Multicomponent Polyanions

II. A Potentiometric, Polarimetric, and Spectrophotometric Study of Mannitoldimolybdates in 3 M Na(ClO₄) Medium

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Equilibria between H^+, $MoO_4{}^{2-}$, and D-mannitol have been studied in 3.0 M Na(ClO₄) medium at 25°C by means of potentiometric (glass electrode), polarimetric and to some extent spectrophotometric measurements. The pH-range $1-9$ has been covered. All data could be completely explained with the two ternary complexes $[(H)_2(MoO_4)_2(C_6H_{14}O_6)]^{2-}$ and $[(H)_3(MoO_4)_2(C_6H_{14}O_6)]^-$. The optical rotation has been measured at the four wavelengths 589, 578, 546, and 436 nm. The absorbance has been measured at 5 nm intervals in the wavelength range $205-320$ nm. Data have been treated using the least squares computer program LETAGROPVRID. "Best" equilibrium constants, molar rotations, and molar absorption coefficients obtained are collected in Tables 2, 3, and 4, respectively.

Complex formation between molybdate ions and mannitol, $C_6H_8(OH)_6$, has been described in a number of investigations. A survey of these reports is given below. Summarizing the results from these investigations, we may conclude that the existence of complexes with the molybdate-mannitol ratio 2:1 seems to be well established, whereas number of complexes, equilibrium constants, and charges are unsatisfactorily known.

Reactions between mannitol and molybdate show many similarities with "pure" anion hydrolysis reactions. The system may therefore be of particular interest and can be used for obtaining structural and kinetic details of the binary $H^+ - MoO_4{}^{2-}$ system. Another interesting feature of the molybdate-mannitol system is its high optical activity. This property would be useful for analytical determinations of total mannitol or molybdenum contents in unknown systems. The high optical activity may perhaps also be useful in investigations of complicated molybdate equilibria. Here the molybdate-mannitol system can be used as an aid-system and the free $MoO_4{}^{2-}$ concentration can be indirectly measured by means of the optical activity.

Clarification of equilibria and composition of polyol-molybdate complexes might also be of biochemical interest, especially for the carbohydrate chemists. The aim of the present investigation was to study equilibria

$$p\mathrm{H^+} + q\mathrm{MoO_4^{2-}} + r\mathrm{Ma} \rightleftharpoons (\mathrm{H})_p(\mathrm{MoO_4})_q(\mathrm{Ma})_r^{\,p-2q}$$
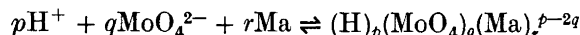
and try to determine complexes (sets of p,q,r) and formation constants (β_{pqr}). Ma stands for mannitol.

The investigation was carried out by using potentiometric, polarimetric and to some extent spectrophotometric methods.

PREVIOUS WORK

Complex formation between molybdate and mannitol was first demonstrated by Gernez [1] in 1891. He found, that the optical rotation of aqueous D-mannitol solutions was considerably increased by addition of acidified molybdate solutions, and that the specific rotation varied as the relative proportions of the two components were changed. Since then the molybdate-mannitol system has been examined by a number of investigators. Different experimental methods have thereby been used, but most frequent are polarimetric, potentiometric, and conductometric methods.

Optical activity data. In 1921, Tanret [2] demonstrated that a maximum specific rotation was reached when the molybdenum to mannitol ratio is about two. Later, Honnelaitre [3] observed that the rotation varied with the pH of the solution, and Frèrejacque [4] noticed that at one and the same molybdenum concentration the specific rotation of strongly acidified solutions was constant when the molybdenum to mannitol ratio was kept above 2.8. Richtmyer and Hudson [5] made a comparison of the optical activity of 14 different polyols in acidified ammonium molybdate solutions. They found for all polyols, that the optical activity increased considerably in acidified molybdate solutions compared with solutions with solely the polyol. For D-mannitol in acid molybdate solution they reported $[\alpha]_\mathrm{D}^{20} = 141°$. Bourne *et al.*[6] examined the effect of pH and found a maximum specific rotation at $\mathrm{pH} \approx 2$. They also found that the molybdenum to mannitol ratio in the complex is about two. A detailed study by Hamon *et al.*[7] of the optimum conditions for analytical determination of mannitol as a molybdate-mannitol complex has shown that at $\mathrm{pH} \approx 1.5$ and for molybdate-mannitol ratios greater than 3 the optical activity is proportional to the mannitol concentration and they reported a specific rotation $[\alpha]_\mathrm{D}$ of $143° \pm 2°$. Voelter *et al.*[8] have studied optical rotatory dispersion of acidified molybdate-mannitol solutions and found evidence for the existence of two different complexes, one at about pH 5 and the other about pH 2.5, both having the molybdenum-mannitol ratio of 2.

Potentiometric and conductometric data. Among the potentiometric [9-14] and conductometric [11,12,14-16] investigations the following may especially be mentioned. In a study of the changes of pH with dilution, Souchay [10] established the existence of a complex $\mathrm{Mo_2O_7C_6H_{14}O_6^{2-}}$. From breaks in pH and spectrophotometric titration curves, Chalmers and Sinclair [13] proposed that in the pH-range 2.5 – 9, two molybdate-mannitol complexes are formed both having a ratio of molybdenum to mannitol of 2. They found that the formation of one of the complexes occurs in approximately neutral solution and requires an absorption of one proton per every complexed $\mathrm{MoO_4^{2-}}$. For formation of the other complex, formed in more acid solution, 1.5 protons are required. From considerations of the absorbance spectra in the near ultraviolet they state that the "neutral" complex contains a dimolybdate group. In the "acid" complex they propose that the degree of condensation of the molybdate changes to either a tetra- or an octamolybdate. Furthermore, they believe that the complex formation is caused by hydrogen bonds.

From conductometric titration data Soubarew-Châtelain [15] found evidence for the species $[\mathrm{Mo_2O_7(HC_6H_{14}O_6)}]^-$. Using the same method Frey [16] came to the same conclusion and gave the species the formula $[\mathrm{HMo_2O_7 \cdot C_6H_{14}O_6}]^-$.

Solid phases obtained from aqueous molybdate-mannitol solutions. All solid phases described have, with one exception, the molybdate—mannitol ratio of 2 ($\mathrm{MoO_3/Ma} =$

$q/r = 2$), and there seems to be three types of crystals, one with $M_2^IO:MoO_3:Ma$ ratio 1:2:1, another with the ratio 0.5:2:1, and a third with the ratio 0:2:1 (M^I is most often K^+ and/or NH_4^+).

1 : 2 : 1-ratio ($p,q.r = 2,2,1$): $NH_4.NH_3[HMo_2O_7.Ma]$;[16] $K.NH_3[HMo_2O_7.Ma]$.[16]

0.5 : 2 : 1-ratio ($p,q,r = 3,2,1$): $K[HMo_2O_7.Ma]$;[16] $NH_4[HMo_2O_7.Ma]$;[16]

$[(7NH_3.13MoO_3.7Ma) - 6H_2O].3H_2O$.[2]

0 : 2 : 1-ratio ($p,q,r = 4,2,1$): $H_2Mo_2O_7.Ma.H_2O$;[18] $(Mo(OH)_4O_2)C_6H_{10}O_2(O_2Mo(OH)_4)$.[19]

The phase in Ref. 19 was prepared from an aqueous solution of $MoO_3.2H_2O$ and mannitol, exposed to fumes of concentrated HCl. It was shown that the unit cell is orthorhombic, containing two formula units, density 2.179 g cm^{-3} and with the dimensions: $a = 8.23$ Å, $b = 12.32$ Å, $c = 6.86$ Å.

EXPERIMENTAL

The present study has been carried out in close connection with Part I [20] in this series.
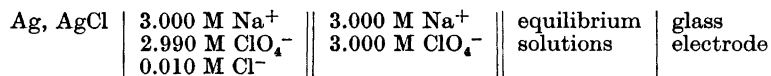
Chemicals and analyses. Solutions of $NaClO_4$ and $HClO_4$ were prepared and analysed as described by Sjöberg,[21] and solutions of Na_2MoO_4 as described in Part I.[20] D-Mannitol (Difco Laboratories and Bakers, *p.a.* quality) was in most cases recrystallized. No difference in the titrations was found between recrystallized and not recrystallized mannitol. Mannitol solutions were prepared by weighing out known amounts. We found that the solutions should be freshly prepared. When standing they give irreproducible values (probably due to contamination from the paraffin and the glass vessels used).

Apparatus. The emf equipment and arrangement used were the same as described by Sjöberg.[21] The polarimeter used was a Perkin-Elmer Model 141. The sample cell was a 10 cm Standard Cell No. 017044. During the measurements the cell was thermostatted at $(25.0 \pm 0.1)°C$. The spectrophotometer was a Bausch and Lomb Spectronic 505. The cells were of quartz and with 1 mm path length constructed to suit a titration procedure. The sample compartment was thermostatted at $(25.0 \pm 0.2)°C$.

Method

The present study has been carried out as a series of emf, polarimetric, and spectrophotometric titrations at 25°C and in 3 M $Na(ClO_4)$ medium. In each titration the total concentrations of molybdenum, B, and mannitol, C, have been kept constant and $[H^+] = h$ has been varied by the addition of H^+ (or OH^-). B and C have been varied within the limits: 0.5 mM $\leq B \leq$ 160 mM and 5 mM $\leq C \leq$ 160 mM. The free hydrogen ion concentration, h, has been measured with a glass electrode with an accuracy of ± 0.2 mV. The range of pH ($= -\log h$) has been kept within the limits $1 < pH < 9$. However, for pH < 3 the B to C ratio was kept below or equal to 2 in order to avoid experimental difficulties due to precipitation of acid polymolybdates and also partly by the lack of exact knowledge of the binary molybdate equilibria in this range (the binary $H^+ - MoO_4^{2-}$ complexes were found to be negligible when $B/C \leq 2$). In order to check the reversibility of equilibria both backward (increasing pH) and forward (decreasing pH) titrations have been carried out.

Emf measurements. The free H^+-concentration was determined by measuring the emf of the cell:

Ag, AgCl	3.000 M Na$^+$		3.000 M Na$^+$		equilibrium	glass
	2.990 M ClO$_4^-$		3.000 M ClO$_4^-$		solutions	electrode
	0.010 M Cl$^-$					

Assuming the activity coefficients to be constant the following expression is valid for the measured emf:

$$E = E_0 + 59.157 \log h + Ej \tag{1}$$

For the liquid junction potential, E_j, we have used $E_j = -16.3.h$ (mV). The quantity E_0 is a calibration constant. Unfortunately there is no possibility of determining E_0 directly in the titrations. It was determined in separate experiments before and/or after every titration in 3 M $Na(ClO_4)$ solutions with known H^+-concentration.

There were indications of a small systematic error in the separately determined E_0-values (especially at high B,C-concentrations). In the search for complexes the E_0-values were supposed to be correct but in the final calculations they were slightly adjusted in order to obtain the "best" explanation of the data.

From h, calculated by using eqn. (1), and from H, the excess concentration of hydrogen ions over the zero level (MoO_4^{2-}, mannitol and H_2O) one can calculate Z, the average number of H^+ bound per B, using the relation:

$$Z = (H - h)/B \qquad (2)$$

The emf titrations thus give series of data sets $H(\log h)_{BC}$ and $Z(\log h)_{BC}$.

Polarimetric measurements. In the beginning of the polarimetric investigation the solutions sometimes had been stored for up to a few weeks. As the investigation proceeded we found that the optical activity in stored solutions had changed somewhat. After that observation the measurements were made on freshly prepared solutions in close connection with the emf measurements.

The angle of optical rotation, α, was measured at points with known Z, $\log h$, B, and C, at the four wavelengths: $\lambda_1 = Na$ 589 nm, $\lambda_2 = Hg$ 578 nm, $\lambda_3 = Hg$ 546 nm, and $\lambda_4 = Hg$ 436 nm. We also tried to use the fifth wavelength of the polarimeter $\lambda_5 = Hg$ 365 nm but had some difficulties in obtaining stable values especially for $B/C > 2$ (molybdenum excess). The measured α-values have been corrected for zero effects (obtained for the sample cell filled with 3 M $NaClO_4$). The relationship between angle of optical rotation, α, and equilibrium concentrations in the solution is assumed to follow the formula:

$$\alpha = l \sum \phi_i c_i$$

where l is the pathlength and the summation is taken over all species containing mannitol. The equilibrium concentration and the molar rotation for the i:th mannitol species are denoted c_i and ϕ_i, respectively. The polarimetric measurements thus give for each wavelength data $\alpha(\log h)_{BC}$.

Spectrophotometric measurements. The measurements were made so that both absorbance and $[H^+]$ were measured in one and the same titration. This was achieved by using a special titration procedure. Description of the measuring technique will be given in a forthcoming paper by L. Lyhamn. For each point in a titration the equilibrium emf was first measured and then the absorbance, OD, at about 5 nm-intervals covering the wavelength region $205 - 320$ nm (25 OD-values for each equilibrium point). The spectrophotometric measurements are preliminary and only two B,C combinations have been studied hitherto namely $B = 0.5$, $C = 5.0$ (mM); $B = 1.0$, $C = 10.0$ (mM) in the pH-range $2 - 7$. For $B = 0.5$ mM pure ionic medium has been used as reference solution but for $B = 1.0$ mM a reference solution consisting of a 0.5 mM molybdate solution with known $OD(\lambda)$ has been used in order to obtain a suitable value of the absorbance. The relation between the absorbance, OD, and the concentrations, c_i, of the various absorbing species is given by the equation: $OD = l \sum \varepsilon_i c_i$, where ε_i is the molar absorption coefficient for the absorbing species i at the wavelength λ. The spectrophotometric measurements thus give data $OD(\lambda)_{\log h,B,C}$.

Equilibria, assumptions and comments. In the present study in addition to the three-component equilibria:

$$pA + qB + rC \rightleftharpoons A_pB_qC_r \qquad (3)$$

we need to consider the binary equilibria:

$$pA + qB \rightleftharpoons A_pB_q \qquad (4)$$

In eqns. (3) and (4), $A = H^+$, $B = MoO_4^{2-}$ and $C =$ mannitol ($C_6H_8(OH)_6$). The complex $A_pB_qC_r$ will mostly be referred to as the (p,q,r) species or complex.

On the whole for determining the three-component complexes it is necessary that the two-component equilibria are exactly known. In the present case accurate equilibrium data for $H^+ - MoO_4^{2-}$ (25°C and 3 M Na(ClO_4)) have already been presented by Sasaki and Sillén.[22] They report the following species and formation constants (valid for pH > 2.5):

$HMoO_4^- (\log \beta_{1,1} = 3.89)$, $H_2MoO_4 (\log \beta_{2,1} = 7.50)$,
$Mo_7O_{24}^{6-} (\log \beta_{8,7} = 57.74)$, $HMo_7O_{24}^{5-} (\log \beta_{9,7} = 62.14)$,
$H_2Mo_7O_{24}^{4-} (\log \beta_{10,7} = 65.68)$, $H_3Mo_7O_{24}^{3-} (\log \beta_{11,7} = 68.21)$.

For pH < 2.5 a large complex (34,19) with log $\beta_{34,19} = 196.30$ and a cation (5,2) with log $\beta_{5,2} \approx 19$ are proposed. In the present paper these $(H^+ - MoO_4^{2-})$-equilibria will be considered as "known" and no attempts will be made to adjust constants or to introduce new $(H^+ - MoO_4^{2-})$-species. For further details (check of the system and impurities in the Mo-stock), see Part I in this seris.[20] We have found that within the pH-range 1 < pH < 9 mannitol does not react either with H^+ or OH^-.

Equilibria between the species and the medium molecules must to some extent also be considered. However, according to the principles of the ionic medium method this influence can be considered as constant when 3 M $Na(ClO_4)$ medium is used.

The law of mass action and the conditions for the concentrations. Applying the law of mass action to equilibria (3) and (4) the conditions for the concentrations give:

$$B = b + B_1 + \sum q \beta_{pqr}\, h^p b^q c^r \tag{5}$$

$$C = c + \sum r \beta_{pqr}\, h^p b^q c^r \tag{6}$$

$$H = h + B_1 Z_1 + \sum p \beta_{pqr}\, h^p b^q c^r \tag{7}$$

where $b = [MoO_4^{2-}]$, $c = [C_6H_8(OH)_6]$, $h = [H^+]$, $\beta_{pqr} = [A_p B_q C_r]\, h^{-p} b^{-q} c^{-r}$, and B_1, $B_1 Z_1$ are the "known" quantities for the binary equilibria:

$$B_1 = \beta_{1,1}hb + \beta_{2,1}h^2b + 7\beta_{8,7}h^8b^7 + 7\beta_{9,7}h^9b^7 + 7\beta_{10,7}h^{10}b^7 + 7\beta_{11,7}h^{11}b^7 \tag{8}$$

$$B_1 Z_1 = \beta_{1,1}hb + 2\beta_{2,1}h^2b + 8\beta_{8,7}h^8b^7 + 9\beta_{9,7}h^9b^7 + 10\beta_{10,7}h^{10}b^7 + 11\beta_{11,7}h^{11}b^7 \tag{9}$$

The summations are made over all ternary species present.

Data treatment. The refinement of constants and the error calculations have been made with the least squares program LETAGROPVRID.[23] For the emf data the version ETITR [24] and for the polarimetric and spectrophotometric data the version SPEFO [25] have been used. On treating the emf, the polarimetric and the spectrophotometric data, the error squares sums $U = \sum(H_{\text{calc}} - H)^2$, $U = \sum(\alpha_{\text{calc}} - \alpha)^2$, and $U = \sum(OD_{\text{calc}} - OD)^2$ have been minimized, respectively. The standard deviations are defined and calculated according to Sillén.[26],[27] The computation has been performed both on CD 3600 (Uppsala) and on CD 3200 (Umeå).

DATA, CALCULATIONS AND RESULTS

Emf data. In Fig. 1 are plotted experimental data $Z(\log h)_{BC}$ for a section at $B = 80$ mM and with $C = 0$, 10, 20, 40, 80, and 160 mM. From the figure is seen that in the Z-range $0 < Z < 1$ different curves are obtained for different C-concentrations, thus clearly indicating that at least one mixed complex $A_p B_q C_r$ must be formed. At higher Z-values $1 < Z < 1.5$ and with $C \geq 40$ mM ($B/C \leq 2$), the points seem to fall on a single curve independent of the value of C. However, for $C < 40$ mM. ($B/C > 2$), different curves are obtained for different C, and as C decreases, these curves approach the limiting curve for the pure molybdate system ($C = 0$). This behaviour of the $Z(\log h)_{BC}$ curves would indicate the existence of two predominating homonuclear (in B and C) complexes, $(AB)_q C_r$ and $(A_{1.5}B)_q C_r$. Similar diagrams were obtained also for the other B sections studied ($B(C)$ in mM: 160 (80,160); 40 (10, 40,160); 20 (5,20); 10 (10,20)) but for clarity these data have been omitted in the figure.

In order to find q and r in the complex $(AB)_q C_r$ we calculated quotients $(\Delta \log c / \Delta \log h)_{B,Z}$, using data with $0 < Z < 1$ and $B/C \leq 2$ (mannitol excess). We found that the quotients were approximately constant and equal to -2.

From eqns. (2) and (5)−(7), assuming formation of a single complex $A_p B_q C_r$, it can be shown that $(\partial \ln c / \partial \ln h)_{B,Z} = -p/r$. The result $p/r \approx 2$ thus points to the existence of the complex $(AB)_2 C$.
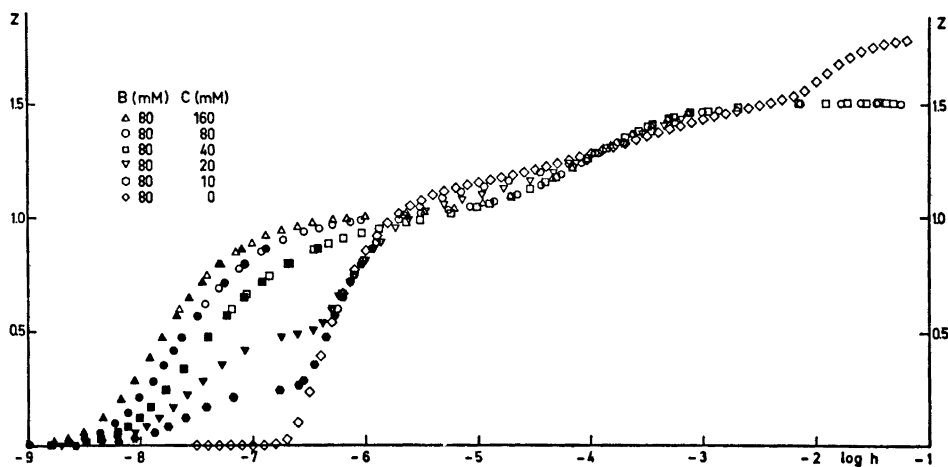
Fig. 1. Experimental emf data, $Z(\log h)_{BC}$ for a cut at $B = 80$ mM and with $C = 160, 80,$ 40, 20, 10 and 0 mM. Filled symbols are obtained in forward titrations (decreasing pH) and unfilled in reverse titrations.

In order to obtain further confirmation of this complex we constructed a diagram Z *versus* X, where $X = 2 \log h + \log B + \log (C - H/2)$, using data $Z < 1$ and $B/C \leq 2$. If the hypothesis of the complex $(AB)_2C$ is correct, the plot, $Z(X)_{BC}$, would give a single curve independent of B and C. This has also been found (see Fig. 2), and the plot strongly confirms the complex $(AB)_2C$.
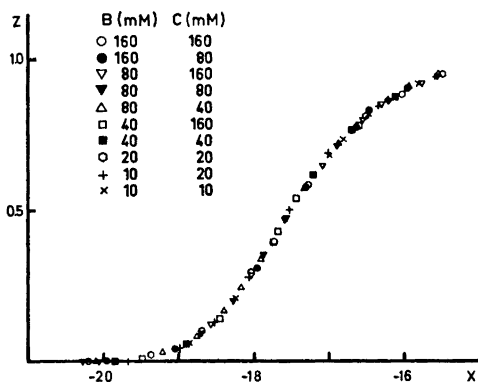
Fig. 2. Experimental emf data, $Z(X)_{BC}$, using data with $Z < 1$ and $B/C \leq 2$. $X = 2 \log h + \log B + \log (C - H/2)$.

By using the LETAGROP computer program the constants were determined and refined. Since the version ETITR at CD 3200 in Umeå at present has a maximum capacity of 25 titrations and 390 equilibrium points, all collected data could not be treated at the same time. It was found convenient to divide the data into two parts:

Table 1. Experimental emf data $H(\log h)_{BC}$. For each point the quantities $-\log h$, H, Δ_0, Δ_1, and Δ_2 are given (in mM). The quantity Δ is the residual $H_{calc} - H$. The indices 0, 1, and 2 refer to three different assumptions.

0. Only binary $H^+ - MoO_4{}^{2-}$ complexes with constants according to Sasaki and Sillén.[22]
1. Binary molybdate complexes and constants as under 0 together with proposed ternary complexes with constants given in Table 2.
2. The same complexes as in 1. From a covariation of E_0 and ternary constants the "best" $\log \beta$ obtained (Table 2) have been used in the calculation of Δ_2.

Data I. The following ΔE_0 for the 25 sets of titrations were obtained: 1.0, -0.1, 0.7, -0.9, 0.7, 0.7, -0.8, 0.9, 1.5, 0.5, -0.3, 0.3, 0.8, 0.3, 0.1, 0.2, -0.1, -1.1, -0.1, -0.8, 0.7, -1.8, -0.2, 1.5, -0.8.

Data II. The following ΔE_0 for the 7 sets of titrations were obtained: 0.0, 0.5, 0.9, 0.8, 0.2, 1.2, -3.0.

Note that the $-\log h$ values in the table do not exactly correspond to the residuals given.

DATA I :

SATS 1. B=0.010 C=0.010

-log h	H	Δ_0	Δ_1	Δ_2
7.747	0	.00	.19	.18
7.529	.29	-0.29	.18	.15
7.412	.58	-0.57	.18	.14
7.240	1.24	-1.23	.16	.09
7.096	2.07	-2.06	.10	.01
6.971	2.90	-2.89	.06	-0.04
6.822	3.96	-3.95	.04	-0.06
6.699	4.86	-4.84	.02	-0.09

SATS 2. B=0.010 C=0.010

-log h	H	Δ_0	Δ_1	Δ_2
3.211	15.00	-0.34	.04	-0.01
3.311	14.71	-0.33	.03	.02
3.508	14.15	-0.27	.07	.05
3.687	13.64	-0.15	.08	.06
3.877	13.05	.05	.10	.07
4.048	12.50	.25	.11	.08
4.240	11.91	.47	.12	.09
4.439	11.37	.61	.10	.07
4.584	11.04	.63	.08	.06
4.745	10.72	.55	.06	.04
4.925	10.42	.31	.04	.03
5.126	10.14	-0.25	.03	.02
5.331	9.88	-1.29	.01	.01
5.513	9.62	-2.78	-0.01	-0.01
5.773	9.15	-5.97	-0.03	-0.03
5.941	8.73	-7.87	-0.04	-0.03
6.117	8.16	-8.05	-0.06	-0.05
6.238	7.66	-7.61	-0.07	-0.05
6.406	6.83	-6.80	-0.08	-0.06
6.524	6.16	-6.13	-0.11	-0.09

SATS 3. B=0.010 C=0.020

-log h	H	Δ_0	Δ_1	Δ_2
7.980	0	.00	.13	.12
7.703	.30	-0.30	.13	.12
7.634	.45	-0.45	.13	.11
7.534	.74	-0.73	.11	.09
7.401	1.28	-1.27	.11	.06
7.272	2.02	-2.01	.06	.00
7.159	2.79	-2.78	.03	-0.04
7.004	4.01	-4.00	-0.05	-0.12

SATS 4. B=0.010 C=0.020

-log h	H	Δ_0	Δ_1	Δ_2
6.677	6.35	-6.33	-0.05	.05
6.582	7.04	-7.02	-0.17	-0.07
6.407	7.90	-7.87	-0.14	-0.07
6.300	8.33	-8.29	-0.13	-0.07
6.151	8.80	-8.72	-0.11	-0.06
6.027	9.11	-8.81	-0.09	-0.06
5.888	9.39	-7.93	-0.08	-0.05
5.739	9.62	-5.91	-0.07	-0.05
5.595	9.81	-3.98	-0.06	-0.05
5.415	10.00	-2.13	-0.05	-0.03
5.219	10.19	-0.83	-0.03	-0.02
4.978	10.47	.07	-0.02	-0.01
4.822	10.69	.37	.00	.01
4.688	10.91	.51	.02	.03
4.569	11.15	.55	.03	.04
4.389	11.56	.52	.05	.06
4.196	12.11	.36	.06	.07

-log h	H	Δ_0	Δ_1	Δ_2
4.035	12.60	.18	.06	.08
3.865	13.13	-0.01	.06	.07
3.713	13.59	-0.16	.05	.07
3.546	14.09	-0.29	.03	.05
3.355	14.62	-0.36	.00	.02
3.152	15.20	-0.36	-0.03	-0.01
3.058	15.50	-0.36	-0.07	-0.04

SATS 5. B=0.020 C=0.050

-log h	H	Δ_0	Δ_1	Δ_2
7.867	0	.00	.22	.21
7.572	.59	-0.58	.17	.14
7.424	1.15	-1.15	.17	.13
7.212	2.47	-2.46	.12	.06
7.015	4.13	-4.12	.05	-0.03
6.830	5.80	-5.77	-0.03	-0.10
6.545	7.93	-7.88	-0.04	-0.09
6.098	9.72	-6.44	.03	-0.01

SATS 6. B=0.020 C=0.050

-log h	H	Δ_0	Δ_1	Δ_2
2.995	30.00	-0.31	-0.03	-0.10
3.116	29.41	-0.31	.02	-0.05
3.357	28.31	-0.24	.12	.05
3.585	27.28	-0.10	.18	.10
3.843	26.09	.14	.19	.10
4.343	23.82	.68	.09	.01
4.599	22.74	.90	.04	-0.03
4.760	22.07	.99	.02	-0.04
4.905	21.44	1.04	.01	-0.06
5.024	20.85	1.07	.03	-0.04
5.125	20.28	1.07	.03	-0.05
5.201	19.75	1.10	.08	-0.00
5.273	19.25	1.05	.08	-0.02
5.381	18.31	.98	.11	-0.01
5.465	17.46	.87	.12	-0.01
5.558	16.32	.71	.15	-0.00
5.629	15.32	.52	.18	.01
5.735	13.65	.03	.20	.02
5.817	12.31	-0.60	.22	.03

SATS 7. B=0.020 C=0.020

-log h	H	Δ_0	Δ_1	Δ_2
7.982	.37	-0.37	.13	.17
7.755	1.21	-1.21	.07	.15
7.633	2.03	-2.03	-0.01	.11
7.464	3.63	-3.63	-0.08	.09
7.287	5.92	-5.91	'-0.21	.01
7.127	8.08	-8.07	-0.14	.09
6.947	10.79	-10.77	-0.31	-0.10
6.697	13.92	-13.88	-0.34	-0.17
6.442	16.24	-16.16	-0.27	-0.15
6.175	17.88	-16.38	-0.20	-0.13
5.908	18.93	-9.81	-0.16	-0.11
5.608	19.70	-3.49	-0.13	-0.10
5.213	20.45	.32	-0.07	-0.06
4.991	20.94	1.12	-0.05	-0.04
4.739	21.66	1.48	-0.00	.01
4.555	22.37	1.42	.03	.04
4.276	23.74	.99	.08	.09
4.054	25.05	.44	.07	.09
3.776	26.71	-0.24	.05	.06
3.401	28.66	-0.78	-0.05	-0.03
3.052	30.13	-0.73	-0.13	-0.10

SATS 8. B=0.040 C=0.010

-log h	H	Δ_0	Δ_1	Δ_2
8.271	0	.00	.27	.26
7.684	1.17	-1.17	.27	.19
7.731	2.30	-2.30	.27	.16
7.521	4.94	-4.93	.11	-0.07
7.320	8.26	-8.25	.01	-0.21
7.124	11.59	-11.57	.05	-0.17
6.838	15.86	-15.81	-0.02	-0.18
6.348	19.43	-14.21	.07	-0.00
6.072	23.38	-1.63	.65	.19
5.975	26.63	.03	.52	.03
5.889	29.35	.92	.47	.01
5.769	32.69	1.66	.40	.02
5.653	35.38	1.99	.28	-0.03

SATS 9. B=0.040 C=0.010

-log h	H	Δ_0	Δ_1	Δ_2
2.832	60.00	-0.34	.02	-0.17
2.995	58.83	-0.50	.06	-0.13
3.290	56.61	-0.46	.26	.05
3.540	54.56	-0.15	.46	.22
3.816	52.19	.36	.52	.23
4.061	50.02	.92	.47	.17
4.339	47.64	1.57	.37	.10
4.626	45.48	2.07	.25	.03
4.832	44.14	2.24	.14	-0.06
5.020	42.88	2.34	.10	-0.11
5.179	41.69	2.33	.06	-0.17
5.297	40.57	2.36	.11	-0.15

SATS 10. B=0.040 C=0.040

-log h	H	Δ_0	Δ_1	Δ_2
8.521	0	-0.00	.35	.34
8.178	1.17	-1.17	.39	.35
8.042	2.30	-2.30	.41	.34
7.868	4.94	-4.94	.16	.06
7.704	8.26	-8.25	.21	.07
7.574	11.59	-11.58	.19	.03
7.425	15.86	-15.85	.09	-0.08
7.307	19.43	-19.42	-0.12	-0.30

SATS 11. B=0.040 C=0.040

-log h	H	Δ_0	Δ_1	Δ_2
2.874	60.00	-0.70	.13	.13
3.071	58.83	-1.08	.18	.17
3.387	56.61	-1.14	.32	.28
3.621	54.56	-0.70	.37	.32
3.842	52.19	.19	.44	.37
4.027	50.02	1.14	.47	.41
4.233	47.64	2.22	.46	.39
4.443	45.48	3.12	.39	.33
4.596	44.14	3.58	.35	.30
4.783	42.88	3.78	.22	.19
5.015	41.69	3.56	.14	.12
5.341	40.57	1.88	.04	.04
5.735	39.50	-4.17	-0.05	-0.03
6.026	38.49	-14.30	-0.11	-0.08
6.352	36.62	-31.58	-0.22	-0.16
6.540	34.92	-34.50	-0.32	-0.23
6.717	32.64	-32.57	-0.35	-0.24
6.842	30.65	-30.60	-0.42	-0.28
7.011	27.31	-27.28	-0.48	-0.30
7.127	24.62	-24.60	-0.53	-0.33

Table 1. Continued.

SATS 12. B=0.040 C=0.160

-log h	H	Δ₀	Δ₁	Δ₂
8.637	.37	-0.	.42	.41
8.367	2.00	-2.00	.51	.48
8.123	5.60	-5.60	.61	.55
7.911	11.25	-11.25	.27	.18
7.728	17.12	-17.11	-0.07	-0.17
7.507	23.72	-23.71	-0.11	-0.20
7.180	31.18	-31.16	-0.16	-0.21
6.815	35.99	-35.94	-0.16	-0.19
6.551	37.95	-37.59	-0.24	-0.25
6.328	38.89	-32.62	-0.21	-0.22
5.973	39.80	-13.08	-0.20	-0.21
5.713	40.25	-4.33	-0.16	-0.18
5.466	40.69	.13	-0.13	-0.16
5.128	41.56	2.88	-0.06	-0.12
4.922	42.41	3.43	-0.03	-0.11
4.648	44.05	3.38	.07	-0.06
4.457	45.61	2.91	.16	-0.00
4.242	47.81	1.99	.20	.01
3.953	51.17	.47	.19	-0.00
3.689	54.19	-0.79	.07	-0.10
3.265	57.93	-1.60	-0.13	-0.23
4.782	90.05	4.07	-0.11	-0.21
4.546	92.91	3.51	.12	-0.02
4.336	95.95	2.72	.29	.13
4.137	99.19	1.80	.45	.27
3.940	102.66	.74	.46	.29
3.726	106.39	-0.24	.44	.28
3.547	109.36	-0.91	.31	.17
3.349	112.51	-1.50	-0.05	-0.15
3.197	114.71	-1.75	-0.33	-0.42
3.019	117.00	-1.72	-0.54	-0.61

SATS 13. B=0.080 C=0.010

-log h	H	Δ₀	Δ₁	Δ₂
8.579	0	-0.00	.27	.25
8.198	1.16	-1.15	.26	.19
8.050	2.29	-2.28	.25	.14
7.875	-.49	-4.48	.23	.05
7.754	6.61	-6.60	.15	-0.07
7.599	9.64	-9.62	.14	-0.10
7.413	13.43	-13.41	-0.03	-0.25
7.171	16.96	-16.92	.00	-0.13
6.766	19.46	-18.70	.15	.09
6.595	21.65	-12.68	.62	.24
6.554	22.60	-10.18	.59	-0.01
6.459	28.31	-4.39	1.13	-0.00

SATS 14. B=0.080 C=0.010

-log h	H	Δ₀	Δ₁	Δ₂
6.248	47.92	.74	1.00	.55
6.103	59.66	1.65	.62	.27
6.025	64.98	1.70	.25	-0.04
5.904	71.31	2.05	.18	-0.05
5.701	79.03	2.00	-0.25	-0.40
5.513	83.55	1.98	-0.42	-0.53
5.319	86.64	1.99	-0.46	-0.54
5.156	88.61	1.95	-0.46	-0.53
4.953	90.68	1.88	-0.41	-0.49
4.730	92.84	1.77	-0.25	-0.35
4.451	95.88	1.52	.03	-0.09
4.197	99.14	1.13	.29	.15
3.960	102.62	.54	.35	.20
3.716	106.35	-0.08	.28	.15
3.458	110.37	-0.77	-0.09	-0.20
3.252	113.59	-1.33	-0.60	-0.70
3.009	117.00	-1.59	-1.01	-1.09

SATS 15. B=0.080 C=0.020

-log h	H	Δ₀	Δ₁	Δ₂
8.701	0	-0.00	.30	.30
8.344	1.16	-1.16	.33	.33
8.207	2.30	-2.29	.34	.34
8.049	4.50	-4.50	.34	.34
7.948	6.63	-6.62	.24	.24
7.831	9.67	-9.66	.20	.20
7.709	13.47	-13.46	.12	.12
7.586	17.86	-17.85	-0.14	-0.13
7.449	22.66	-22.64	-0.22	-0.22
7.275	28.35	-28.35	-0.39	-0.39
7.071	33.45	-33.40	-0.27	-0.26
6.750	37.97	-37.00	-0.06	-0.05
6.608	39.03	-31.74	-0.01	-0.01

SATS 16. B=0.080 C=0.020

-log h	H	Δ₀	Δ₁	Δ₂
6.291	46.02	-3.92	.35	.20
6.209	53.26	-0.86	.34	.18
6.104	59.77	1.65	.32	.16
6.010	65.08	2.57	.15	.01
5.868	71.41	3.55	-0.02	-0.12
5.732	76.04	4.04	-0.16	-0.24
5.612	79.12	4.27	-0.27	-0.34
5.468	81.88	4.48	-0.27	-0.33
5.307	84.23	4.56	-0.27	-0.33
5.147	86.09	4.57	-0.21	-0.28
4.972	88.03	4.35	-0.22	-0.30

SATS 17. B=0.080 C=0.040

-log h	H	Δ₀	Δ₁	Δ₂
8.799	0	-0.00	.38	.39
8.481	1.16	-1.16	.45	.48
8.351	2.30	-2.29	.50	.55
8.205	4.50	-4.50	.50	.59
8.111	6.63	-6.62	.45	.57
8.010	9.67	-9.66	.33	.47
7.908	13.47	-13.46	.17	.34
7.774	19.52	-19.51	-0.21	-0.00
7.614	27.02	-27.01	-0.08	.14
7.397	37.97	-37.95	-0.43	-0.21
7.231	45.68	-45.64	-0.61	-0.42
7.072	52.02	-51.97	-0.60	-0.44
6.916	57.34	-57.22	-0.57	-0.43
6.679	63.84	-60.96	-0.52	-0.41
6.423	69.08	-40.66	-0.54	-0.46

SATS 18. B=0.080 C=0.040

-log h	H	Δ₀	Δ₁	Δ₂
6.199	72.64	-19.35	-0.73	-0.48
6.035	74.50	-8.47	-0.63	-0.43
5.084	75.95	-1.68	-0.57	-0.40
5.639	77.97	4.75	-0.46	-0.33
5.511	79.03	6.53	-0.43	-0.30
5.241	81.23	8.39	-0.19	-0.09
5.018	83.51	8.43	-0.24	-0.14
4.904	84.76	8.25	-0.18	-0.08
4.713	87.29	7.49	-0.14	-0.03
4.544	89.98	6.46	-0.06	.06
4.314	94.34	4.58	.12	.25
4.168	97.48	3.12	.18	.33
4.021	100.84	1.56	.20	.34
3.865	104.44	-0.00	.12	.26
3.732	107.33	-1.27	.04	.16
3.574	110.37	-2.27	-0.02	.10
3.451	112.50	-2.80	-0.11	-0.01
3.301	114.70	-3.08	-0.22	-0.12
3.112	117.00	-2.93	-0.34	-0.25

SATS 19. B=0.080 C=0.080

-log h	H	Δ₀	Δ₁	Δ₂
8.987	0	-0.01	.32	.33
8.632	1.16	-1.16	.46	.48
8.500	2.29	-2.29	.57	.61
8.359	4.49	-4.49	.58	.65
8.229	7.64	-7.63	.65	.75
8.115	11.57	-11.56	.63	.76
8.013	16.10	-16.10	.48	.64
7.886	22.61	-22.60	.37	.55
7.791	28.31	-28.30	-0.11	.08
7.706	33.38	-33.37	-0.32	-0.13
7.635	37.88	-37.87	-0.79	-0.60
7.494	45.59	-45.57	-0.78	-0.60
7.250	57.23	-57.20	-0.95	-0.81
7.071	63.74	-63.69	-0.86	-0.76
6.884	68.97	-68.81	-0.85	-0.77

SATS 20. B=0.080 C=0.080

-log h	H	Δ₀	Δ₁	Δ₂
6.548	75.07	-61.96	-0.88	-0.67
6.413	76.54	-46.79	-0.79	-0.64
6.295	77.55	-33.90	-0.74	-0.62
6.139	78.59	-20.08	-0.68	-0.59
6.041	79.12	-13.45	-0.65	-0.57
5.655	80.75	1.54	-0.57	-0.53
5.510	81.31	4.27	-0.51	-0.49
5.265	82.46	6.87	-0.42	-0.40
5.078	83.63	7.73	-0.32	-0.29
4.869	85.46	7.87	-0.17	-0.14
4.661	88.03	7.25	-0.02	.01
4.448	91.46	5.97	.19	.24
4.263	95.17	4.32	.32	.37
4.083	99.19	2.44	.40	.45
3.936	102.66	.80	.33	.39
3.769	106.39	-0.80	.30	.35
3.623	109.36	-1.40	.20	.25
3.450	112.51	-2.81	-0.00	.04
3.306	114.71	-3.15	-0.17	-0.13
3.120	117.00	-3.04	-0.34	-0.29

SATS 21. B=0.080 C=0.160

-log h	H	Δ₀	Δ₁	Δ₂
9.081	0	-0.01	.42	.40
8.771	1.17	-1.17	.54	.46
8.646	2.29	-2.29	.64	.52
8.508	4.47	-4.47	.71	.59
8.332	9.64	-9.64	.41	.06
8.173	16.10	-16.10	.58	.09
8.052	22.60	-22.59	.50	-0.07
7.916	30.91	-30.90	.18	-0.43

SATS 22. B=0.080 C=0.160

-log h	H	Δ₀	Δ₁	Δ₂
7.652	47.92	-47.91	-1.42	.33
7.406	59.66	-59.64	-1.40	-0.13
7.302	63.56	-63.53	-1.36	-0.26
7.153	67.99	-67.95	-1.20	-0.34
7.010	71.31	-71.25	-1.08	-0.42
6.884	73.56	-73.40	-1.01	-0.49
6.746	75.46	-74.42	-0.93	-0.54
6.604	76.95	-69.35	-0.89	-0.60
6.286	79.03	-34.37	-0.78	-0.62
6.003	80.11	-12.06	-0.70	-0.61
5.637	81.23	1.55	-0.64	-0.56
5.214	82.96	6.96	-0.49	-0.37
4.963	84.76	7.70	-0.38	-0.20
4.726	87.30	7.35	-0.20	.06
4.541	89.96	6.48	-0.01	.31
4.164	47.48	3.18	.26	.69
3.983	101.73	1.15	.21	.64
3.633	109.34	-1.99	.06	.41
3.459	112.50	-2.91	-0.13	.16
3.314	114.70	-3.25	-0.27	-0.02
3.136	117.00	-3.25	-0.50	-0.29

SATS 23. B=0.160 C=0.080

-log h	H	Δ₀	Δ₁	Δ₂
9.026	.34	-0.35	.74	.77
8.560	6.60	-6.60	1.51	1.71
8.166	29.37	-29.37	1.34	1.84
7.951	44.06	-44.05	1.29	1.88
7.743	70.22	-70.20	.54	1.12
7.529	91.63	-91.59	-1.25	-0.73
7.253	112.39	-112.31	-1.22	-0.83
7.040	125.05	-124.39	-1.48	-1.17
6.787	136.26	-113.03	-1.60	-1.38
6.531	144.34	-59..7	-1.60	-1.45
6.173	151.74	-9.61	-1.40	-1.32
5.934	155.22	5.95	-1.27	-1.73
5.679	158.55	13.94	-1.22	-1.21
5.439	161.75	16.91	-1.14	-1.17
5.138	166.32	17.44	-1.12	-1.20
4.847	172.02	16.07	-0.92	-1.09
4.607	178.57	13.56	-0.70	-0.94
4.381	186.84	9.76	-0.66	-0.96
4.158	196.14	5.42	-0.32	-0.67
3.999	203.39	1.97	-0.33	-0.68

SATS 24. B=0.160 C=0.160

-log h	H	Δ₀	Δ₁	Δ₂
9.298	0	-0.01	.62	.55
8.783	4.68	-4.68	1.48	.91
8.633	9.17	-9.17	2.10	1.13
8.441	19.69	-19.69	2.84	1.19
8.292	32.90	-32.90	2.35	.17
8.167	46.18	-46.17	1.97	-0.52
8.020	63.16	-63.15	1.50	-1.12

SATS 25. B=0.160 C=0.160

-log h	H	Δ₀	Δ₁	Δ₂
2.755	239.00	-3.09	-0.99	-0.93
3.177	232.05	-6.31	-0.59	-0.56
3.426	225.50	-5.84	-0.11	-0.00
3.658	217.32	-3.48	.30	.33
3.877	207.89	.47	.66	.70
4.067	199.24	4.46	.62	.66
4.277	189.77	9.08	.59	.62
4.500	181.16	13.01	.23	.26
4.669	175.84	15.19	-0.02	.00
4.877	170.82	16.81	-0.30	-0.28
5.173	160.08	17.15	-0.58	-0.56
5.729	161.60	9.17	-0.88	-0.84
6.362	157.36	-40.07	-1.02	-0.89
6.670	153.33	-101.80	-1.18	-0.92
6.975	145.86	-143.98	-1.27	-0.79
7.153	139.08	-138.92	-1.40	-0.74
7.327	130.02	-129.96	-1.50	-0.61
7.445	122.07	-122.03	-1.30	-0.25
7.611	108.77	-108.74	-1.27	.03
7.719	98.08	-98.05	-0.72	.74

Table 1. Continued.

DATA II:

SATS 1. B=0.020 C=0.020

-log h	H	Δ_0	Δ_1	Δ_2
4.555	22.37	1.42	.08	.03
4.276	23.74	.99	.14	.09
4.054	25.05	.44	.14	.08
3.776	26.71	-0.24	.11	.05
3.401	28.66	-0.78	-0.01	-0.05
3.052	30.13	-0.73	-0.11	-0.13
2.736	31.53	-0.32	-0.12	-0.14
2.523	32.86	.04	-0.12	-0.13
2.320	34.73	.41	-0.10	-0.11
2.116	37.57	.87	-0.00	-0.02
1.917	41.95	1.58	.11	.09

SATS 2. B=0.020 C=0.080

-log h	H	Δ_0	Δ_1	Δ_2
1.332	75.37	6.21	1.14	.16
1.430	66.18	5.63	1.00	.12
1.544	58.09	4.48	.50	-0.10
1.669	51.08	3.43	.32	-0.12
1.833	44.53	2.05	.11	-0.19
2.005	39.88	1.08	-0.08	-0.29
2.219	36.13	.47	-0.22	-0.35
2.480	33.31	.00	-0.24	-0.32
2.687	31.92	-0.37	-0.26	-0.31
2.868	31.02	-0.64	-0.25	-0.30

SATS 3. B=0.040 C=0.040

-log h	H	Δ_0	Δ_1	Δ_2
4.131	48.37	2.12	1.03	.74
3.932	50.73	1.05	1.00	.71
3.727	53.05	.09	.93	.67
3.383	56.33	-0.84	.70	.52
2.607	61.42	.38	.41	.28

(continued)

-log h	H	Δ_0	Δ_1	Δ_2
2.303	64.25	1.42	.41	.21
1.958	70.33	3.88	.55	.15
1.764	76.48	6.89	.68	.06
1.543	87.87	9.76	.78	-0.26
1.365	101.76	11.77	1.45	-0.13
1.265	112.48	12.69	1.86	-0.14
1.200	120.71	13.51	2.40	.07

SATS 4. B=0.040 C=0.160

-log h	H	Δ_0	Δ_1	Δ_2
1.279	110.37	13.08	2.26	.53
1.482	92.07	10.41	.86	-0.20
1.716	78.99	7.12	.18	-0.44
2.037	69.18	2.32	-0.17	-0.47
2.362	64.38	.41	-0.41	-0.57
2.616	62.23	-0.53	-0.48	-0.59
2.934	60.21	-1.41	-0.40	-0.50
3.147	58.94	-1.77	-0.34	-0.47
3.393	57.13	-1.70	-0.17	-0.34
3.682	54.35	-0.91	.09	-0.14
3.905	51.83	.12	.22	-0.05

SATS 5. B=0.080 C=0.040

-log h	H	Δ_0	Δ_1	Δ_2
4.406	92.36	5.53	.41	.17
4.283	94.86	4.40	.49	.23
4.171	97.27	3.30	.60	.32
4.072	99.59	2.18	.55	.27
3.878	103.97	.22	.55	.28
3.697	108.05	-1.53	.25	.01
3.494	111.85	-2.71	.03	-0.15
3.259	115.40	-3.23	-0.26	-0.40
2.957	118.73	-2.62	-0.51	-0.59
2.686	121.09	-1.22	-0.57	-0.63
2.449	123.34	.28	-0.60	-0.65

SATS 6. B=0.080 C=0.080

-log h	H	Δ_0	Δ_1	Δ_2
2.142	127.55	3.57	-0.59	-0.64
1.916	132.63	10.05	-0.47	-0.55
1.726	139.28	15.61	-0.28	-0.40
1.557	148.38	18.73	-0.16	-0.32
1.463	154.98	20.02	.13	-0.07
1.381	162.11	20.78	.31	.08
1.322	167.85	21.56	.81	.53

SATS 6. B=0.080 C=0.080

-log h	H	Δ_0	Δ_1	Δ_2
4.046	100.00	2.09	.73	.03
3.940	102.74	.67	.43	-0.26
3.816	105.37	-0.39	.56	-0.09
3.499	111.54	-2.47	.38	-0.10
2.861	119.27	-1.87	-0.19	-0.41
2.137	127.05	4.25	-0.19	-0.56
1.760	137.00	15.65	.22	-0.59
1.586	145.34	19.49	.51	-0.70
1.446	154.56	21.99	1.24	-0.43
1.357	162.15	23.29	1.78	-0.28
1.287	168.49	25.09	3.10	.67
1.228	176.29	25.24	2.91	.11
1.180	182.55	26.07	3.50	.37

SATS 7. B=0.160 C=0.080

-log h	H	Δ_0	Δ_1	Δ_2
1.491	276.29	38.39	-2.92	1.52
1.709	262.74	33.98	-2.87	-0.21
1.898	255.43	25.71	-2.88	-1.17
2.130	249.49	10.75	-2.66	-1.61
2.354	245.68	1.29	-2.55	-1.83
2.635	241.98	-3.10	-2.43	-1.86
2.953	237.51	-6.37	-2.13	-1.48
3.213	232.36	-7.50	-1.62	-0.74
3.454	225.84	-6.88	-1.14	.07
3.707	216.71	-4.10	-0.68	.92

Data I. The main part of the data consisting of experimental points in the pH-range $3 < \mathrm{pH} < 9$ and with no restrictions in the B/C ratios.

Data II. Points in the pH-range $1 < \mathrm{pH} < 4$ and with $B/C \leq 2$.

The Letagrop calculation was started in the data I region. The following "best" log $(\beta_{p,q,r} \pm 3\sigma)$ values were obtained:

$$\log \beta_{2,2,1} = 17.484 \pm 0.007, \quad \log \beta_{3,2,1} = 21.547 \pm 0.012.$$

The data used in the refinement and the residuals $\Delta_1(=H_{\mathrm{calc}}-H)$ obtained are given in Table 1. The residuals show that the data within the experimental errors (in emf, in analyses and in the effects due to the impurity level) are satisfactorily explained.

In order to test the influence of an error in E_0 a covariation of the setwise E_0-values and the ternary constant values was made. This calculation lowered the error squares sum and the standard deviations but did not change the picture. The results are given in Tables 1 and 2.

In the calculations of the Data II region, the $\beta_{2,2,1}$ value determined in Data I calculation was kept constant and $\beta_{3,2,1}$ was varied. A "best" value of log $(\beta_{3,2,1} \pm 3\sigma) = 21.56 \pm 0.04$ was obtained. The data used and the residuals obtained are given in Table 1. In this acid region a small error in the E_0-determination causes large changes in H_{calc} and consequently gives large residuals. A covariation of E_0 and $\beta_{3,2,1}$ lowered the error squares sum considerably. The results of this calculation are given in Tables 1 and 2.

Table 2. Results from LETAGROP calculations on potentiometric and polarimetric data.

Emf data	U	$\sigma(H)$ mM	log $(\beta_{2,2,1} \pm 3\sigma)$	log $(\beta_{3,2,1} \pm 3\sigma)$
Data I (390 points):				
Δ_1-calculation	117.2	0.55	17.484 ± 0.0074	21.547 ± 0.0120
Δ_2-calculation	71.2	0.43	17.489 ± 0.0059	21.539 ± 0.0094
Data II (85 points):				
Δ_1-calculation	120.1	1.20	17.484	21.559 ± 0.037
Δ_2-calculation	26.7	0.59	17.484	21.549 ± 0.021
Polarimetric data		$\sigma(\alpha)°$	$\log(\beta_{2,2,1} \pm 3\sigma)$	$\log(\beta_{3,2,1} \pm 3\sigma)$
119 solutions		0.006	17.506 ± 0.0057	21.546 ± 0.0014

Conclusively it can be said that the emf data within the whole range studied are well explained with the two ternary complexes (2,2,1) and (3,2,1).

Polarimetric data. Our optical data collecting was started with a series of measurements on pure mannitol in the 3.0 M $Na(ClO_4)$ medium. We found that at pH-values between 1 and 10 the optical activity was linearly dependent on the mannitol concentration but independent of the pH-values. For pH > 10, however, the optical activity was dependent also on pH and was found to increase with [OH^-]. The "best" values of the molar rotation of mannitol, obtained in a Letagrop calculation, are given in Table 3.

Table 3. The molar rotations $\phi(\lambda) \pm \sigma(\phi_\lambda)$ of mannitol, the (2,2,1) and the (3,2,1) complexes, results from LETAGROP calculations. ϕ is given as degrees dm^{-1} M^{-1}.

λ (nm)	$\phi_{Mannitol} \pm \sigma(\phi)$ (deg dm^{-1} M^{-1})	$\phi_{2,2,1} \pm \sigma(\phi)$ (deg dm^{-1} M^{-1})	$\phi_{3,2,1} \pm \sigma(\phi)$ (deg dm^{-1} M^{-1})
589	-0.109 ± 0.003	1.358 ± 0.022	26.887 ± 0.026
578	-0.119 ± 0.003	1.351 ± 0.023	28.082 ± 0.027
546	-0.142 ± 0.003	1.207 ± 0.025	32.170 ± 0.030
436	-0.329 ± 0.004	-1.541 ± 0.044	57.583 ± 0.053
365	-0.750 ± 0.007	—	—

Measurements on molybdate-mannitol solutions were performed at the following concentrations $B(C)$ in mM: 160 (160,80); 80 (160,80,40,20); 40 (160,40,10); 20 (80,20) and in the pH-range 9 − 3.

For most of the B,C-concentrations with $B/C \le 2$ (mannitol excess) the pH-range was extended to pH ≈ 1 and a few of them were measured at still lower pH. However, for pH < 1 the pH-values are approximate.

In Fig. 3 we have plotted the angle of optical rotation α as a function of log h for $B = 20$, $C = 20$ mM at five different wavelengths. Plots for the other B,C combinations studied are very similar. As can be seen in the figure the
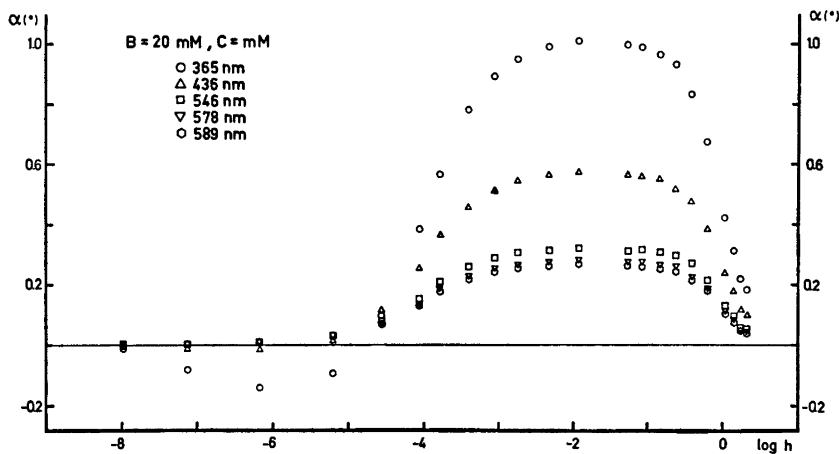
Fig. 3. The angle of optical rotation α is plotted as a function of log h for $B = 20$ mM, $C = 20$ mM at five wavelengths.

optical rotation is strongly dependent both on wavelength and pH. The following ranges can be distinguished:

(i) $5 \lesssim pH \lesssim 8$, the optical activity is low except for $\lambda = 365$ nm.
(ii) $3 \lesssim pH \lesssim 5$, the optical activity is strongly increasing.
(iii) $1 \lesssim pH \lesssim 3$, the optical activity is high and constant.
(iv) $pH \lesssim 1$, the optical activity is strongly decreasing.
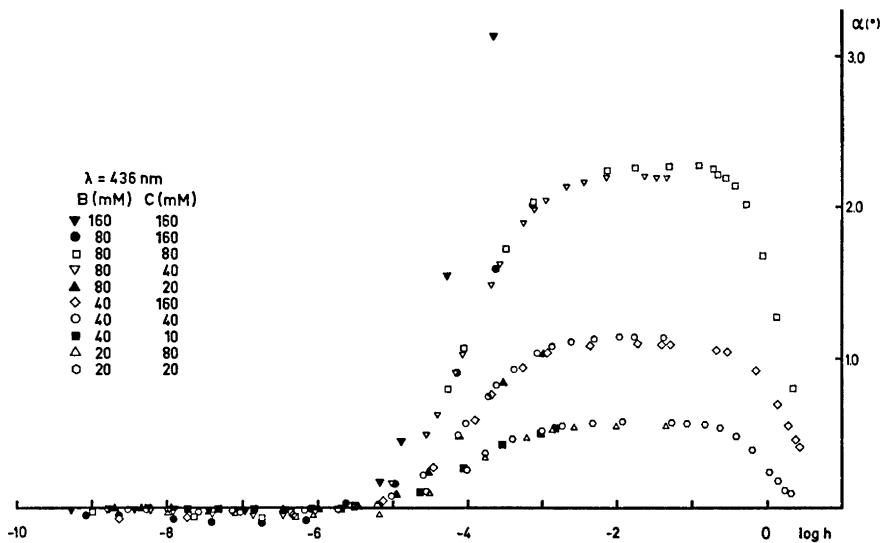
Fig. 4. Polarimetric data $\alpha(\log h)_{BC}$ at the wavelength 436 nm are given for all the B,C-combinations studied.

In Fig. 4 all experimental data, $\alpha(\log h)_{BC}$, are plotted for the wavelength 436 nm. It was found that in all solutions with $Z = 0$, the optical activity was the same as for pure mannitol of the corresponding concentration, thus indicating that no molybdate-mannitol complexes were present in these solutions.

When comparing the polarimetric data $\alpha(\log h)_{BC}$ with the emf data Z $(\log h)_{BC}$ (Figs. 1 and 4) one may note that large emf effects are found in the range $5.5 < \mathrm{pH} < 9$ ($0 < Z < 1$) when the first three-component complex is built up, while on the other hand the rotation effects are small, indicating that the molar rotation of the complex is rather low. It is quite the contrary in the range $1 < \mathrm{pH} < 3$ ($Z \approx 1.5$) where the emf effects are small whereas the rotation effects are large and constant. Here there must exist a second three-component complex with a high molar rotation, and from considerations of the α-level of the plateau for different B,C-concentrations one can conclude that the ratio of molybdenum to mannitol in the complex is about two.

In an accurate treatment of the polarimetric data with the least squares program LETAGROPVRID[23] version SPEFO[25] we found that all data in the pH-range $1 < \mathrm{pH} < 9$ could be well explained with the same complexes as found from emf data.

In the calculations the formation constants of the ternary complexes were allowed to vary together with the molar rotations of the optical active species. The error was put on the angle of optical rotation and the error squares sum $U = \sum(\alpha_{\mathrm{calc}} - \alpha)^2$ was minimized. The results giving "best" values of equilibrium constants and molar rotations are collected in Tables 2 and 3. The standard deviation in α was $\sigma(\alpha) = \pm 0.006$, as expected from the experimental accuracy.

Concerning the pH-range less than 1, we have not yet gathered enough data to be able to make a detailed analysis. The strong decrease in the optical activity may be due either to formation of a new three-component complex, for instance (4,2,1) or to decomposing of (3,2,1) into $H^+ - MoO_4^{2-}$ species and mannitol.
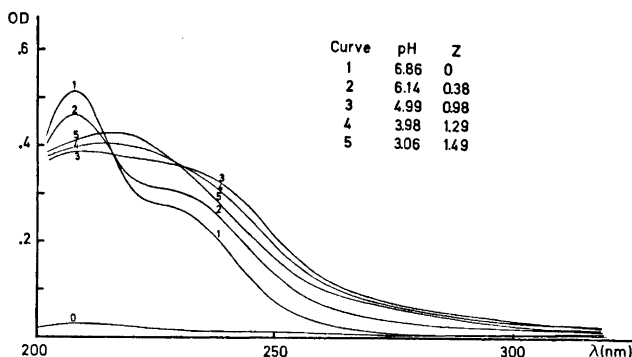
Fig. 5. Absorbance curves $\mathrm{OD}(\lambda)_Z$ for solutions with $B = 0.5$ mM, $C = 5.0$ mM at some chosen Z-values. (Ionic medium as reference solution.) Curve 0 is the difference between the sample and the reference cells when both are filled with ionic medium.

Spectrophotometric data. Since the spectrophotometric measurements are still in progress, the data that will be discussed are only preliminary. We have found that in the $H^+ - MoO_4{}^{2-}$ system the heptamolybdate complexes absorb in the whole wavelength region (205 – 320 nm), whereas the $MoO_4{}^{2-}$-ion absorbs only for λ less than 280 nm.[28] Mannitol has no absorbance in the wavelength region studied. In the titrations we have used an excess of mannitol in order to make the contributions from the $H^+ - MoO_4{}^{2-}$ species negligible.

In Fig. 5, a set of curves, $OD(\lambda)$, is given for a titration with $B = 0.5$, $C = 5.0$ mM. As reference solution pure ionic medium was used. For the sake of clarity only curves at some chosen Z-values are plotted. Concerning curve 1 no ternary complexes have yet been formed ($Z = 0$) and as mannitol does not absorb, the curve is identical to that of a pure $MoO_4{}^{2-}$-solution. On acidification the typical molybdate ion peak diminishes and for curve 3 ($Z = 0.98$) it has totally disappeared, which means that practically all molybdenum must be bound in a ternary complex which obviously has a broad absorbance peak. On further acidification there is no marked displacement of the peak, it just narrows somewhat and becomes more distinct as can be seen in curve 5 ($Z = 1.49$, pH = 3.06). When lowering the pH to 2.49 (the most acid solution measured in this titration) the curves obtained are identical to curve 5.

Table 4. The molar absorption coefficients $\varepsilon(\lambda)$ of the molybdate ion (determined by L. Lyhamn) are tabulated together with $\varepsilon \pm \sigma(\varepsilon)$ of the ternary complexes. ε is given for 25 different wavelengths and the result has been obtained in a LETAGROP computation.

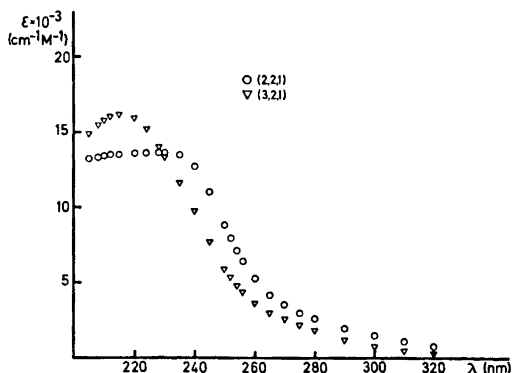| λ (nm)	$\varepsilon_{MoO_4{}^{2-}} \times 10^{-3}$ (cm^{-1} M^{-1})	$(\varepsilon_{2,2,1} \pm \sigma(\varepsilon)) \times 10^{-3}$ (cm^{-1} M^{-1})	$(\varepsilon_{3,2,1} \pm \sigma(\varepsilon)) \times 10^{-3}$ (cm^{-1} M^{-1})
205	9.30	13.18 ± 0.04	14.81 ± 0.03
208	9.91	13.32 ± 0.07	15.40 ± 0.06
210	9.71	13.39 ± 0.08	15.71 ± 0.07
212	9.07	13.53 ± 0.08	15.99 ± 0.07
215	7.76	13.50 ± 0.08	16.14 ± 0.06
220	5.77	13.57 ± 0.04	15.90 ± 0.04
224	5.17	13.61 ± 0.05	15.16 ± 0.05
228	5.04	13.63 ± 0.04	14.00 ± 0.04
230	4.95	13.63 ± 0.05	13.32 ± 0.04
235	4.34	13.46 ± 0.05	11.61 ± 0.04
240	3.25	12.71 ± 0.04	9.72 ± 0.03
245	2.01	11.04 ± 0.04	7.68 ± 0.04
250	1.15	8.86 ± 0.04	5.88 ± 0.03
252	0.90	7.96 ± 0.05	5.34 ± 0.04
254	0.72	7.11 ± 0.04	4.73 ± 0.03
256	0.57	6.43 ± 0.04	4.31 ± 0.03
260	0.35	5.26 ± 0.04	3.62 ± 0.03
265	0.18	4.16 ± 0.04	3.00 ± 0.03
270	0.08	3.51 ± 0.04	2.58 ± 0.03
275	0.03	2.95 ± 0.04	2.17 ± 0.03
280	0.01	2.56 ± 0.03	1.84 ± 0.03
290	0.00	1.91 ± 0.03	1.20 ± 0.02
300	0.00	1.45 ± 0.03	0.72 ± 0.02
310	0.00	1.07 ± 0.03	0.42 ± 0.02
320	0.00	0.77 ± 0.03	0.25 ± 0.02

Fig. 6. Molar absorption coefficients, $\varepsilon(\lambda)$, plotted for the ternary complexes (2,2,1) and (3,2,1). ε is given as 10^{-3} cm^{-1} M^{-1}.

Using the LETAGROPVRID [23] version SPEFO [25] and assuming the same complexes and constants as found from emf and polarimetric data, the spectrophotometric data could be completely explained. The molar absorption coefficients of the ternary complexes obtained in the calculation are given in Table 4 and visualized in Fig. 6. The error was put on the measured absorbance and the error squares sum $U = \sum(OD_{calc} - OD)^2$ was minimized. The standard deviation in the measured absorbance values $\sigma(OD)$ obtained was ± 0.004.

The molar absorption coefficients of the molybdate ion used in the calculations are those given in Table 4. The values have been determined in a spectrophotometric examination of the $H^+ - MoO_4^{2-}$ system by L. Lyhamn (not yet published).

CONCLUSION

The present investigation has clearly shown that in the system $H^+ - MoO_4^{2-}$-mannitol the ternary complexes (2,2,1) and (3,2,1) are formed in addition to the binary $H^+ - MoO_4^{2-}$ species. This has been demonstrated by using emf, polarimetric, and spectrophotometric methods. Of these the emf result may be considered to be the most accurate one, but is strongly supported by the polarimetric measurements. Composition and equilibrium constants of the ternary complexes are well established. A good criterion for this is the low standard deviations of the calculated equilibrium constants (Table 2). The values of the equilibrium constants obtained from emf and polarimetric data agree very well (within 0.02 log units) and there is approximate overlap within their three sigmas. The residuals obtained both for emf and polarimetric data can be considered as being within the experimental accuracy. Concerning emf data, see Table 1.

The preliminary spectrophotometric data are too meagre to make a detailed data analysis but could be completely explained with our "emf model". The magnitude of and the wavelength dependence on the molar absorption coefficients for the two ternary complexes are very much alike (Fig. 6) and there

is no reason to suspect a big change of condensation of the molybdate in the two complexes as proposed by Chalmers and Sinclair.[13] One may notice that they made their measurements at 370 nm, which is far away from the absorbance peaks.
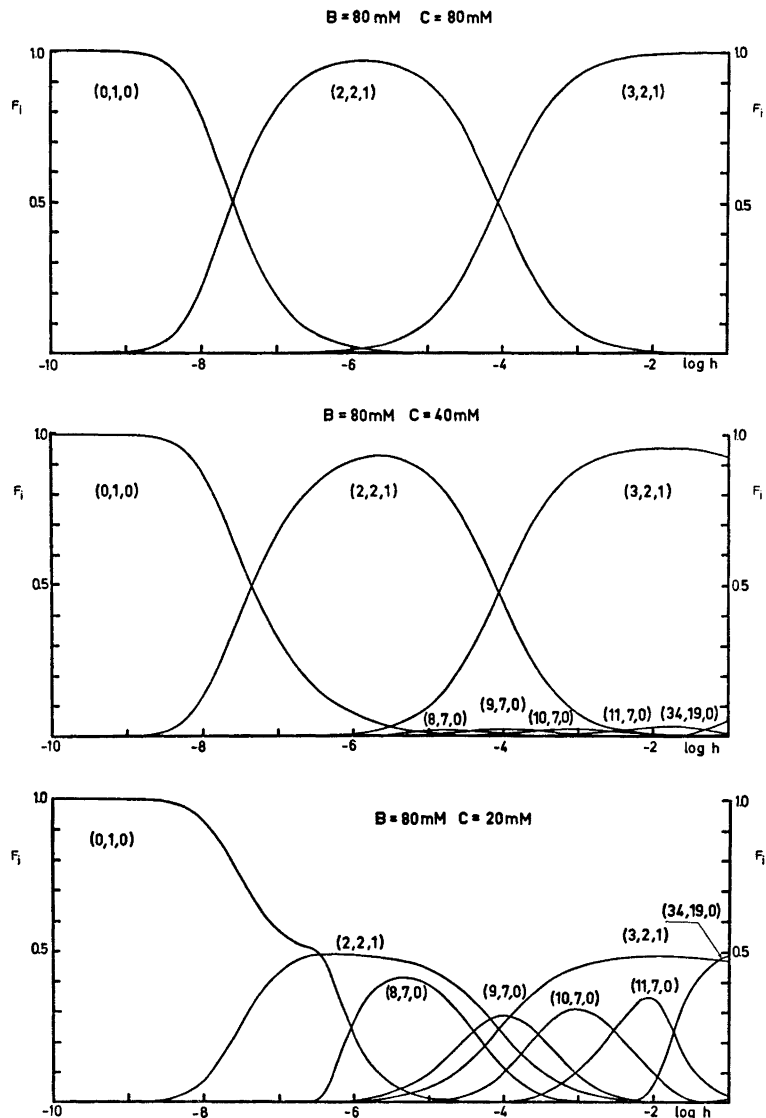

Fig. 7. Distribution diagrams $F_i(\log h)_{BC}$. For a, $B = 80$ mM, $C = 80$ mM; b, $B = 80$ mM, $C = 40$ mM; c, $B = 80$ mM, $C = 20$ mM. F_i is defined as the ratio between molybdenum in a species and total molybdenum. HALTAFALL [29] was used for the calculation using the constants in Table 2 and Ref. 22.

Strengths and concentrations of the ternary complexes in the pH-range 1 – 10 are well illustrated by the distribution diagrams given in Fig. 7, a – c. In 7a, where $B/C = 1$ (mannitol excess), all molybdenum bound appears in the ternary complexes. In 7b, where $B/C = 2$ (the same ratio as in the ternary complexes), at most 5 % of the molybdenum is present as binary $H^+ - MoO_4^{2-}$ complexes (clearly demonstrating the large strengths of the ternary complexes). In 7c, where $B/C = 4$ (molybdenum excess), one may note that the first ternary complex (2,2,1) appears about two log h units before the first binary complex (8,7,0). This explains the large emf effects in the pH-region where the first three-component complex is formed.

Work in progress. In order to attain confirmatory information and a possible structure for the proposed molybdate-mannitol complexes an X-ray scattering study of solutions is going on, together with Georg Johansson, KTH, Stockholm.

Furthermore through slow self-evaporation of different equilibrium solutions we have tried to obtain well-defined crystalline phases of the complexes (2,2,1) and (3,2,1). For solutions with $Z \lesssim 1.2$ we were not successful but for $Z > 1.2$ crystals were obtained. In a powder X-ray analysis they were all found to be identical, and a single crystal X-ray study is in progress (Britt Hedman). The unit cell is monoclinic, space group $P2_1$, $a = 12.234$, $b = 6.899$, $c = 8.388$ Å, $\beta = 99.77°$, two formula units, density $= 2.40$ g cm^{-3}. Chemical analysis has given the composition $(MoO_3)_2(C_6H_{14}O_6)(H_2O)_2$ which corresponds to (4,2,1), a complex not found from equilibrium data in the pH-region studied.

Additional potentiometric, polarimetric, and spectrophotometric titrations are in progress in order to extend the data range to B/C ratios greater than two (molybdenum excess) for pH less than 3. From these titrations we hope to be able to determine the complicated $H^+ - MoO_4^{2-}$ equilibria in this region.

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