Multicomponent Polyanions

I. On Yellow and Colourless Molybdophosphates in 3 M Na(ClO₄).
 A Determination of Formation Constants for Three Colourless
 Pentamolybdodiphosphates in the pH-range 3—9

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Emf data (glass electrode, 25°C, 3 M Na(ClO₄)) for the reaction between H⁺, MoO₄²⁻ and HPO₄²⁻ in the pH-range 3–9 indicated formation of two types of species, yellow and colourless. The colourless products found are (H)₈(MoO₄)₅(HPO₄)₂⁶⁻, (H)₉(MoO₄)₅(HPO₄)₂⁵⁻, and (H)₁₀(MoO₄)₅(HPO₄)₂⁴⁻ with log $\beta_{8,5,2}$ =61.97±0.02, log $\beta_{9,5,2}$ =67.07±0.08, and log $\beta_{10,5,2}$ =70.86±0.09. The errors given are 3σ . The complexes have been found using a Letagrop-search (see Table 2 and Fig. 4). For the yellow-coloured complexes, the data range available is too limited to allow a distinct answer. Efforts to extend the data range are in progress.

Assume the molybdophosphates was first given in 1826 by Berzelius. Assince then, the molybdophosphates have been the object of very extensive research activity. In spite of that, the results and conclusions found in the literature give a rather diffuse and incomplete picture of the behaviour and characteristics of these ions. This is especially so for aqueous solutions. In this case, exact knowledge (verified with enough data) about the number and composition of the various species formed seems to be lacking. Also the equilibrium conditions, under which the ions are formed, are poorly defined. The molybdophosphates belong to a group of inorganic compounds, often named heteropolyanions. These ions may be regarded as composed of three components: protons (A), and two anions (B and C). Their formulas may generally be written $A_p B_q C_r$, where p, q, and r may attain values greater than or equal to unity. The formation equilibria and stability constants may be written:

$$p\mathbf{A} + q\mathbf{B} + r\mathbf{C} \rightleftharpoons \mathbf{A}_{p}\mathbf{B}_{q}\mathbf{C}_{r} \tag{1}$$

$$\beta_{pqr} = [A_p B_q C_r] [A]^{-p} [B]^{-q} [C]^{-r}$$
 (1a)

The component with the lowest nuclearity is usually denoted as the heteroion, and is considered being the central group within the complex (C in the

present paper). The B-component is mostly an anion of elements in groups 5A and 6A. Examples most frequently encountered are molybdates, tungstates, vanadates, niobates, and tantalates. The ability to act as the central atom is widely spread, not only amongst the acid forming elements, but also among the metals of the transition series. Borates, silicates, germanates, phosphates, arsenates, tellurates, and periodates are common examples. Further details about the heteropolyanions may be found in reviews in Gmelin,² Mellor,³ and Emeleus-Anderson.⁴

We will now shortly consider some of the difficulties often encountered in studies of aqueous heteropolyanions. We may summarize these difficulties under the following three main points:

(i) Firstly, if one considers the complexity of the system, we may note that in most of the aqueous heteropolyanion systems, not only 3-component complexes $A_pB_qC_r$, but also a series of binary complexes, e.g. A_pB_q (isopolyanions) and A_nC (weak acids), are present. Thus it is necessary to consider binary equilibria (2), (3) in addition to equilibria (1).

$$p\mathbf{A} + q\mathbf{B} \rightleftharpoons \mathbf{A}_{b}\mathbf{B}_{a} \tag{2}$$

$$nA + C \rightleftharpoons A_nC$$
 (3)

Consequently, before a successful attack can be made upon a heteropolyanion system, the binary systems A-B and A-C must be studied separately, and accurate determinations of the species formed and their formation constants made. In some situations it may also be necessary to consider complex formation between formed complexes and medium ions.

(ii) Secondly, considering the experimental methods. Of suitable experimental methods, one may mention: emf, spectrophotometry, conductometry, X-ray diffraction, ultracentrifugation, NMR- and Raman-spectroscopy. Among these methods, emf is without doubt the only one of sufficient accuracy to be useful in studying complicated heteropolyanion systems. It is then necessary to be able to measure at least one equilibrium concentration with highest accuracy. The concentration most readily measurable is that of H^+ . Activity coefficient variations, impurity contents, slow equilibria and liquid junction potentials must be under exact control. The accuracy of the determination would be considerably increased if it were possible to measure also some additional species, e.g. some of the molybdate or phosphate ions. Suitable electrodes for such measurements are, however, at present not available. In order to partly compensate for this lack of measurable quantities it is therefore necessary to extend the measurements over as wide concentration ranges as possible (without causing activity coefficient variations). An emf method alone cannot provide a complete explanation of a complicated heteropolyanion system. Complementary types of measurements are mostly necessary.

(iii) Thirdly, considering the data treatment. The computational problem is to determine from a great amount of experimental data, the various pqr-triplets present, and the corresponding equilibrium constants β_{pqr} . This computation is usually difficult to carry out using hand calculational methods (see eqns. (7), (8), and (9) on p. 1965). For success it seems necessary to use

electronic computer methods.

Points (i), (ii), and (iii) clearly show that an equilibrium analysis of aqueous heteropolyanion systems is generally rather complicated. To obtain detailed information about such a system, very accurate and distinct experimental and calculational methods are necessary. It is no exaggeration to state that 10-15 years ago, such methods were not available or, if so, they were unsatisfactorily developed. That might be a possible reason why we know so little about the equilibria in aqueous heteropolyanion systems. However, during the last years, very accurate experimental and calculational methods have been developed. The emf and the computer methods, developed in Stockholm by Sillén and his group, seem to be especially useful.

The aim of the present study is to apply these methods to determine the composition and formation constants of the various polyanions formed in the system $H^+-MoO_4^{2-}-HPO_4^{2-}$. Thus the equilibria that will be studied are

$$pH^{+} + qMoO_{4}^{2-} + rHPO_{4}^{2-} \rightleftharpoons (H^{+})_{p}(MoO_{4}^{2-})_{q}(HPO_{4}^{2-}),$$
 (4)

EXPERIMENTAL

Chemicals and analysis. Stock solutions of sodium perchlorate have been prepared and analysed as described by Sjöberg.⁵ The dilute perchloric acids used were standardized against KHCO₃. All solutions were made using boiled distilled water.

For preparing molybdate stock solutions, crystalline sodium molybdate, Na₂MoO₄.2H₂O (Mallinckrodt p.a.) recrystallized once, was used. The molybdenum content of the stocks was determined gravimetrically as PbMoO₄ according to Vogel.⁶ This analysis agreed within 0.1 %. In order to check this method, some Mo-analyses were made by evaporating the water from a known amount of stock solution, drying the residue at 110°C and then weighing as anhydrous Na₂MoO₄. The results from these two Mo-determinations agreed within 0.2 %.

All solutions containing molybdate ions were carefully protected from contact with glass. This is necessary in order to prevent dissolution of silicate ions from the glass which contaminate the molybdate solution by forming, e.g., dodecamolybdosilicate ions. Therefore, the insides of the bottles and vessels used for storing molybdate solutions were always coated with a paraffin layer. Two different qualities of paraffin were used. One of them caused "errors" in our titrations, indicating some sort of complex formation between a compound in the paraffin and the molybdate ions. The effect of this complex formation on our results will be discussed later in this paper.

Phosphate stock solutions were prepared either by using recrystallized NaH₂PO₄.2H₂O (analytical reagents of BDH quality) or Na₂HPO₄.12H₂O (Merck p.a.). The stock solutions were analysed for phosphate and excess H⁺ (over the chosen zero level HPO₄²⁻), using electrometrical titration methods in combination with a graphical Gran extrapolation technique. The determinations of phosphorus were checked by gravimetric determinations as magnesium ammonium phosphate according to Vogel.⁷

Apparatus. The emf measurements were carried out, using the same electrometrical equipment and arrangement described by Sjöberg. The free H⁺-concentration has been measured with a glass electrode (Beckman, type 40498) and the cell used was

The thermostating and all additional equipment are as described in Ref. 5.

The free hydrogen ion concentration, h, was calculated from the measured emf, E, using the equation

$$E = E_0 + 59.157 \log h + E_i \tag{5}$$

where E_0 is a constant determined separately in a solution with known h. For the liquid junction potential, E_j , we have used $E_j = -16.3 \ h$ (expressed in mV M⁻¹).

METHOD

The emf measurements. The present determination has been carried out experimentally as a series of emf titrations. In each of these titrations, the total analytical molybdenum and phosphorus concentrations, B and C, have been kept constant, and the hydrogen ion concentration has been varied by addition of H^+ (or OH^-).

The free hydrogen ion concentration has been measured electrometrically with a glass electrode (with an accuracy of ± 0.2 mV) as described in Experimental. To keep the activity factors as constant as possible during the measurements, a "constant" salt medium background consisting of 3 M Na(ClO₄) has been used.

In order to check the reversibility of equilibria both backward (increasing pH) and forward (decreasing pH), titrations have been carried out, and this check has been made for each B,C-combination. From the free hydrogen ion concentration, h, calculated by using eqn. (5), and from H, the excess concentration of hydrogen ions over the zero level MoO_4^{2-} , HPO_4^{2-} and H_2O , one can calculate A, the total concentration of bound H^+ , by using the following relation:

$$A = H - h \tag{6}$$

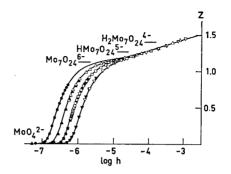
The titrations thus give a series of data sets $A(\log h)_{B,C}$ or $H(\log h)_{B,C}$. The total concentrations have been varied within the following limits: 5 mM < B < 160 mM, 5 mM < C < 80 mM, and 0 < H < (1.5B + 1.1C). This means that for the most extreme concentration cases, about 16 % of the perchlorate ions have been replaced by phosphate and molybdate ions. Biedermann and Sillén 8 have shown that up to around 16 % of Na⁺ or ClO₄⁻ in a 3 M NaClO₄-medium may be replaced with 1- or 2-charged ions without producing any detectible changes in activity coefficients. In the present case, most of the anions formed are highly charged, and it is probable that for the highest B and C concentrations one may obtain effects due to activity coefficient variations. However, in the first instance, we will assume that we have no activity coefficient variations, and all effects will be explained by using the law of mass action. The range of $pH = -\log h$ has been kept within the limits 3 < pH < 9. This range has a lower limit determined by experimental difficulties due to precipitation of acid polymolybdates and also partly by the lack of exact knowledge of the binary molybdate equilibria in more acid solutions. The upper limit is given by the fact that for pH > 8, no ternary complexes seem to be formed.

The binary equilibria — assumptions and comments. In order to obtain composition and concentration of the various ternary species as accurately as possible, the binary complexes must first be determined in separate experiments. However, in the present work, no separate study of the system $\mathrm{H^+-MoO_4^{2^-}}$ was made. Accurate data for this system has already been presented by Sasaki and Sillén 9 (25°C and 3 M Na(ClO₄)). They report the following species and formation constants:

HMoO₄⁻ (log β_{1,1}=3.89); H₂MoO₄(log β_{2,1}=7.50); Mo₇O₂₄⁶⁻ (log β_{8,7}=57.74); HMo₇O₂₄⁵⁻ (log β_{9,7}=62.14); H₂Mo₇O₂₄⁴⁻ (log β_{10,7}=65.68): H₃Mo₇O₂₄³⁻ (log β_{11,7}=68.21).

Curves $(Z(\log h)_B)$ calculated using their proposals are given in Fig. 1. The points given are those obtained in some control titrations, and we see that our experimental points fit the calculated curves satisfactorily. However,

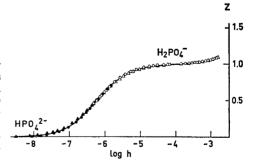
Fig. 1. Curves $Z(\log h)_B$ for the binary system $\mathrm{H^+-MoO_4^{2^-}}$. The full curves have been calculated using the complexes and formation constants proposed by Sasaki and Sillén. The points are experimentally obtained from some control titrations. The symbols stand for the following total molybdenum concentrations B (in mM): $\nabla 20$; $\Delta 80$; $\Delta 80$; O160. Filled symbols are obtained in forward titrations (decreasing pH), and unfilled in reverse titrations.



a more careful analysis shows small systematic deviations in H, which increase when the molybdenum concentration increases. Initially, it was difficult to decide whether this effect depended on the formation of additional polymolybdate complexes or on some impurity. As the investigation proceeded, we found that the deviations were probably caused by an impurity in the paraffin used. The effects can be found in most of our titrations and are more pronounced when a molybdate excess is used. However, to a good approximation the impurity effects can be neglected compared with the effects due to formation of the molybdophosphates.

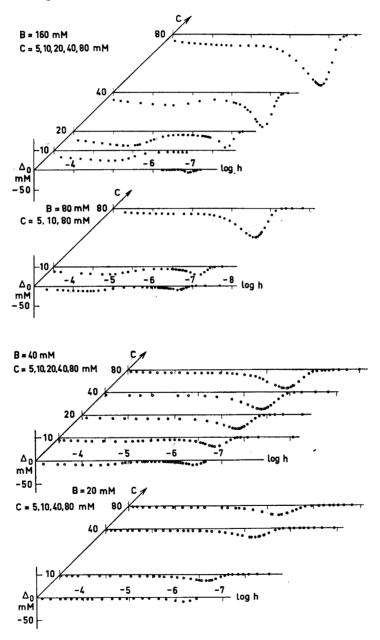
For the "mononuclear" phosphate equilibria we have made a separate determination. We found that different phosphate concentrations gave small systematic changes in the equilibrium constants. However, the difference could be neglected in the pH-range studied. In a Letagrop calculation, using

Fig. 2. Curves $Z(\log h)_C$ for the binary system $\mathrm{H^+-HPO_4^{2-}}$. The full curve has been calculated, using the complexes and formation constants given in the text. The symbols stand for the following total phosphorus concentrations C (in mM): O10; \triangle 80. Filled symbols are obtained in forward titrations (decreasing pH), and unfilled in reverse titrations.



data with $C \le 80$ mM, we obtained the following "best" $\log \beta_n \pm 3\sigma$: $\log \beta_2 = 8.067 \pm 0.019$; $\log \beta_1 = 6.240 \pm 0.008$; and $\log \beta_{-1} = -10.72 \pm 0.03$. Calculated curve and experimental points (C = 10 and 80 mM) are shown in Fig. 2.

Data treatment (pqr-analysis). The equilibria that must be taken into account have been discussed earlier in this paper and are defined by eqns. (1), (2), and (3). Applying the law of mass action to these equations, the conditions for the concentrations give:



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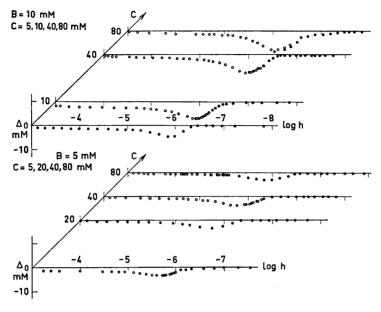


Fig. 3. Residual diagrams $\Delta_0(\log h)_{B,C}$. The residuals $\Delta_0 = 1000(H_{\rm calc} - H)$ have been calculated assuming that only binary phosphates and molybdates are formed. The constants used are those given in Table 1. Filled symbols are obtained in forward titrations (decreasing pH), and unfilled in reverse titrations.

$$B = b + B_1 + \sum_{1}^{p} \sum_{1}^{q} q \beta_{pq} h^p b^q c^r$$
 (7)

$$C = c + C_1 + \sum_{1}^{p} \sum_{1}^{q} r \beta_{pqr} h^p b^q c^r$$
 (8)

$$H = h + B_1 Z_1 + C_1 Z_2 + \sum_{1}^{p} \sum_{1}^{q} \sum_{1}^{r} p \beta_{pqr} h^p b^q c^r$$
(9)

where $b = [\text{MoO}_4^{2^-}]$, $c = [\text{HPO}_4^{2^-}]$, $h = [\text{H}^+]$, $\beta_{pqr} = [\text{A}_p \text{B}_q \text{C}_r] h^{-p} b^{-q} c^{-r}$, and B_1 , C_1 , $B_1 Z_1$ and $C_1 Z_2$ are the "known" quantities for the binary equilibria:

$$\begin{split} B_1 &= [\mathbf{A}\mathbf{B}] + [\mathbf{A}_2\mathbf{B}] + 7[\mathbf{A}_8\mathbf{B}_7] + 7[\mathbf{A}_9\mathbf{B}_7] + 7[\mathbf{A}_{10}\mathbf{B}_7] + \\ 7[\mathbf{A}_{11}\mathbf{B}_7] &= \beta_{1,1}hb + \beta_{2,1}h^2b + 7\beta_{8,7}h^8b^7 + 7\beta_{9,7}h^9b^7 + \\ 7\beta_{10,7}h^{10}b^7 + 7\beta_{11,7}h^{11}b^7 \end{split} \tag{10}$$

$$B_{1}Z_{1} = [AB] + 2[A_{2}B] + 8[A_{8}B_{7}] + 9[A_{9}B_{7}] + 10[A_{10}B_{7}] + 11[A_{11}B_{7}] = \beta_{1,1}hb + 2\beta_{2,1}h^{2}b + 8\beta_{8,7}h^{8}b^{7} + 9\beta_{9,7}h^{9}b^{7} + 10\beta_{10,7}h^{10}b^{7} + 11\beta_{11,7}h^{11}b^{7}$$
(11)

$$C_1 = [A^{-1}C] + [AC] + [A_2C] = \beta_{-1}h^{-1}c + \beta_1hc + \beta_2h^2c$$
 (12)

$$C_1 Z_2 = -[A^{-1}C] + [AC] + 2[A_2C] = -\beta_{-1}h^{-1}c + \beta_1 hc + 2\beta_2 h^2c$$
 (13)

The main problem of the present data treatment is to try to find out which equilibrium model (set of pqr-triplets) and corresponding equilibrium constants (β_{pqr}) can "best" explain the experimental data, $H(\log h)_{B,C}$. For this search a trial and error method was used based on the least squares program LETA-GROPVRID ¹⁰ (mainly using version ETITR ¹¹). Assuming that only one pqr-complex is present, different values of p, q, and r were tested. That pqr-set giving the lowest error squares sum was considered being the "best" one. When proved necessary, additional pqr-complexes will be added and tested. However, the main aims of the search will be to explain the data with as few complexes as possible.

In the Letagrop calculations we have assumed that the emf E is without error and that all errors are in H. The quantity $(H_{\rm calc}-H)^2$ is calculated on all experimental points giving the error squares sum:

$$U = \sum (H_{\text{calc}} - H)^2 \tag{14}$$

As "best" β_{pqr} -values we consider those giving the lowest error squares sum. U_{\min} . The standard deviations $\sigma(H)$ and $\sigma(\beta_{pqr})$ given are defined and calculated according to Sillén.^{12,13} The computer calculations have been carried out by using both the CD 3600 (Uppsala) and the CD 3200 (Umeå).

DESCRIPTION OF DATA

It is difficult from the data, $H(\log h)_{B,C}$ or $A(\log h)_{B,C}$, to decide directly whether ternary complexes are formed or not. In order to make this decision easier, we have made use of plots $\Delta_0(\log h)_{B,C}$, where $\Delta_0 = H_{\text{calc}} - H$. H_{calc} have been calculated assuming that only binary phosphates and molybdates are formed (species and constants given above). These plots, including all our experimental points, are given in Fig. 3. By inspecting the plots we see that over the pH-range studied there are marked "effects", which in some cases rise up to over 100 mM. We will consider that these effects are caused by formation of ternary complexes. One may note particularly that for most sets of BC there are two characteristic pits, a sharp one at around pH 6 and a broader one between pH 3 and 5. The two pits are changed systematically through all the B and C concentrations studied. They will, in the following, be denoted as the alkaline and the acid pit respectively. The plots $\Delta_0(\log h)_{B,C}$ in Fig. 3 seem to indicate formation of at least two types of complexes. Both are strongly dependent on the total molybdenum concentration. The type that corresponds to the alkaline pit seems, however, to be more dependent on the total phosphorus concentration than the type corresponding to the acid pit. Furthermore, the residual plots show that there is good reversibility between forward and backward titrations (filled and unfilled symbols in Fig. 3).

In order to simplify the data treatment and also to obtain a more detailed data description, it was found convenient to devide data into five different groups:

Data I. Experimental points from pH \approx 7.5 to the bottom of the alkaline pit. Uncoloured solutions.

Data II. The remaining part of the alkaline pit (from the bottom to $pH \approx 6-5$). Uncoloured solutions.

Data III. Data between the two pits. Uncoloured solutions.

Data IV. Points in the acid pit region and with $B/C \ge 4$. Yellow coloured solutions. The Δ_0 -changes indicate the existence of complexes with B/C ratio between 8 and 12.

Data V. Data from the same pH-range as data IV but with $B/C \le 2$. Uncoloured solutions. For this case, one can find no typical pit, but there are still Δ_0 residuals. In this region, the existence of uncoloured complexes with B/C < 4 seems probable.

The data of the present work consist of over 1200 experimental points, and in order to simplify the data treatment (and save computer time) only a restricted number of the total number of points in each of the groups will be used in the calculations. These points have been arbitrarily chosen so that they are evenly distributed over the B and C concentrations. However, in the final calculations, most of the data have been used.

LETAGROP SEARCH FOR COMPLEXES

The Letagrop-search was started in the data I region. The results of the calculations of main interest are given in Table 2 and Fig. 4. The lowest error squares sum was obtained for the complex $A_8B_5C_2$. By extending the calculations to include data II and then testing successively additional complexes we found that a model with $A_8B_5C_2$ and $A_9B_5C_2$ gave the best explanation of the alkaline pit.

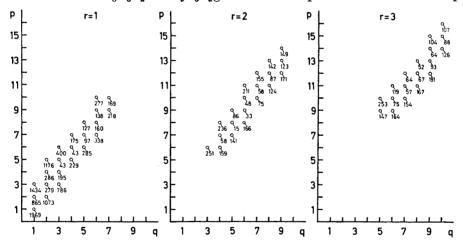


Fig. 4. Letagrop-search. Results of the calculations using Data I. Error squares sums $10^5 U_{\min}$ as a function of various (p,q,r)-sets. All details of the calculations are given in Table 2.

An analysis of the remaining data with uncoloured solutions (data III and V) gave evidence for an additional complex $A_{10}B_5C_2$. A refinement of data III and V together with data I and II, assuming formation of $A_8B_5C_2$, $A_9B_5C_2$, and $A_{10}B_5C_2$, gave the following "best" log $(\beta_{\rho qr} \pm 3\sigma)$ values:

log
$$(\beta_{8,5,2} \pm 3\sigma) = 61.97 \pm 0.02$$

log $(\beta_{9,5,2} \pm 3\sigma) = 67.07 \pm 0.08$

$$\log (\beta_{10.5.2} \pm 3\sigma) = 70.86 \pm 0.09$$

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

Table 1. Experimental $H(\log h)_{B,C}$ data for molybdophosphate equilibria (colourless solutions). For each point, the quantities $-\log h$, H, Δ_0 , Δ_1 and Δ_2 are given. The quantity Δ is the residual $H_{\rm calc}-H$. The indices 0, 1, and 2 refer to three different assumptions. 0. Only binary complexes with the following constants: $\log \beta_{1,1,0} = 3.89$, $\log \beta_{2,1,0} = 7.50$, $\log \beta_{8,7,0} = 57.74$, $\log \beta_{9,7,0} = 62.14$, $\log \beta_{10,7,0} = 65.68$, $\log \beta_{11,7,0} = 68.21$. $\log \beta_{-1,0,1} = -10.72$, $\log \beta_{1,0,1} = 6.24$, and $\log \beta_{2,0,1} = 8.07$.

1. Binary complexes and constants given under 0 together with proposed ternary complexes with the following constants.

plexes with the following constants:

log $\beta_{8,5,2} = 61.97$, log $\beta_{9,5,2} = 67.06$, and log $\beta_{19,6,2} = 70.86$. 2. The same complexes as in 1. First, the setwise E_0 -values were adjusted, and then the The same complexes as in 1. First, the setwise E_0 -values were adjusted, and then the ternary constants together with the binary phosphate constants were refined. The following "best" $\log (\beta \pm 3\sigma(\beta))$ were obtained and used in the calculation of A_2 : $\log \beta_{1,0,1} = 6.241 \pm 0.005$, $\log \beta_{2,0,1} = 8.08 \pm 0.05$, $\log \beta_{8,6,2} = 62.043 \pm 0.012$, $\log \beta_{9,5,2} = 67.12 \pm 0.05$, $\log \beta_{10,6,2} = 70.92 \pm 0.07$. $(\sigma(H) = 0.38 \text{ mM}, U = 0.05 \times 10^{-3}.)$ ΔE_0 in mV for the various 19 sets of titrations were: 0, -0.5, 0.3, -0.4, -0.2, -0.7, -0.3, -0.5, 0.7, 0.6, -0.2, -0.4, -0.5, -0.3, 0.9, 0.2, 1.1, 0.5, 0.5. Note that the -log h values given in the table do not exactly correspond to the residual given.

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B= 0.020 C= 0.005	B= 0.040 C= 0.310	B= 0.005 C= 0.040
7.001 0.00 0.11 0,11 0,11	8.059 0.00 0.13 0.13 0,15	2.944 52.00 -0.82 -0.34 -0.20
7.245 0.38 0.08 0.08 0.08	7.305 0.74 0.06 0.07 0.08	3.007 51.49 -0.86 -0.33 -0.21
6.475 0.74 0.05 0.06 0.05	7.064 1.47 -0.14 -0.11 -0.09	3.073 50.98 -0.88 -0.30 -0.28
6.796 1.11 0.01 0.03 0,03	6.921 2.18 -0.42 -0.20 -0.11	3.237 50.00 -0.96 -0.27 -0.20
6.687 1.46 -0.11 -0.01 0.01		3.457 49.06 -1.03 -0.24 -0.19
6.613 2.15 -0.62 -0.30 -0.24		3.758 48.15 -1.11 -0.21 -0.18
6.448 3.45 -1.62 -0.08 0.12	6.704 8.02 -5.39 -0.68 0121 6.603 14.50 -11.29 -1.00 0112	3,964 47.71 -1.15 -0.19 -0,18
6.429 5.23 -3.19 =0.18 0.11 6.319 8.76 -6.26 =0.35 =0.01	6.454 24.30 -19.05 -1.18 -0,18	4.174 47.28 -1.21 -0.18 -0.17
6.319 8.76 -6.26 -0.35 =0.01 5.202 12.31 -8.63 =0.37 =0.07	6.240 32.41 -19.24 -0.90 -0,21	4.358 45.85 -1.29 -0.17 -0,16
6.055 15.09 -8.33 -0.28 -0.07	5.100 38.91 -12.95 -0.48 -0.09	4.530 46.44 -1.37 -0.15 -0.14
5.912 18.60 -6.17 -0.16 -0.04	5.942 43.72 -8.95 -0.22 0.05	4.064 46.03 -1.47 -0.13 -0.13
5.680 22.41 -3.62 -0.00 0.02		4.765 45.62 -1.54 -0.08 -0.00
31010 1100 0100 0100		4.434 44.84 -1.77 -0.04 -0.03 5.806 44.08 -2.07 -0.03 -0.02
	B= 0.040 C= 0.020	
B= 0.020 C= 0.310	5.236 0.00 0.08 0.08 0,16	5.164 43.34 -2.39 •0.01 •0.00 5.321 41.95 -2.97 0.05 0.07
2.933 43.00 -2.27 -0.18 -0.14	7.026 0.85 -0.07 -0.06 -0.05	5,486 40.01 -3.89 0.07 6,11
3.020 42.57 -2.45 -0.11 -0.07	7.152 1.69 -0.25 -0.23 -0.22	5.633 37.70 -4.65 0.17 0.22
3.147 42.16 -2.75 -0.11 -0.07	7.1/6 2.54 -0.44 -0.42 -0.41	5.770 35.15 -5.01 0.13 0,21
3.204 41.75 -2.95 -0.08 -0.04	7.0/1 3.31 -0.71 -0.63 -0.61	5.418 31.73 -4.57 0.10 0122
3.759 41.35 -3.16 -0.07 -0.03	7.066 3.37 -0.75 -0.66 +0.64	6.029 28.91 -4.10 -0.11 0.04
3.021 40.5/ -3.39 -0.01 0.02	6.439 4.8/ -1.50 -0.89 -0.73	0.108 26.55 -3.49 -0.14 0:04
3.855 39.82 -3.58 -0.01 0.02	6.838 7.82 -3.74 -1.00 -0143	6.201 23.66 -2.72 -6.27 -0.07
4.084 39.10 -3.73 -0.03 -0.01	6./4/ 13.12 -8.31 -0.81 0,20	6.273 21.33 -2.07 -0.37 -0:15
4.307 38.40 -3.86 -0.05 -0.04	6.664 19.85 -14.27 =0.67 0,51	
4.536 37.73 -4.05 =0.14 =0.14 4.727 37.08 -4.17 =0.18 =0.18	6.574 27.90 -21.30 -0.83 0132 6.505 33.57 -25.83 -0.74 0132	
		B= 0.005 C= 0.040
2011	6.447 38.23 -28.97 -1.02 -0.06 6.342 42.13 -30.56 -1.07 -0.20	
5.02/ 35.84 -4.51 -0.23 -0.22 5.142 35.26 -4.75 -0.23 -0.21	A. 114 4A. 9H -30. 77 -1.19 -0.45	8.441 0.00 0.04 0.04 8.25
5.243 34.69 -5.00 -0.25 -0.21	6.241 50.76 -29.28 -1.18 -0155	8.038 0.51 0.03 0.04 0:13
5.404 33.61 -5.82 -0.26 -0.19		7.615 1.02 -0.03 -0.02 0.04 7.660 1.51 -0.05 -0.06 -0.01
5.524 32.59 -6.65 -0.25 -0.14		7,545 2.00 -0.14 +0.13 +0.08
5.001 31.17 -8.02 -0.28 -0.12	B= 0.040 C=0.320	7,369 2.94 -0.18 -0.16 -0.11
5.813 29.03 -9.94 -0.23 0.02	- 1	7.24/ 3.84 -0.27 -0.24 -0,19
5.939 26.91 -12.04 -0.42 -0.07	2.624 86.00 -4.45 -0.92 -0.84	7.148 4.72 -0.32 -0.29 -0.23
6.047 24.45 -13.56 -0.48 -0.04	3.107 84.31 -5.86 -0.73 -0,66	6.497 6.37 -0.41 -0.37 -0.30
6-135 21.93 -13.98 -0.46 0.07 6-207 19.55 -13.34 -0.44 0.16	3.403 82.69 -6.85 -0.60 -0.53 3.673 81.13 -7.40 -0.54 -0.46	0.030 d.65 -0.46 -0.40 90 <u>1</u> 32
	3.673 81.13 -7.40 -0.54 +0.46 3.625 79.63 -7.74 +0.56 +0.48	6.671 11.36 -0.52 -0.44 -0.34
6.262 17.63 -12.27 -0.53 0113	4.177 78.18 -8.06 -0.65 -0.60	6.495 14.83 -0.52 -0.29 -0.14
	4.422 76.78 -8.31 -0.76 -0.73	6.32/ 19.47 -1.44 -0.26 0104
B= 0.020 C= 0.010	4.650 75.44 -8.49 -0.86 -0.85	6.17/ 24.31 -2.83 -0.14 0.17 6.050 27.90 -3.78 -0.03 0.24
8.118 0.00 0.11 0.11 0.13	4.253 74.14 -8.65 -0.94 -0194	6.050 27.90 -3.78 -0.03 0 ₁ 24 5.959 30.66 -4.35 0.10 0 ₁ 33
7.525 0.43 0.07 0.07 0.07	5.104 72.27 -9.04 -1.00 -0.99	34.24 00:00 -103 0'IN 4Ind
7.261 0.84 0.03 , 0.04 0,03	5.431 69.35 -10.72 -1.03 "0194	
7.000 1.25 0.02 0.04 0.02	5.687 66.15 -13.94 +1.03 +0.81	B= 0,010 C= 0.040
6.956 1.65 -0.02 -0.01 -0.03	5.695 62.32 -18.47 -1.04 -0164	D= 01010 C- 01040
6.648 2.04 -0.04 -0.01 -0.03 6.717 2.81 -0.28 -0.04 -0.05	6.052 58.10 -23.14 -1.06 -0145	2.943 59.50 -1.11 =0.09 =0:10
	6.172 53.75 -27.10 -1.06 -0.25	3:020 58.91 -1.25 -0.12 -0.13
6.627 3.90 -0.95 +0.04 +0.01 6.543 5.92 +2.55 +0.03 0.08	6.278 48.86 -30.13 -1.14 -0.11 6.363 43.78 -30.67 -0.89 0.36	3.006 58.34 -1.23 =0.01 =0102
6.543 5.92 -2.55 -0.03 0i0B 6.451 9.39 -5.51 -0.10 0i07	6.363 43.78 -30.67 *0.89 0:36 5.434 39.09 -29.36 *0.91 0:52	3.173 57.77 -1.31 0.01 0:01
6.344 13.93 -9.36 -0.15 0.03	6.486 35.24 -27.09 -0.96 0161	3.260 57.22 -1.32 0.10 0:09
6.244 17.95 -12.39 -0.22 -0.05		3.536 56.14 -1.62 0.02 0.01
5.141 21.48 -13.73 -0.22 -0.08		3.678 55.61 -1.66 0.07 0.06
-5.997 25.36 -12.63 -0.16 -0.00		3.647 55.10 -1.73 0.08 0109 4.035 54.59 -1.82 8.07 8105
		4.035 54.59 -1.82 8.07 8:85 4.220 54.10 -1.90 0.07 8:04
	į	4.378 53.61 -1.94 0.11 0,07
	1	4.540 53.13 -2.07 6.09 0.04
	į i	4.005 52.00 -2.17 0.11 0,05
	'	*****

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Table 1. Continued.

4.787 52.20 -2.36 0.07 -0.01	5.847 53.45 -14.09 -0.51 =0.34 5.947 50.57 -16.12 -0.22 =0.00	
4.049 51.30 -2.57 8.14 8:04	5.847 53.45 -14.09 -0.51 =0.34 5.947 50.57 -16.12 -0.22 =0.00	B= 0.020 C= 0.380,
5.082 50.44 -2.91 0.16 0.05	A 101 45 A4 _19.37 _0 20 0.05	= ' = '
5.189 49.60 -3.29 0.18 0.05	6.22V 40.68 -19.68 -0.38 0.09 6.32V 35.99 -17.83 -0.49 0.11	2.928 118.00 -2.12 -0.09 -0.19 2.995 116.83 -2.11 0.11 0.03
5.273 48.78 -3.65 0.23 0.09	6.329 35.99 -17.83 -0.49 0,11	2.995 116.83 -2.11 0.11 0.03
5.410 47.24 -4.46 0.31 0:14	6.425 30.68 -14.79 -0.50 0,23	1 3.092 115.69 -2.41 0.07 -0.01
5.521 45.79 -5.43 0.29 0.10		3.182 114.57 -2.46 0.24 0,16
5.675 43.13 -6.98 0.43 0.20	_	3.305 113.47 -2.71 0.23 0:16
5.e18 40.22 -8.72 0.41 0.14 5.439 37.21 -9.67 0.38 0.09	B= 0.040 C= 0.040	3.442 112.39 -2.69 0.27 0120 3.596 111.33 -3.04 0.32 0125
5.439 37.21 -4.67 0.38 0.09 6.054 33.85 -9.39 0.37 0.05		3.596 111.33 -3.04 0.32 0.25
6.054 33.85 -9.34 0.37 0.05 6.158 30.38 -8.40 0.27 •0.06	8.454 0.00 -0.00 -0.00 0,23 7.42/ 1.13 -0.17 -0.16 *0,10	3.745 110.29 -3.13 0.38 0.31
6.158 30.38 -8.40 0.27 *0.08 6.245 27.07 -7.14 0.20 *0.14	7.82/ 1.13 -0.17 -0.16 -0,10	3,765 110.29 -3.13 0,38 0,31 3,953 109.27 -3.25 0.40 0,32 4,151 108.27 -3.39 0,38 0,29
6.711 24.41 -6.00 0.11 -0.23	7.561 2.22 -0.42 -0.40 -0.35	4.151 108.2/ -3.39 0.38 0.29 4.339 107.29 -3.51 0.37 0.25
6.711 24.41 -6.00 0.11 *0,23	7.26/ 4.15 -0.72 -0.68 -0.63 7.093 6.11 -1.18 -0.98 -0.86	
	6.446 9.82 -3.21 -1.31 -0,68	
B and a second	6.841 16.48 -8.42 -1.46 -0.05	4.624 105.38 -3.59 0.52 0.34 4.635 103.53 -3.70 0.66 0.42
B= 0.010 C= 0.040	6.241 16.48 -8.42 -1.46 -0.05 6.752 24.93 -15.45 -1.25 0.49 6.27 35.15 -23.97 -1.44 0.27	4.995 101.75 -3.94 0.76 0,46
8.445 0.00 0.04 0.04 0.24	6.657 35.15 -23.97 -1.44 0.27	5.120 100.02 -4.25 0.86 0.52
	6.556 42.19 -29.54 -1.35 0,20	5.305 96.75 +5.10 1.05 0,60
8.005 0.59 0.01 0.02 0.07 7.755 1.16 -0.02 -0.01 +0.00	6.522 48.01 -33.73 -1.29 0.08	5.782 V5.19 -5.61 1.13 0,64
7.559 1.73 -0.04 -0.03 +0.05	6 463 52.90 -36.63 -1.33 -0.13	5.500 92.22 -6.64 1.35 0.78
7.889 1.73 -0.04 -0.03 -0.05 7.4/0 2.28 -0.08 -0.06 -0.10 7.771 2.83 -0.09 -0.07 -0.13	6.378 58.89 -38.21 -1.27 -0.29 6.297 63.74 -37.00 -1.21 -0.42	5.656 86.80 -9.49 1.34 0,63
7.371 2.83 -0.09 -0.07 -0.13	6.297 63.74 -37.00 -1,21 -0,42	5.882 79.72 -14.19 1.01 0.14
7.301 3.36 -0.18 -0.15 -0.22	, , , , , , , , , , , , , , , , , , ,	6.084 70.28 -19.48 0.77 -0.25
7.301 3.36 -0.18 -0.15 -0.22 7.1/3 4.40 -0.22 -0.19 -0.29		6.245 61.51 -21.19 8.13 +0.97
7.070 5.40 -0.25 -0.21 -0.34	B= 0.040 C= 0.040	6.422 48.81 -16.98 0.76 -0.43
A. URY A. 37 =0.28 =0.24 =0.38	D- 0.040 C= 0.040	• • • • • • • • • • • • • • • • • • • •
6.854 8.20 -0.36 +0.29 +0.48	2.829 106.93 -3.65 -0.10 0.03	
6.750 9.90 -0.45 +0.32 +0.53	2.444 105.75 -4.24 0.02 0.13	B= 0.040 C= 0.080
6.e52 11.50 -0.50 -0.16 -0.40	3.207. 103.85 -5.54 0.02 0.10.	-
6.599 13.00 -0.00 -0.04 +0.28	3.207.103.85 -5.54 0.02 0.10. 3.432.101.89 -6.28 0.17 0.24	8.456 0.00 -0.01 -0.01 0,44
6.510 15.73 -1.73 0.25 +0.01	3.768 100.00 -6.81 0.19 0.25	7.490 1.45 -0.20 -0.19 -0.07
6.421 19.28 -3.36 0.43 0,16	4.025 98.48 -7.00 0.30 0.33	7./26 2.85 -0.42 -0.40 -0.37
6.311 24.06 -5.65 6.46 6.19	4.554 94.73 -7.59 0.10 0,07	7.990 1.45 -0.20 -0.19 -0.07 7.726 2.85 -0.42 -0.40 -0.37 7.558 4.27 -0.65 -0.62 -0.64
A.200 28.49 -7.49 0.58 0.31	1	/.434 5.05 -0.86 +0.82 =0.68
6.106 31.93 -8.74 0.55 0.28 6.019 34.69 -9.36 0.61 0.35	1 E 142 On. 66 _B. 61 = 6.68 = 6.12	7.343 6.99 -1.15 -1.10 -1.19
6.019 34.69 -9.36 8.61 0.35	5.398 87.09 -10.34 -0.12 =0.13 5.732 81.81 -15.89 -0.20 =0.11	/.261 8.31 -1.35 -1.26 1.37
	5.732 81.81 -15.89, -0.20 =0.11	7.193 9.60 -1.55 -1.40 -1.53
	5.437 77.14 -22.09 -0.33 -0,12	7.087 12.12 -2.15 -1.39 -1,52
	6.082 72.97 -28.20 -0.76 -0.43	6.997 15.73 -3.79 -0.89 -0.95
B= 0.020 C= 0.040	0.196 68.35 -32.94 -0.73 -0.26	6.412 22.34 -8.33 -0.49 -0.44
****	6.253 64.28 -36.42 -1.01 -0.41	6.808 33.88 -16.81 0.28 0.37
8.447 0.00 0.04 0.04 0.25	6.354 59.99 -37.70 -0.86 -0.12	6.694 47.62 -26.74 0.78 0.82
7.438 0.74 -0.02 -0.01 0.06	0.42/ 55.10 -37.23 -0.86 0.03	5.5/U 61.48 -35.70 D.74 D.67
7.424 1.46 -0.08 -0.06 -0.03		6.464 /1.94 -40.75 0.23 0.07
7,505 2:18 -0.13 -0.11 -0.09	6.559 44.26 -30.97 -0.87 0133	6.301 80.12 -41.07 0.36 0.13
7.355 2.87 -0.21 -0.19 •0.17 7.255 3.56 -0.27 •0.24 •0.23	1 . 21.22	6.20/ 85.70 -38.01 0.42 0.15
7.258 3.56 -0.27 -0.24 -0.23		
7.200 4.23 -0.27 -0.24 -0.23	l	
7.075 5.53 -0.43 -0.38 -0.37	B= 0.150 C= 0.040	B= 0.040 C= 0.080.
6.475 6.79 -0.56 -0.47 -0,45	1	3.065 147.00 -4.90 -0.01 0.02
6.835 9.17 -1.05 -0.55 -0.43	8.368 0.00 0.12 0.13 0.29 7.458 2.83 -0.52 -0.27 -0.36	3.189 145.55 -5.42 0.05 0,07
6.753 11.39 -1.98 -0.41 =0.10 6.009 15.42 -4.52 -0.50 0.04	7.458 2.83 -0.52 -0.27 -0.36 7.330 5.60 -2.54 -0.29 -0.58	3.324 144.12 -5.85 0.14 0,14
6.009 15.42 -4.52 -0.50 0.04 6.525 24.23 -10.52 -0.33 0.31		3.474 142.73 -6.23 0.20 0119
6.525 24.23 -10.52 -0.33 0.31 6.413 31.28 -15.12 -0.40 0.14	7.276 8.32 -4.88 0.47 •0.86 7.208 15.15 -12.19 1.37 0.38	3.000 141.35 -6.47 0.30 0,27
6.413 31.28 -15.12 +0.40 0.14 6.300 37.37 -18.47 -0.41 0.01	7.208 16.16 -12.19 1.37 0.38 7.15/ 25.96 -21.50 1.91 0.60	3.790 140.01 -6.71 0.32 0.29
0.145 44.12 -19.81 -0.32 -0.05	7.157 25.96 -21.50 1.91 0.60 7.103 39.39 -34.31 2.24 0.73	3.424 138.69 -6.65 0.55 0.58
0.145 44.12 -14.01 -0.32 -U_U		
	7.026 62.43 -56.03 1.06 =0.51 6.514 92.66 -80.76 0.97 =0.40	1 4.278 136.13 -7.06 0.45 0.34
B	6./92 119.61 -88.69 0.73 *0.34	1 4.431 134.85 -/.23 0.39 0.27
B= 0.020 C= 0.040	6.662 139.97 -75.53 1.20 0128	
2 44 5 40 2 20 4 40 217	6.417 158.65 -44.77 1,93 0,42	/ 4.710 133.33 m2.44 0.37 m 3m
3.014 24.80 -2.79 -0.49 +0.37 3.114 24.06 -3.01 -0.46 +0.36	1	4./70 131.2/ -/.3/ 0.71 0.32
3.114		4.477 128.97 -7.55 0.61 0.38 5.126 126.75 -7.96 0.65 0.39
	D	5.126 126.75 -7.96 0.65 0.39
3.322 72.62 -3.23 -0.25 *0.1/	B= 0.020 C= 0.080	1 5.24Y 124.A1 -8.55 D.05 A.4A'
3.472 /1.93 -3.50 -0.29 *0.25 3.578 /1.24 -3.43 *0.09 *0.05		1 5.349 100 57
3.578 71.24 -3.43 -0.09 -0.03 3.728 70.57 -3.56 -0.07 =0.02	8.512 0.00 -0.04 -0.06 0.42	5.515 118.59 -11.19 0.85 0.52
7.897 AO.O1 — 3.78 _A NO A. N.] 2.544 114.55 -13.45 0.73 0.75
4.072 69.27 -3.59 -0.17 -0.14	7.814 2.31 -0.33 -0.31 -0.24	1 5.753 111.41 -16.20 0.82 0.43
4.232 68.63 -3.99 -0.17 -0.16	7.646 3.43 -0.47 -0.44 -0.42	5.843 108.13 -19.04 0.72 0,32
4.381 68.01 -4.07 -0.16 -0.15	7.526 4.53 -0.64 -0.60 -0.61	5.418 105.05 -21.75 0.71 0.29 6.049 99.38 -27.68 0.30 0.13
4.072 69.27 -3.89 +0.17 +0.14 4.232 68.63 -3.99 +0.17 +0.15 4.281 68.01 -4.07 +0.16 +0.15 4.248 67.40 -4.30 +0.29 +0.29	7.426 5.61 -0.75 -0.71 -0.74	
4.671 66.80 -4.40 -0.28 -0.28		
4./59 66.21 -4.44 -0.21 +0.22	7.214 8.73 -1.06 *1.00 *1.07. 7.112 10.71 -1.24 *1.15 *1.25	0.321 83.58 -40.59 -0.15 -0.55 6.431 75.06 -41.73 -0.10 -0.45
4.865 65.63 -4.56 .0.20 .0.21	7.112 10.71 -1.24 -1.15 -1,25	
5.030 64.50 -4.91 -0.19 =0.20	6.45/ 14.47 -1.58 -1.27 -1.39	6.532 66.88 -38.88 0.07 •0,25 6.586 60.30 -35.22 0.26 •0,02
5.102 63.41 -5.35 -0.17 =0.17	6.618 19.64 -2.89 -0.89 -0.90	0.500 60.30 -35.22 0.26 -0.02
5.248 62.35 +5.86 +6.43 +0.12	6./10 25.78 -5.72 -0.18 =0:07	Ţ
5.435 60.34 -7.05 -0.04 0.00	6.630 32.45 -4.26 0.25 0136	l
5.555 58.46 -8.50 -0.08 0.00	6.546 39.29 -12.86 0.31 0139	j
5.715 55.84 -10.86 -0.01 0.10	0.429 48.54 -17.02 0.51 0150	I
	6.307 57.13 -10.04 0.57 0.47 6.103 69.19 -19.80 0.81 0.63	i
	6.103 69.19 -19.80 0.81 0163	i
	1	,

In order to test the influence of an error in E_0 , a calculation was made where the E_0 -values were setwise adjusted. This calculation lowered the error squares sum, but did not change the overall picture. The results are given in Table 1. Data of the data IV region (yellow coloured solutions) were treated separately. The results of this pqr-analysis are given in Fig. 5. It is seen that

although the lowest error squares sum is obtained for the complex $A_{19}B_{12}C$, equally valid explanations with other pqr-values cannot be ruled out.

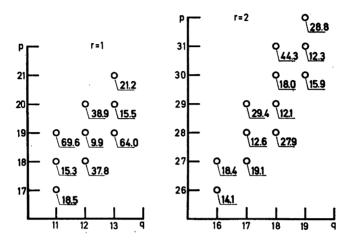


Fig. 5. Letagrop-search. Results of the calculations using Data IV. Error squares sums $10^4 U_{\min}$ as a function of various (p,q,r)-sets.

A relatively good fit was obtained by assuming $A_{18}B_{12}C$, $A_{19}B_{12}C$, and $A_{20}B_{12}C$ (log $\beta_{18,12,1}=125.15\pm0.16$, log $\beta_{19,12,1}=129.34\pm0.24$, log $\beta_{20,12,1}=132.92\pm0.21$, $U_{\min}=1.9\times10^{-4}$). However, attempts to connect this result with the result from the calculation on uncoloured solution data failed completely. Before we can analyse the data for the yellow coloured solutions successfully, it is necessary to extend the pH-range to more acid solutions and also to complement the emf data with, for instance, spectrophotometric data. Investigations in this direction are in progress.*

CONCLUSIONS

The present equilibrium analysis has given clear indications for the existence of two types of complexes, one yellow and one colourless. Moreover, through the present work, composition and equilibrium constants for main complexes of the colourless type have been well established. A good criterium for that is the low standard deviations of the determined equilibrium constants (Table 2). Strengths and concentrations of these complexes are well illustrated by the distribution diagrams given in Fig. 6.

Concerning the yellow complexes it may be said that the range studied is too limited to allow a distinct conclusion. What can be said at present is that the B/C ratio of the complexes probably lies between 8 and 12. Attempts

^{*} Note added in proof. Some recent results on yellow coloured solutions are presented elsewhere. 14

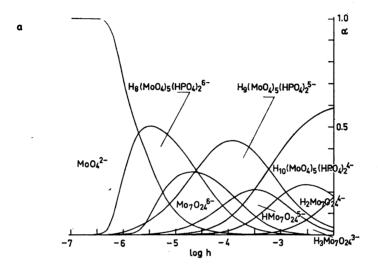
Table 2. Results of pqr-analysis for colourless solutions, using LETAGROP. The binary constants used are those under 0 in Table 1.

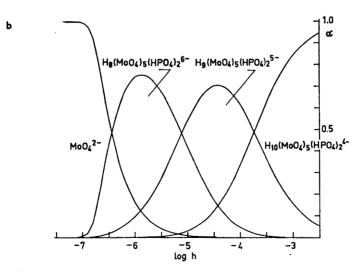
	$\begin{array}{c} \text{Species tested} \\ (p,q,r) \end{array}$	$\begin{array}{c} U_{\rm min} \\ \times 10^3 \end{array}$	$\sigma(H) \text{ mM}$	$\log \left(eta_{pqs} \pm 3\sigma ight)$
Data I	(1,1,1)	19.69	15.89	8.42 ± 0.48
(79 points)	(2,1,1)	8.65	10.53	14.85 ± 0.15
, ,	(3,1,1)	14.34	13.56	21.37 ± 0.18
	(2,2,1)	10.73	11.73	16.13 ± 0.22
	(3,2,1)	2.79	5.98	22.79 ± 0.09
	(4,2,1)	2.86	6.06	29.47 ± 0.09
	(5,2,1)	11.76	12.28	36.08 ± 0.21
	(3,2,1) $(4,2,1)$	2.11	5.24	22.52 + 0.27, 29.14 + 0.30
	(3,3,1)	7.86	10.04	24.02 ± 0.21
	(4,3,1)	1.95	5.00	30.73 ± 0.09
	(5,3,1)	0.43	2.35	37.47 ± 0.05
	(6,3,1)	4.00	7.16	44.17 + 0.14
	(5,4,1)	2.29	5.42	38.71 ± 0.12
	(6,4,1)	0.43	2.33	45.47 ± 0.05
	(7,4,1)	1.75	4.74	52.20 ± 0.09
	(6,5,1)	2.85	6.04	46.71 ± 0.15
	(7,5,1)	0.97	3.53	53.48 ± 0.09
	(8,5,1)	1.27	4.04	60.24 ± 0.09
	(7,6,1)	3.38	6.58	54.73 ± 0.21
	(8,6,1)	1.60	4.53	61.51 ± 0.12
	(9,6,1)	1.38	4.21	68.28 ± 0.12
	(6,3,2)	2.51	5.68	45.81 ± 0.12
	(6,4,2)	1.59	4.52	47.08 + 0.12
	(7,4,2)	0.58	2.73	53.83 + 0.07
	(8,4,2)	2.36	5.50	60.56 + 0.17
	(7,5,2)	1.41	4.26	55.08 ± 0.13
	(8,5,2)	0.15	1.36	61.85 ± 0.04
	(9,5,2)	0.86	3.33	68.60 ± 0.09
	(8,6,2)	1.66	4.62	63.09 ± 0.15
	(9,6,2)	0.33	2.06	69.87 + 0.06
	(10,6,2)	0.48	2.47	76.64 + 0.07
	(10,7,2)	0.75	3.11	77.90 ± 0.10
	(11,7,2)	0.58	2.72	84.68 ± 0.09
	(10,6,3)	0.75	3.10	78.28 + 0.11
ì	(11,6,3)	1.19	3.91	85.04 ± 0.17
	(10,7,3)	1.54	4.44	79.52 ± 0.18
	(11,7,3)	0.57	2.70	86.31 ± 0.09
	(12,7,3)	0.64	2.86	93.08 ± 0.10
	(11,8,3)	1.67	4.62	87.54 ± 0.19
	(12,8,3)	0.67	2.94	94.34 ± 0.12
Data I+II	(3,2,1)	10.94	10.85	22.95 ± 0.17
(94 points)	(4,2,1)	9.82	10.27	29.31 ± 0.16
-	(3,2,1) $(4,2,1)$	3.82	6.31	$22.71 \pm 0.20,\ 28.82 \pm 0.15$
	(8,5,2)	0.25		61.85
	(8,5,2) (9,5,2)	0.12	1.14	$61.79 \pm 0.04, 66.93 \pm 0.16$
Data I+II+III+V (359 points)	(8,5,2) (9,5,2) (10,5,2)	0.12	0.58	$61.97 \pm 0.02, 67.07 \pm 0.08, 70.86 \pm 0.09$

to explain these data with e.g. dodecamolybdophosphates — a proposal often found in the literature — were however not successful. Complimentary works on the yellow solutions (emf and spectrophotometry) are in progress.

The present paper contains no review or comparison with earlier studies. We suggest that such a survey may be worth-while when the information concerning the yellow complexes becomes clearer.

From present studies, using other experimental methods, we hope, in the near future, to collect complementary and confirmatory information about proposed complexes. At present, the following studies are in progress:





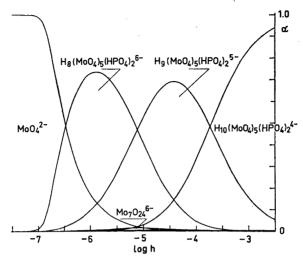


Fig. 6. Complex distribution diagrams, $\alpha(\log h)_{B,C}$ for a) B=40 mM, C=10 mM (The curves have been calculated neglecting the existence of yellow coloured species); b) $B=50\,$ mM, $C=20\,$ mM; c) $B=40\,$ mM, $C=20\,$ mM. α is defined as the ratio between molybdenum in a species and total molybdenum. Species with $\alpha < 0.008$ have been omitted.

- i. Molecular weight determinations using ultra-centrifugation.
- ii. "Structure" determination of the aqueous species by X-ray solution studies.
- iii. Structure determinations of molybdophosphates crystallized from aqueous solutions, using X-ray diffraction.
- iv. Spectrophotometric measurements in UV.

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