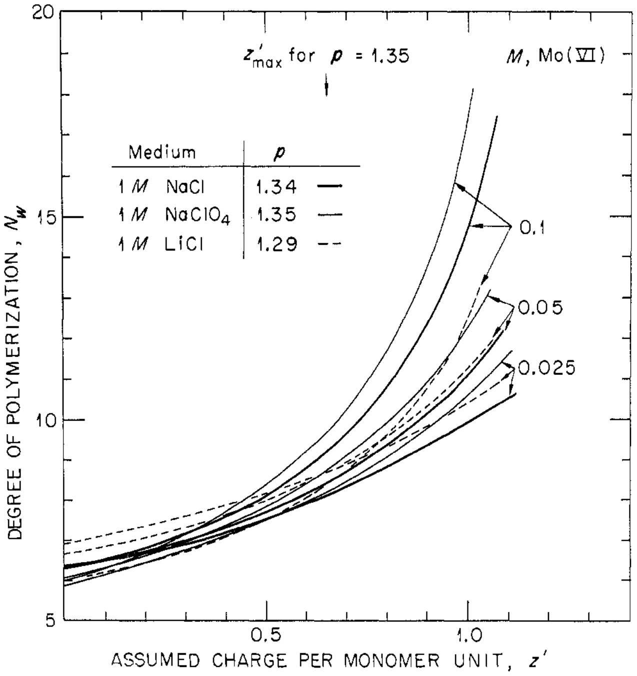

Fig. 6.—Weight average degree of polymerization of Mo(VI) computed as a function of assumed charge per monomer unit.

Use of eq. 4 for estimation of ion binding thus rests mainly on the assumption that Γ is constant, and it is of interest to see what our measurements indicate in this respect. A shift of $\Delta \log c_H$ between our results in 3 *M* NaCl and Sasaki's in 3 *M* $NaClO_4$ of *ca.* 0.28 unit clearly shows the assumption is not completely good. Further, from eq. 4, for the (8,7) species, one would compute for complete counterion binding (six sodiums) a shift of 0.36 unit. We observed a shift of 0.44 unit (Fig. 4). Since complete binding, *i.e.*, zero charge, would not be expected, 0.36 unit is in any case an upper limit, and changes in Γ between the media must account for part of the shift. These results confirm that a shift in Γ large enough to make a substantial contribution to the observed $\Delta \log c_H$ between 1 and 3 *M* Na^+ is plausible, and in view of the magnitude of this term, no firmer conclusions can be drawn concerning counterion binding from the acidity measurements than from ultracentrifugation results.

From all results, however, it does appear to us likely that part of the shift is accounted for by complexing and that probably Li^+ is less bound. There is a shift of 0.14 between 1 *M* LiCl and 1 *M* NaCl in the direction indicating higher charge in Li^+ media, and a smaller shift between 1 and 3 *M* LiCl (0.31 unit) than between 1 and 3 *M* Na^+.

(5) **Raman Spectra.** (a) **Paramolybdate and Octamolybdate.**—The ultracentrifugation and acidity

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[27] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 1st Ed., Butterworth Scientific Publications, London, 1955, Table of Osmotic Coefficients, p. 468.

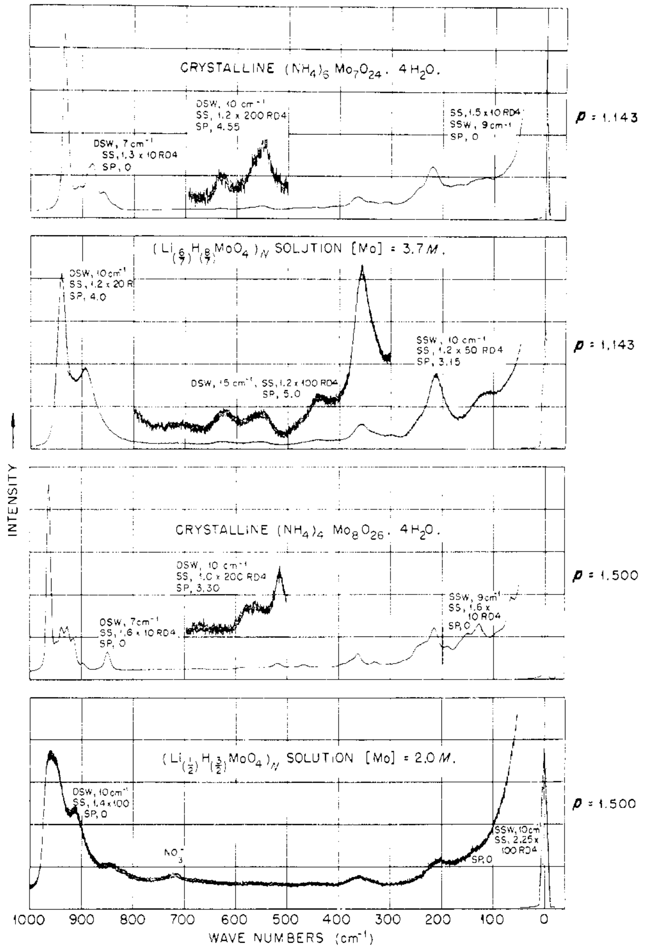

Fig. 7.—Comparison of Raman spectra of solid polymolybdates with solutions. Cary Model 81; lamp current 13.5 amp.; scan speed 0.25 cm.$^{-1}$/sec.; period control setting 0.5. Abbreviations: SS, sensitivity setting; SP, suppression setting; SSW, single slit width; DSW, double slit width.

results presented so far indicate that either heptamolybdates or octamolybdates, or both, are present in acidified molybdate solutions, below $p = 1.5$, although neither method appears to permit a clear decision between possibilities. In a recent publication,[28] Keller points out that it is possible to identify species in solution by Raman spectroscopy, if a direct comparison can be made between the spectra of the solutions and the spectra of crystals of known structure. The structures of both $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ and $(NH_4)_4Mo_8O_{26}\cdot5H_2O$, based on X-ray analysis, have been reported by Lindqvist.[29] He concludes that the molybdenum atoms are arranged in heptameric and octameric units, respectively, in these two solids. It seemed worthwhile to compare the Raman spectra of these solids with those of solutions having the same value of p, in an attempt to establish if either or both are prominent in solution. Because of the complexity and low symmetry of the structural units, and the consequent complexity of predicted spectra, we do not attempt a fundamental analysis of the results, but employ the spectra simply to identify the aggregates in question.

Lithium molybdate solutions were used, for solubility reasons, but with the solution analogous to the paramolybdate it was additionally possible to compare the spectra of ammonium and lithium solutions, and they were found to be the same. Ammonium solids were used in both cases, since these can be obtained more easily in good crystalline form and were the salts used by Lindqvist. Our octamolybdate preparation appeared to have four waters per unit (see Experimental section), rather than the five reported by Lindqvist; we do not feel that this is a serious difference (even if real), since he states that the water in both solids is present as lattice water, not an integral part of the polymolybdate aggregates.[11]

The comparison is shown in Fig. 7 and in Table IV. There is obviously considerable difference between spectra of the two solids, and the differences between the two solutions are more than one would expect simply from protonation of a polymeric species without a rearrangement of the basic structure. If Lindqvist's structure of the heptamolybdate is correct, its point group is C_{2v} and thus contains no degenerate vibrations. All the $3N-6 = 87$ vibrations should be Raman active. The addition of protons to these ions should have no effect on the skeletal vibrations. The only effect should be on OH vibrations, outside the region discussed here.

TABLE IV

RAMAN SPECTRA OF CRYSTALS AND SOLUTIONS OF POLYMOLYBDATES

$\Delta\nu$, cm.$^{-1}$ from 4358 Å. Hg

$(NH_4)_6Mo_7O_{24}\cdot4H_2O$ solid	$(Li_{6/7}H_{8/7}MoO_4)_N$ soln.	$(Li_{1/2}H_{3/2}MoO_4)_N$ soln.	$(NH_4)_4Mo_8O_{26}\cdot4H_2O$ solid	Mo(VI) in concd. HCl
115	115		68	225, m, sp[a]
220	215		90	250, m, sp
245	245		130	313, w, br
308	300		150	403, w, br
340		200	190	919, s, sp
363	358		216	958, vs, sp
415			240	
450	444		330	
550	550	360	363	
630	628		469	
840			520	
860			575	
880		850	850	
890	893		896	
908		916	916	
934	940		928	
			939	
			950	
		961	963	

[a] w, weak; m, medium; s, strong; br, broad; sp, sharp.

Lines found in the solid paramolybdate (top, Fig. 7) at 220 and 363 cm.$^{-1}$, which are shifted slightly in solution to 215 and 358 cm.$^{-1}$ (second from top), also occur at similar frequencies in both the crystalline octamolybdate (second from bottom) and the corresponding solution (bottom, Fig. 7); they are therefore no help in assigning structures to the ions in solution. On the other hand, the most intense lines in the

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(28) O. L. Keller, Jr., *Inorg. Chem.*, **2**, 783 (1963).
(29) I. Lindqvist, *Arkiv Kemi*, **2**, 325, 349 (1951).

spectra of the crystalline heptamolybdate ($\mathbf{p} = 1.143$) and octamolybdate ($\mathbf{p} = 1.5$), which occur at 934 and 963 cm.$^{-1}$, respectively, and which probably correspond to the Mo–O stretching frequency in the two solids, also occur at similar frequencies in solutions of corresponding $\mathbf{p}$ values; the shift for the solutions indicates a difference in the molybdenum species at these values of $\mathbf{p}$, and the correspondence with the solids suggests that the same species are present in solid and solution at the same $\mathbf{p}$. The lines at 890 and 893 cm.$^{-1}$ appear far more prominent for $\mathbf{p} = 1.14$ than for 1.5. Another correspondence between the two top spectra of weaker peaks, absent in the bottom two, are the lines at 550 and 630 cm.$^{-1}$ in the crystal, which are found within about 2 cm.$^{-1}$ in the solution. It is therefore clear that the paramolybdate ion is present in the solution with $\mathbf{p} = 1.142$.

It is clear also that the predominant Mo(VI) species in solution at $\mathbf{p} = 1.14$ is not present in great amount at $\mathbf{p} = 1.5$; there is further a correlation between this solution and the octamolybdate crystal, though a somewhat less positive one. The most striking correspondence is between the 961 and 963 cm.$^{-1}$ peaks already mentioned. The distinct line at 850 cm.$^{-1}$ in the crystal also occurs at the same frequency in solution, but is absent in the paramolybdate solution and apparently also in the solid. The asymmetry of the 961 cm.$^{-1}$ line in the $\mathbf{p} = 1.5$ solution shows that unresolved lines are present on the low frequency side. Since the lines are broadened in solution, it is plausible to suppose that the resolved lines of $(NH_4)_4Mo_8O_{26}\cdot 4H_2O$ occurring at 928, 939, and 950 cm.$^{-1}$ are hidden by the intense 961 cm.$^{-1}$ line. The 916 cm.$^{-1}$ line, which is not seen in the paramolybdate crystal or solution spectra, is resolved, however. From these similarities, we conclude that the octamolybdate probably occurs in solution at $\mathbf{p} = 1.5$.

Examination of the correspondence of lines in Table IV, which includes many weak ones not apparent in Fig. 7, leads to the same conclusions. In summary, from the Raman spectra, we conclude that both heptamers and octamers are formed on the acidification of sodium molybdate solution and that scheme H of Table III expresses more closely than the others the actual situation in solution up to $\mathbf{p}$ about 1.5. Computed degrees of polymerization for this scheme are given in Fig. 3, and computed acidities are compared with the experimental values in Fig. 4.

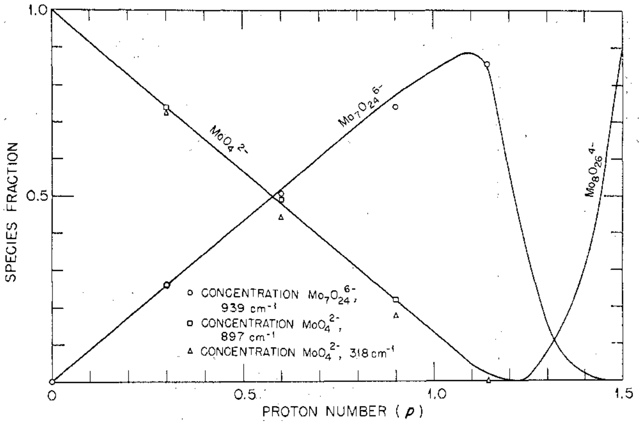

Fig. 8.—Fraction of total molybdate as MoO_4^{2-}, $Mo_7O_{24}^{6-}$, and $Mo_8O_{26}^{4-}$ computed for 2 *M* total Mo(VI) by scheme H. Points are fractions obtained by Raman intensities. Intensity–concentration relation for $Mo_7O_{24}^{6-}$ established at $\mathbf{p} = 0.3$. Curves for other postulated heptamers not shown.

(b) **Raman Spectra between $\mathbf{p} = 0$ and $\mathbf{p} = 1.143$.**—There is no suggestion from the ultracentrifugation or the acidity results that species intermediate between monomers and heptamers are important in the concentration ranges studied, but it seems worthwhile to try to confirm this with Raman measurements. Consequently, the spectra of a few lithium molybdate solutions with values of $\mathbf{p}$ between 0 and 1.143 were examined. The Mo(VI) concentration was 2 *M* and $LiNO_3$ was added to bring the total NO_3^- concentration up to 3 *M* in each case to provide an internal intensity standard.[30] An attempt was then made to compute from the intensities (relative to NO_3^-) of peaks associated with various species (here only MoO_4^{2-} and $Mo_7O_{24}^{6-}$ are important) the amounts of the species present in the different solutions; these were then compared with the amounts predicted on the assumption of no intermediate species. The approximate concentration of free molybdate was obtained, for example, from the equation

$$c_{MoO_4^{2-}} = \frac{2I_pI_0'}{I_p'I_0} \qquad (5)$$

where $c_{MoO_4^{2-}}$ is the concentration of MoO_4^{2-}; I_p is the intensity of the molybdate line at 318 cm.$^{-1}$ at the $\mathbf{p}$ in question; I_0 is the intensity of the same line measured at $\mathbf{p} = 0$ and Mo(VI) = 2 *M*; I_0' is the intensity of the nitrate line at 1040 cm.$^{-1}$ in the unhydrolyzed molybdate solution; and I_p' its intensity in the polymolybdate solution. The same procedure was followed for the 897 cm.$^{-1}$ line, which is prominent in normal molybdate, but in this case it was necessary to correct for the intensity contributed by the $Mo_7O_{24}^{6-}$ ion, which is evaluated when $c_{MoO_4^{2-}}$ is zero, *i.e.*, at high $\mathbf{p}$. An approximate measure of the concentration of the paramolybdate ion was similarly found from the 940 cm.$^{-1}$ line intensity by relating the measured intensity at $\mathbf{p} = 0.3$ to the concentration of $Mo_7O_{24}^{6-}$ computed from the scheme being tested. The other concentrations of paramolybdate were obtained from the intensities with this relation.

The results are compared (Fig. 8) with curves of the species fractions computed for 2 *M* Mo(VI) with the constants of scheme H, Table III. (These constants are not strictly applicable to such a concentrated solution, but in the $\mathbf{p}$ region and Mo(VI) concentration in question, since essentially only two species are present, their fractions follow directly from the value of $\mathbf{p}$.)

The approximate correlation of the monomeric and heptameric concentrations computed from the Raman

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(30) D. D. Tunnicliff and A. C. Jones, *Spectrochim. Acta*, **18**, 579 (1962).

intensities, together with the absence of additional Raman lines which might be attributed to intermediate species, confirms that $Mo_7O_{24}^{6-}$ is the first important hydrolytic species formed on acidification of MoO_4^{2-}, at least at high Mo(VI) concentration.

(c) **Raman Spectra in Strongly Acid Solution.**—The six observed Raman bands for solutions of molybdic acid (H_2MoO_4) in HCl are given in Table IV. The 403 cm.$^{-1}$ line appears asymmetric, indicating the presence of a seventh unresolved line on the high frequency side. The spectra were independent of Mo(VI) concentration over the range 1–4 *M* for a total HCl concentration of 11.6 *M* (or 9.6–3.6 *M* stoichiometric HCl in excess of component MoO_2Cl_2) but began to change at lower acidities. Our ultracentrifuge results indicate that the molybdate species is monomeric over most of this acidity range; the anion-exchange work of Kraus, Nelson, and Moore[31] suggests that, at least at low Mo(VI) concentrations, the (average) Mo(VI) species is either neutral or anionic above 4 *M* HCl, though the value of the charge is not established by their results. The Raman spectra exclude the presence of major amounts of uncomplexed MoO_2^{2+}, but are consistent with MoO_2Cl_2, point group symmetry C_{2v}, which would require nine fundamentals. Neumann and Cook,[32] on the basis of ultraviolet spectra, favor MoO_2Cl_2 as the principal species in this acidity range. If the 403 cm.$^{-1}$ line is not asymmetric, MoO_3Cl^-, group C_{3v}, six Raman fundamentals, is not excluded.

Discussion

In summary, our conclusions are that on acidification of Na_2MoO_4 solutions at appreciable concentration, the first important species formed is $Mo_7O_{24}^{6-}$; at higher acidification the octamer $Mo_8O_{26}^{4-}$ forms; above 1.5 protons bound per molybdenum, more aggregated species occur and chemical processes become slow; polymeric species are present in solutions containing several molar HCl in excess of molybdic acid. In addition, to obtain agreement with acidity measurements, other protonated forms of the monomeric and polymeric molybdates must be postulated; whether those listed in scheme H are the ones which actually exist is less certain. Whether appreciable binding of Na^+ or Li^+ by the polymers occurs is not clear from our results.

We were able to eliminate by ultracentrifugation and acidity measurements many possibilities suggested by others. However, in the final analysis, the conclusions rest on the comparison of Raman spectra of solutions and solids coupled with the identification of heptameric and octameric units in polymolybdate solids by Lindqvist. The Raman identification seems convincing for the paramolybdate, and attribution of heptameric units to the solid by Lindqvist is consistent with the analytical ratio of alkali:Mo(VI). Although correspondence of Raman patterns for the octamer is somewhat weaker, it should be remembered that if a substantial amount of a species with $\mathbf{p} = 1.5$ is formed in solution, ultracentrifugation values of molecular weights indicate that it must be an octamer, rather than a tetramer or dodecamer.

The scheme seems reasonable in the over-all context of Mo(VI) chemistry, and also has been found the most satisfactory by others. (Indeed, it would be difficult to propose anything really new for this system; the problem is to select the right answer from the numerous alternatives in the literature.) The fundamental polymeric species were suggested by Lindqvist.[11] Tyree[33] and co-workers, on the basis of light scattering and other measurements, have reached similar conclusions. Glemser and Holznagel,[6j] from acidity measurements, spectrophotometry, and ultracentrifugation, also list the heptamer and octamer; their work has to our knowledge been reported only in abstract form, and it is not clear how they arrived at definite conclusions by these techniques in the face of some of the difficulties we have outlined.

We believe the present study illustrates again[16] the value of using more than one technique in study of the complicated equilibria frequently encountered in hydrolysis. In the present case, even the combination of a weight sensitive method, equilibrium ultracentrifugation, with acidity measurements, interpreted by a nonlinear least-squares program, did not suffice for a conclusion in which reasonable confidence could be placed, and an additional technique was necessary.

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[31] K. A. Kraus, F. Nelson, and G. E. Moore, *J. Am. Chem. Soc*,. **77**, 3972 (1955).

[32] H. M. Neumann and N. C. Cook, *ibid.*, **79**, 3026 (1957).

[33] S. Y. Tyree, private communication.