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Equilibrium and Structural Studies of Silicon(IV) and Aluminum(III) in Aqueous Solution. 21. A Potentiometric and ^{27}Al NMR Study of the System $H^+–Al^{3+}–MoO_4^{2-}$

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Equilibria in the $H^+–Al^{3+}–MoO_4^{2-}$ system have been studied by potentiometry and ^{27}Al NMR spectroscopy in 0.6 M Na(Cl) medium at 25 °C. The total concentration of aluminum, B, and molybdate, C, were varied within the limits $0.9 \le B/\mathrm{mM} \le 10$, $5.5 \le C/\mathrm{mM} \le 120$, and $2 \le C/B \le 12$ within the range $1.5 \le -\log [H^+] \le 6.0$. All data unambiguously show that one single ternary species, $Al(OH)_6Mo_6O_{18}^{3-}$, is formed. According to potentiometric data, the formation constant for this species (as related to the reaction $6H^+ + Al^{3+} + 6MoO_4^{2-} \rightleftarrows Al(OH)_6Mo_6O_{18}^{3-}$) is $\log (\beta_{6,1,6} \pm 3\sigma) = 50.95 \pm 0.04$. Independent ^{27}Al NMR data yielded the value 50.96 ± 0.06, i.e. in full agreement with emf data. The high thermodynamic stability of the complex was manifested in a model calculation, showing that even at $B = 10^{-5}$ M, $C = 6 \times 10^{-5}$ M, and $-\log [H^+] = 3.7$, 40% of B and C remained bound in this species. In acidic media, equilibration times of approximately 6 h were observed, while in near-neutral solutions the decomposition rate is higher by several orders of magnitude. With $-\log [H^+] \le 2$, the complex decomposes with the formation of free aluminum ions and isopoly molybdates, while in near-neutral solutions ($-\log [H^+] \ge 5$) the decomposition yields amorphous aluminum hydroxide and molybdate ions. The solubility product for this phase, defined by the reaction $Al^{3+} + 3H_2O \rightleftarrows Al(OH)_3(s) + 3H^+$, was determined to be $\log (K_{-3,1,0} \pm 3\sigma) = -10.49 \pm 0.08$. Data were analyzed with the computer programs LETAGROPVRID and SOLGASWATER.

Introduction

In two current research projects in this department, speciation and equilibria in systems containing Al(III)[1] and Mo(VI)[2] are being investigated. The title system might therefore be regarded as a link between these projects.

Literature information concerning equilibria in the system $H^+–Al^{3+}–MoO_4^{2-}$ is quite confusing. Thus, thermodynamic data available in ref 3 and 4 seem to indicate that a species containing six molybdenum atoms per aluminum atom is formed. However, the reported charge for this species ranges from −3 to −9, and equilibrium constants differing by 15 orders of magnitude have been reported.

On the other hand, according to the comprehensive review on heteropoly and isopoly oxymetalates given by Pope,[5] the occurrence of an aqueous complex $Al(OH)_6Mo_6O_{18}^{3-}$ is well established. On the basis of an assumed resemblance with the compound $Na_3(CrMo_6O_{24}H_6)\cdot 8H_2O$,[6] even the structure for this species was postulated[7] to be of the so-called "Anderson" type, given in Figure 1. In the literature, ^{27}Al[8] and ^{17}O NMR[9] characteristics for this species have also been reported.

Whether or not this species is the only heteropoly anion formed in the title system as a function of aluminum/molybdenum ratio and pH has never been investigated. Neither have any true stability constants for the species formed been reported. For such an investigation to be successful, a necessary prerequisite is that the binary subsystems $H^+–Al^{3+}$ and $H^+–MoO_4^{2-}$ are well characterized. As such data, valid in 0.6 M Na(Cl) medium, recently have been determined within our research projects,[10,11] it was decided to undertake this investigation. The unbiased interpretation of data will be based on precise potentiometric titration as well as on quantitative ^{27}Al NMR data.

Table I. Binary Species in the System $H^+–Al^{3+}–MoO_4^{2-}$ [a]

proposed formula[b]	(p,q,r)	log $\beta_{p,q,r}$	proposed formula[c]	(p,q,r)	log $\beta_{p,q,r}$
Al^{3+}	(0,1,0)		MoO_4^{2-}	(0,0,1)	
$Al(OH)^{2+}$	(−1,1,0)	−5.52	$HMoO_4^-$	(1,0,1)	3.39
$Al(OH)_2^+$	(−2,1,0)	−11.3	H_2MoO_4	(2,0,1)	7.35
$Al(OH)_3$	(−3,1,0)	−17.3	$Mo_7O_{24}^{6-}$	(8,0,7)	52.42
$Al(OH)_4^-$	(−4,1,0)	−23.46	$HMo_7O_{24}^{5-}$	(9,0,7)	57.23
$Al_3(OH)_4^{5+}$	(−4,3,0)	−13.57	$H_2Mo_7O_{24}^{4-}$	(10,0,7)	60.78
$Al_{13}O_4(OH)_{24}^{7+}$	(−32,13,0)	−109.2	$Mo_8O_{26}^{4-}$	(12,0,8)	71.62
			$HMo_8O_{26}^{3-}$	(13,0,8)	73.38
			$H_3Mo_8O_{26}^-$	(15,0,8)	76.34

[a] (p,q,r) notations and formation constants are related to the reaction $pH^+ + qAl^{3+} + rMoO_4^{2-} \rightleftarrows H_pAl_q(MoO_4)_r^{p+3q-r}$. [b] Reference 10. [c] Reference 11.

Experimental Section

Solutions and Analysis. Stock solutions of sodium molybdate were prepared from $Na_2MoO_4\cdot 2H_2O$ (Merck p.a.) and analyzed through potentiometric titrations, considering the hydrolysis model in Table I as known. The titrated values were within 0.3% of those expected from the weighings. The preparation and analysis of other solutions is described in ref 12.

Apparatus. The automatic system for precise emf titrations, the thermostat, and the cell arrangement are fully described elsewhere.[12] The calibration of the glass electrode was performed separately in solutions of known hydrogen ion concentration before and after each titration. The ^{27}Al NMR spectra were measured on a Bruker WM-250 spectrometer equipped with a 10-mm multinuclear probehead. X-ray powder diffractograms of solids precipitating in near-neutral solutions were recorded on a Rigaku/"Geigerflex"D/MAXIIA diffractometer using Cu Kα radiation.

Temperature and Medium. The present investigation was carried out at 25.00 ± 0.05 °C in a constant ionic medium of 0.6 M Na(Cl).

Methods. The potentiometric measurements were carried out as a series of titrations at a constant ratio of the total concentration of aluminum, B, and molybdate, C. The titration procedures have been described earlier in this series.[12] The equilibration time between titrant additions was adapted so that stable emf readings, remaining constant to ±0.02 mV for hours, were recorded. In the present system, it was found that equilibration times of up to 6 h were needed. The reversibility of equilibria were tested by performing titrations in acidic as well as in alkaline directions.

The ^{27}Al NMR measurements were carried out on batch solutions equilibrated for at least 24 h. The short spin–lattice relaxation times for the quadrapolar nucleus ^{27}Al and the high stability of the spectrometer made it possible to collect data without D_2O lock of the instrument. Spectra were recorded using 8K data over a frequency domain of 2500

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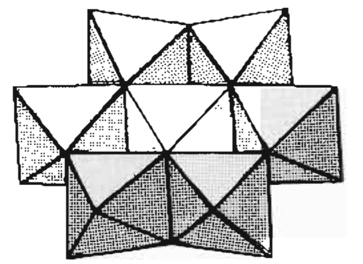

Figure 1. View of the "Anderson" structure drawn as linked octahedra.

Hz. For a spectrum, 1024 transients were collected, and an exponential line-broadening function of 0.5 Hz was applied in order to improve the signal to noise ratio. By calibration of the instrument versus a 0.0100 M Al^{3+} solution at $-\log [H^+] = 2$ and operation of it in the absolute intensity mode, quantitative information about the concentration of each species was determined. This sample was also used as an external chemical shift standard, by using the high-frequency-positive convention.

Data Treatment. The equilibria under consideration in the present study can be divided into three groups as follows: (1) hydrolysis of Al^{3+}, (2) hydrolysis of MoO_4^{2-}, and (3) formation of three-component complexes according to the general reaction $p\mathrm{H}^+ + q\mathrm{Al}^{3+} + r\mathrm{MoO_4}^{2-} \leftrightarrow \mathrm{H}_p\mathrm{Al}_q(\mathrm{MoO_4})_r{}^{p+3q-2r}$.

In earlier parts of our research projects, formation constants for dominating hydrolytic species of Al(III)[10] and Mo(VI)[11] have been determined. These constants are given in Table I. In the evaluation of three-component data, these binary complex models were considered as known, and all effects above this level were treated as being caused by three-component species.

Computer Programs. The mathematical analysis of emf data in homogeneous solutions was performed with the least-squares program LETAGROPVRID,[13] version ETITR.[14,15] In these computations, the error squares sum $U = \sum(H_{\text{calcd}} - H_{\text{exptl}})^2$, where H is the analytical proton concentration with H_2O, Al^{3+}, MoO_4^{2-} as zero level, was minimized. The analysis of NMR data and emf data in the presence of aluminum hydroxide was performed by using the modeling computer program SOLGASWATER.[16] $U = f(\log \beta)$ curves were constructed through a stepwise variation of $\log \beta$, and the minimum value in U was evaluated manually. In these cases, the minimized functions were $\sum((F_{\mathrm{Al}^{3+}})_{\text{calcd}} - F(_{\mathrm{Al}^{3+}})_{\text{exptl}})^2$ ($F_{\mathrm{Al}^{3+}}$ stands for the fraction of the species Al^{3+}) and $\sum((-\log [H^+])_{\text{calcd}} - (-\log [H^+])_{\text{exptl}})^2$, respectively. All standard deviations reported are defined according to Sillén.[17,18]

The program SOLGASWATER was also used for the construction of distribution, predominance area, and solubility diagrams. The computations were all performed on a CD Cyber 850 computer.

Data, Calculations, and Results

Before a successful attack on a ternary system can be made, a thorough knowledge about the binary subsystems underlying it is a necessity. In the present case, these systems show quite divergent qualities. Thus, while the H^+–Al^{3+} system becomes increasingly complicated in near-neutral solutions, the H^+–MoO_4^{2-} system exhibits its most complicated behavior in strongly acidic solutions. The present investigation was therefore started by a series of ^{27}Al NMR measurements on solutions of intermediate acidity ($-\log [H^+] = 3.0$) containing 10.0×10^{-3} M Al(III) and variable concentrations of Mo(VI). The result of these measurements is illustrated in Figure 2 and shows that, as the molybdenum concentration increases, the peak corresponding to Al^{3+} ($\delta = 0$ ppm; $\gamma_{1/2} = 4$ Hz) is successively replaced by a second Al(III) peak ($\delta = 15.5$ ppm; $\gamma_{1/2} = 55$ Hz) and that this peak corresponds to a species with a C/B ratio of 6. It can also be concluded that, at this $-\log [H^+]$ value, no species of any other C/B ratio is formed. Finally, as this plot shows that the species is formed in near-stoichiometric amounts, it can be concluded that its equilibrium constant is hard to evaluate at this $-\log [H^+]$.

To investigate whether complexes of different stoichiometries were formed at other $-\log [H^+]$ values, two series of solutions at $C/B = 6$ and 12 ($B = 10.0 \times 10^{-3}$ M) were prepared and measured by ^{27}Al NMR. The results of these measurements are illustrated in Figure 3 and show that in neither case can any "new" peak be observed. Furthermore, as the chemical shift and the line width for the peak corresponding to the "AlMo$_6$" species remained constant throughout, a strong indication for a constant degree of protonation in this species was obtained. These figures, however, also illustrate that the complex is decomposed in solutions of high and low acidities. At low acidities, this decomposition was connected to the formation of a white precipitate, presumably aluminum hydroxide. It was therefore concluded that the stability of this ternary species preferably should be determined in solutions of high acidities.

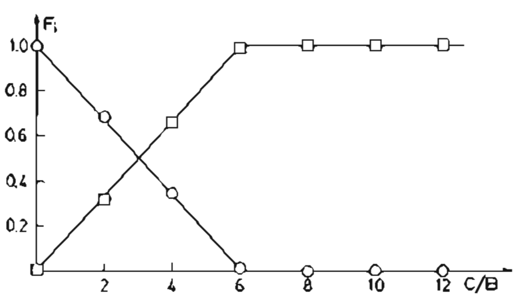

Figure 2. Fraction of Al(III) found as Al^{3+} (○) and "AlMo$_6$" (□) as a function of C/B at $B = 10.0 \times 10^{-3}$ M and $-\log [H^+] = 3.0$. The curves were calculated by using the final equilibrium model.

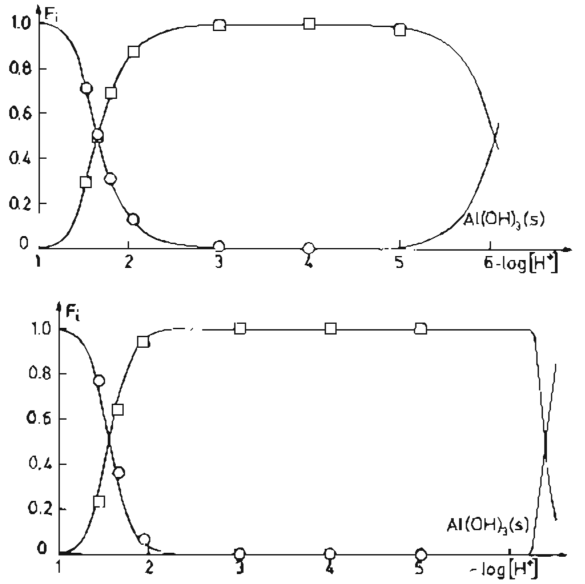

Figure 3. Fraction of Al(III) in Al^{3+} (○) and "AlMo$_6$" (□) as a function of $-\log [H^+]$ at $B = 10.0 \times 10^{-3}$ M and $C =$ (a, top) 60.0×10^{-3} M or (b, bottom) 120×10^{-3} M. The curves represent the final equilibrium model.

For this reason, potentiometric titrations at $C/B = 6$; $0.9 \leq B/\text{mM} \leq 10$ and $1.5 \leq -\log [H^+] \leq 5$ were performed. These titrations were run in the acidic as well as in the alkaline direction, and it was found that equilibration times of 6 h were needed. A total of 48 equilibrium data were collected. As NMR data had clearly indicated the presence of a species with a C/B ratio of 6, the computational work to evaluate the full stoichiometry and stability of this complex was highly simplified; i.e., only the number of protons attached and the multiplicity had to be considered.

These computations were made by using the LETAGROP[13] program, and the complex resulting in the lowest error squares sum U was considered the "best". From the results obtained ((p,q,r), $\log (\beta \pm 3\sigma)$, U, $\sigma(H/\mathrm{M})$: (5,1,6), 48.6 ± 0.4, 765, 0.0040; (6,1,6), 50.95 ± 0.04, 5.8, 0.0003; (7,1,6), 53.9 ± 0.6, 558, 0.0034; (12,2,12), 104.1 ± 0.15, 22.5, 0.0007), it was concluded that the ternary species had the composition $H_6Al(MoO_4)_6{}^{3-}$. An independent validation of this equilibrium constant was also obtained

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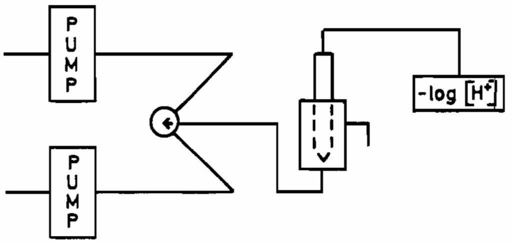

Figure 4. Schematic figure of the flow system used for kinetic experiments.

from NMR data yielding the value log ($\beta_{6,1,6} \pm 3\sigma$) = 50.96 ± 0.06. At this point it might also be pointed out that as the species (6,1,6) and (12,2,12) only differ in their d(−log [H^+])/dC while (5,1,6) and (7,1,6) give rise to different amounts of attachable protons, it is by no means surprising that (12,2,12) provides a much closer fit to emf data than (5,1,6) or (7,1,6).

To study the characteristics of the precipitate formed in near-neutral solutions, several batches of suspensions were prepared, filtered, washed, and analyzed by X-ray powder diffractometry. Through these measurements, the amorphous nature of the solid formed was proved. In this area, a potentiometric titration at $C/B = 6$ ($B = 0.008$ M and −log [H^+] ≤ 6.0) was also performed. This titration yielded increasing amounts of the white precipitate with increasing −log [H^+]. As it was found that reasonable stable emf readings ($dE/dt \leq 0.05$ mV/h after 4 h) were obtained, an attempt was made to evaluate the stoichiometry and solubility for this solid phase. These calculations were carried out with the program SOLGASWATER,[16] and it was found that experimental data could be explained by the reaction $Al^{3+} + 3H_2O \rightleftarrows Al(OH)_3(s) + 3H^+$ with log ($K_{-3,1,0} \pm 3\sigma$) = −10.49 ± 0.08. This value is quite in accordance with earlier data[3,4] regarding the solubility of freshly precipitated amorphous aluminum hydroxide.

In the present investigation, attempts have also been made to study the deprotonation of $H_6Al(MoO_4)_6^{3-}$ by means of kinetic experiments. By quick addition of base to a solution dominated by $H_6Al(MoO_4)_6^{3-}$ and with −log[H^+] monitored as function of time, such information could be gained if the kinetics of the deprotonation step exceed the kinetics for the decomposition step. At first, this experiment was simply performed by using an Oxford pipet and a glass electrode (cf. ref 10), but as it turned out that $Al(OH)_3(s)$ started to form already within 5 s, a more sophisticated technique had to be used. For this reason, a flow system consisting of two peristaltic pumps, a mixing cavity, a single-bead string reactor and a flow-through glass electrode cavity was constructed (cf. Figure 4). The flow of solution containing $H_6Al(MoO_4)_6^{3-}$ was kept constant at 7 mL/min while the flow of sodium hydroxide was varied to obtain different degrees of neutralization. Through this arrangement, steady −log [H^+] readings, valid 0.3–0.5 s after mixing, were recorded. The results of these experiments are illustrated in Figure 5. At low degrees of neutralization, these data seem to indicate that the protons attached can be assigned an average pK_a of 6.2 (cf. the theoretical dashed curve). At higher neutralization degrees, however, the expected loss of buffer capacity at six OH^- added per $H_6Al(MoO_4)_6^{3-}$ does not occur. Instead, this buffer loss occurs at the addition of 9–10 OH^- ions, corresponding to a deprotonation of the species plus the formation of $Al(OH)_3(s)$ and/or $Al(OH)_4^-$. It is therefore doubtful whether the pK_a indicated at low neutralization degrees is real or whether these data also reflect a partial formation of $Al(OH)_3(s)$. What the present kinetic data definitely do show is, however, that the protons surrounding the $AlMo_6$ moiety are vital parts for stabilizing this complex. Compared to the formation and decomposition kinetics in acid media, the decomposition rate in neutral solutions is higher by several orders of magnitude.

Discussion

In the present study, data from potentiometric and ^{27}Al NMR measurements have been used for somewhat different purposes.

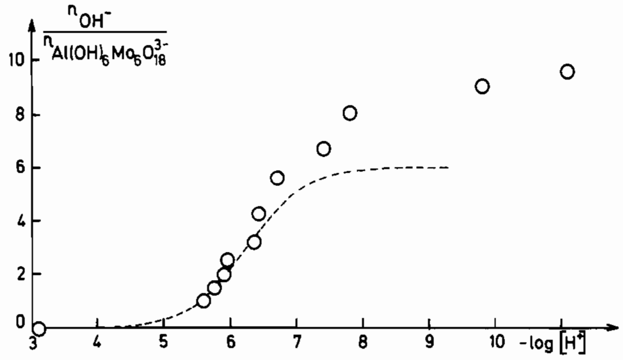

Figure 5. Experimental results for the kinetic experiments. The dashed curve has been calculated by assuming a single average acidity constant of $10^{-6.2}$.

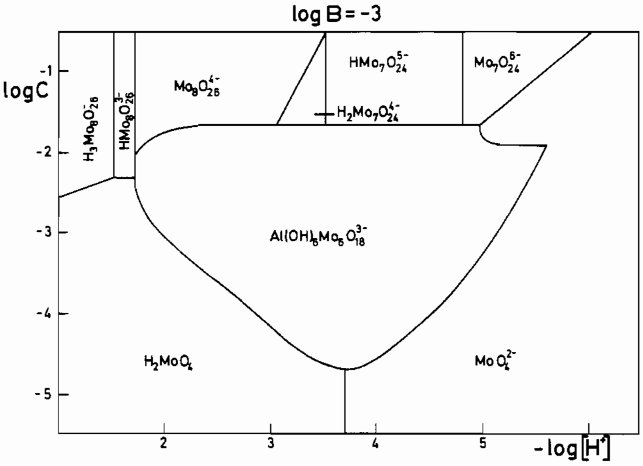

Figure 6. Diagram showing predominance areas of Mo(VI)-containing complexes at $[Al]_{tot} = 10^{-3}$ M. In each area, the species containing the highest content of Mo(VI) has been marked.

Thus, from NMR data, information concerning the number of magnetically nonequivalent Al surroundings as a function of C/B and −log [H^+] was obtained. NMR data also yielded valuable information concerning the C/B ratio in the species formed. Potentiometric data, on the other hand, were used to evaluate the number of protons attached to the complex as well as to determine the stoichiometric multiplicity in the species formed. Finally, both types of data were used to independently evaluate the formation constant for the species formed.

In view of the apparent simplicity of the present results, the question that naturally arises is why published thermodynamic data are so enormously scattered. The main reason to this scatter can probably be deduced from Table I. Without a proper characterization of the binary subsystems underlying the system under investigation, in this case especially the H^+–MoO_4^{2-} system, the investigation will be out of control. This is illustrated in Figure 6, which is a diagram showing predominating Mo(VI)-containing species as function of −log [H^+] and total molybdate concentration at $B = 10^{-3}$ M. This figure also illustrates the real complexity of the present system.

Another possible cause for divergent results in the present system is the relative slowness by which the ternary species is formed and decomposed in acidic solutions. Unless a proper equilibration time (≥6 h) has been allowed between changes in solution composition, the measured quantity will give rise to erroneous results.

With respect to structures of different species formed, an investigation of this kind gives no direct information. As, however, the composition of the ternary species found, $H_6Al(MoO_4)_6^{3-}$, exactly matches the formula $Al(OH)_6Mo_6O_{18}^{3-}$, there is little doubt that this complex is of the "Anderson" type, illustrated in Figure 1. The reasons for assuming that the six protons are attached to the oxygen atoms surrounding the aluminum ion have been given by Perloff.[6] In thermodynamic terms, these protons

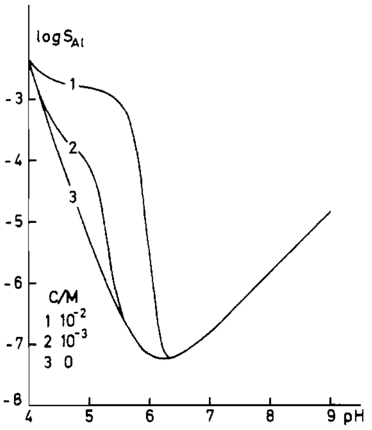

Figure 7. Solubility of gibbsite expressed as $\log S_{Al}$ versus $-\log$ [H$^+$] for different total concentrations of Mo(VI), *C*.

behave fully nonacidic; i.e. when $-\log$ [H$^+$] is increased, the complex decomposes with the formation of $Al(OH)_3(s)$ and MoO_4^{2-} without signs of deprotonation.

The formation of $Al(OH)_3(s)$ from an aqueous solution is normally an extremely slow process. One of the reasons for this behavior is the formation of metastable polynuclear hydrolysis products in the aqueous phase. Due to the complex-forming ability of the molybdate ions, this supersaturation never occurs in the present system. Therefore, it was possible to collect reasonably stable emf data ($dE/dt \le 0.05$ mV/h) in the presence of this solid. From X-ray powder diffractograms, but also from the solubility product evaluated, $\log {}^*K_{s0} = 10.49$, the amorphous nature of this phase was demonstrated. The slow drift in emf potentials registered can probably be attributed to a slow rearrangement of the solid into a more crystalline form of aluminum hydroxide.

In the present study, attempts were also made to evaluate kinetic acid–base qualities for the species $Al(OH)_6Mo_6O_{18}^{3-}$. The idea was to test whether the deprotonation rate of this species exceeded its decomposition rate. A flow system, by which steady $-\log$ [H$^+$] values could be recorded 0.3–0.5 s after mixing, was constructed. At low neutralization degrees, data indicated an average pK_a of 6.2 for these protons, but at the same time, data collected at higher degrees of neutralization indicated a simultaneous formation of $Al(OH)_3(s)$ and/or $Al(OH)_4^-$. It was therefore concluded that data collected were nondecisive but that they definitely showed the decomposition rate of $Al(OH)_6Mo_6O_{18}^{3-}$ to be several orders of magnitude higher in near-neutral solutions than in acidic solutions. It can therefore be concluded that the protons surrounding the $AlMo_6$ moiety are vital parts for stabilizing the complex.

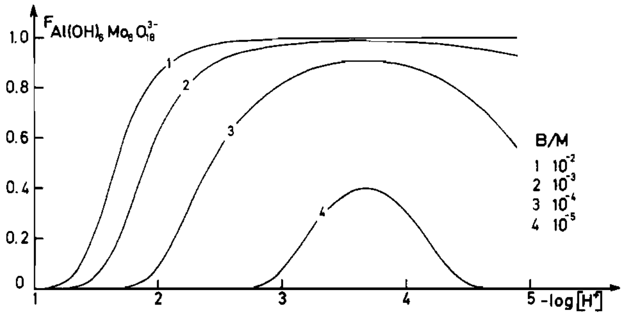

Figure 8. Fraction of aluminum in the form of $Al(OH)_6Mo_6O_{18}^{3-}$ at *C*/*B* = 6 as a function of total concentrations and $-\log$ [H$^+$].

To illustrate the thermodynamic stability of the species $Al(OH)_6Mo_6O_{18}^{3-}$, a series of model calculations using the program SOLGASWATER[16] were performed. In the first series of calculations, the potential ability of molybdate ions to raise the solubility of gibbsite, $\log {}^*K_{s0} = 9.60$,[19] was examined. These calculations, illustrated in Figure 7, showed that the main influence can be expected to occur at $-\log$ [H$^+$] = 4–6 but also that the molybdate concentration has to exceed $\approx 0.3 \times 10^{-3}$ M to result in any significant solubilization. Compared to that of other substances previously investigated within this series, the complexation ability of molybdate ions thus shows their closest resemblance to phthalate ions.[20]

In a second series of calculations, the fraction of aluminum in the form of $Al(OH)_6Mo_6O_{18}^{3-}$ was calculated at $C/B = 6$ as function of total concentration and $-\log$ [H$^+$]. These calculations are illustrated in Figure 8 and show that still at a very high dilution ($B = 10^{-5}$ M; $C = 6 \times 10^{-5}$ M) approximately 40% of *B* and *C* remain bound in the ternary species at $-\log$ [H$^+$] = 3.7. As, however, this complex decomposes (predominantly into Al^{3+} and MoO_4^{2-}) at $-\log$ [H$^+$] values slightly above 4, the negligible solubilization effect of low molybdate concentrations indicated above can also be understood.

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