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Studies in the Determination of Silica

II. The Separation of Phosphomolybdate from α-Silicomolybdate

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Experiments described in this paper show that it is possible to separate quantitatively phosphomolybdate from α-silicomolybdate by extracting water phases with *n*-butanol or *n*-butanol-benzene mixtures under certain specified conditions.

When silica is determined spectrophotometrically as α-silicomolybdate, phosphorus in the form of orthophosphate ion interferes seriously. Among the methods used to separate the heteropolymolybdic acids of silicon and phosphorus, extraction of water phases with different organic solvents has repeatedly been investigated [1–4]. Probably because the authors cited have worked with solutions in which equilibrium between α- and β-silicomolybdates has not been reached, definite conclusions cannot always be drawn from their data.

King *et al.*[5] precipitated phosphate as ferric phosphate by the "basic ferric acetate method" prior to the determination of silica as silicomolybdate.

In this paper some experiments with the extraction of heteropolymolybdic acids of phosphorus and silicon are described. An elementary theoretical account of the extraction is also presented. Experimental data on the formation and some properties of phosphomolybdate are given as are also some experiments on the determination of phosphorus as phosphomolybdic acid extracted into organic phases.

1. EXPERIMENTAL DETAILS

For an account of some of the experimental methods and instruments the reader is referred to the first paper [6] in this series. The chemicals used were of analytical grade; the solvents, however, were also in general distilled once using a small Vigreux column.

pH measurements in solutions, in which the concentration of perchlorate ion is not low enough, can not be performed using saturated calomel electrodes with asbestos or sintered glass plugs, dipping into the solution to be measured, since $KClO_4$ will precipitate in the plug causing a drift of potential. Instead a calomel electrode with a bent-up open tip at the end of the tube dipping into the solution was used in the case of perchloric acid solutions.

The extinction measurements were carried out in 1 cm cells of fused silica, fitted with ground in stoppers.

If not otherwise stated the experiments have been performed at 20.0°C.

2. SOME EXPERIMENTS ON THE FORMATION OF PHOSPHOMOLYBDATE IN AQUEOUS SOLUTIONS

The reaction between orthophosphate and molybdate ions to form phosphomolybdate seems to be too complex to be useful as a basis for a method for phosphorus determination. It has earlier been studied by, *e. g.*, Nydahl [7].

The following experiment shows the complex nature of the system orthophosphate-sodium molybdate-hydrochloric acid.

To two solutions, each containing 3×10^{-5} moles Na_2HPO_4, equal amounts of a Na_2MoO_4 solution was added followed by concentrated hydrochloric acid until the pH in one solution was 3.5 and in the other 0.5; they were then diluted to 50 ml in calibrated measuring flasks. By mixing suitable amounts of these two solutions a series of pH-values in the interval $0.5 \leqq pH \leqq 3.5$ could be obtained. Now varying the amount of Na_2MoO_4 taken and measuring the extinction of the solutions against suitable blanks at 400 mμ the extinction as a function of pH with Na_2MoO_4 as a variable was recorded.

The results are shown in Fig. 1, where the extinction is plotted against pH. Nowhere in the range of molybdate concentration studied is the extinction independent of that variable. Also pH plays an important role.

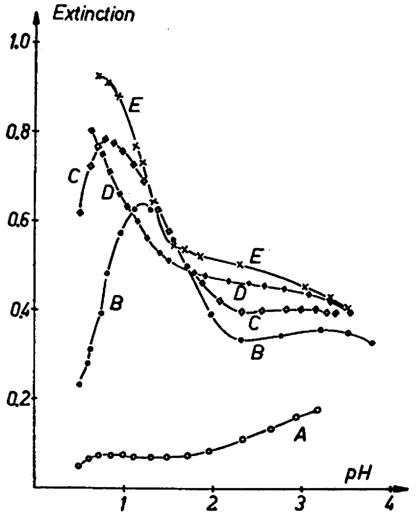

Fig. 1. Extinction of water solutions of phosphomolybdate at 400 mμ.

curve A, $[Na_2MoO_4] = 6 \times 10^{-3}$ M
» B, » $= 1.2 \times 10^{-2}$ M
» C, » $= 3.0 \times 10^{-2}$ M
» D, » $= 1.5 \times 10^{-1}$ M
» E, » $= 0.3$ M.

3. A SIMPLIFIED THEORETICAL TREATMENT OF A CERTAIN TYPE OF EXTRACTION PROCESS

3.1. Notations and simplifying assumptions

The following notations will be used:

Concentrations in the water phase	[ ]
» » » organic »	[ ]'
The i:th acid dissociation constant of H_nA	k_i
Distribution constant for H_nA	γ

To begin with it will be assumed that the acid H_nA dissolves in the organic phase only as such (no polymerisation), dissociation taking place only in the water phase giving the ultimate product A^{-n} In this treatment also activity effects, mutual solubilities of the two phases and the influence of temperature are not taken into consideration.

3.2. The distribution of H_nA as a function of pH

By definition we have

$$k_i = \frac{[H^+]\,[H_{n-i}A^{-i}]}{[H_{n-i+1}A^{-i+1}]} \tag{1}$$

$$\gamma = \frac{[H_nA]'}{[H_nA]} \tag{2}$$

We also define an apparent distribution constant γ_a by

$$\gamma_a = \frac{[H_nA]'}{\sum\limits_{i=0}^{n} [H_{n-i}A^{-i}]} \tag{3}$$

Putting $i = p$ in (1) and solving for $[H_{n-p}A^{-p}]$ we get, using (2)

$$[H_{n-p}A^{-p}] = \frac{1}{\gamma}\,\frac{\prod\limits_{i=1}^{p} k_i}{[H^+]^p}\,[H_nA]' \tag{4}$$

Substituting eqn. (4) in (3) we arrive at the following expression for γ_a as a function of $[H^+]$:

$$\gamma_a = \frac{\gamma}{1 + \sum\limits_{p=1}^{n} \frac{\prod\limits_{i=1}^{p} k_i}{[H^+]^p}} \tag{5}$$

With fixed k_i, γ_a is therefore only a function of $[H^+]$. With the aid of eqn. (5) the function

$$\log \gamma_a = f(\mathrm{pH}) \tag{6}$$

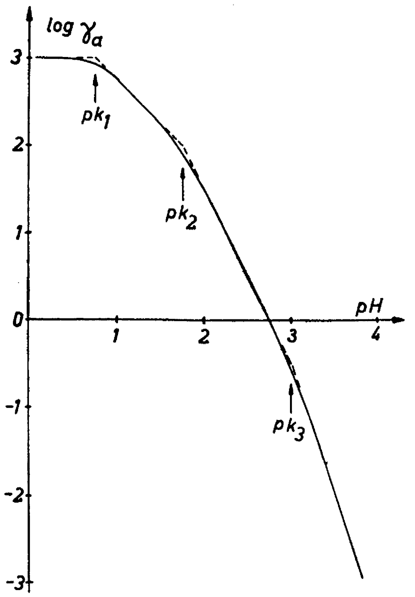

Fig. 2. Logarithm of apparent distribution constant as a function of pH.

can easily be constructed plotting log γ_a along the vertical and pH along the horizontal axis. Such a construction is shown in Fig. 2 for the hypothetical case H_3A with $pk_1 = 0.74$, $pk_2 = 1.75$, $pk_3 = 3$ and $\gamma = 10^3$. When $pH \gg pk_3$ or when $pH \ll pk_1$ the curve approximates to straight lines; if the differences $pk_2 - pk_1$ and $pk_3 - pk_2$ are large enough, the form of the curve in the middle parts of the corresponding intervals will also be approximately straight lines with slopes -1 and $-1/2$, respectively. When $pH \gg pk_3$ the slope of the line is in the limit $-1/3$ and when $pH \ll pk_1$ the line is horizontal. These successive straight lines cut when $pH = pk_1$, $pH = pk_2$ and $pH = pk_3$, respectively.

3.3. Limits of applicability of foregoing treatment

The limits of applicability of the foregoing treatment can be summarised as follows:

a) the mass action law is strictly applicable only when activity is introduced instead of concentration.

b) the value of the distribution constant γ depends on the composition of the phases; this composition changes, *e. g.*, with the mutual solubilities of the two solvents, which depend on their salt contents.

c) polymerisation or other reactions can take place in one or both of the phases.

d) the "constants" k_i and γ are functions of temperature. In spite of these and other restrictions, experiments show that the treatment in 3.2 can to some extent be used to describe the behavior of extraction systems referred to later.

4. QUANTITATIVE EXTRACTION EXPERIMENTS

4.1. Description of experiments

The water phase containing α-silico- or phosphomolybdate, sodium molybdate, acid and when necessary additional salts was mixed in a beaker with the organic solvent using a magnetic stirrer to effect intimate phase contacts. A glass and a calomel electrode were dipped into the mixture being stirred; a reproducible pH-value could then after some stirring be read off the instrument. (pH-values measured in the way just described on solutions containing comparatively large amounts of organic compounds dissolved must only be regarded as relative, since the solvent is no longer water but a mixture of water and organic solvent.) If necessary concentrated acids were added to adjust pH to a desired value; when this was reached, the contents of the beaker were transferred to a graduated cylinder fitted with a ground glass stopper. This cylinder was placed in a thermostate and shaken now and then until equilibrium was reached. The volumes were read when the phases had separated completely; their contents of silicon and phosphorus were determined spectrophotometrically, silicon by the method described in the first paper in this series [6], phosphorus in the way described later in this paper (section 6). Finally the pH of the water phase was checked once more.

In the case of *n*-butanol-benzene mixtures a certain amount of care must be exercised if the original composition of the organic phase is to be maintained during the extraction process, since *n*-butanol and to a smaller extent benzene dissolve in the water phase. A large water phase is therefore first repeatedly shaken with new, small volumes of organic phase at a rather high pH (about = 4) until the water phase is in equilibrium with an organic phase, the composition of which is practically the same as the original organic mixture. The pH is then lowered to the desired value and the intended extractions carried out. This procedure is necessary when the water phase is more than about three times as large as the organic phase.

4.2. Extractions with *n*-butanol

4.2.1. *Preliminary notes.* The paper by Mellon and Wadelin [2] contains much information on the suitability of a number of organic solvents for the purpose of extracting heteropolymolybdic acids of phosphorus, arsenic and silicon. Some of these solvents have been tested and *n*-butanol was selected for more detailed experiments.

4.2.2. *Results of experiments.* The curves in Fig. 3 give the results obtained with water phases containing hydrochloric acid-sodium chloride. 15 ml water solution was extracted with 10 ml *n*-butanol. The water phase was 0.24×10^{-3} M in Si or P; curves B and D refer to water phases, which were also 0.6 M in NaCl. In Fig. 4 are given the extinctions of extracts from blank solutions as a function of pH.

The system nitric acid-sodium nitrate gives results which within experimental error are identical with those in Fig. 3. In the case of perchloric acid-sodium perchlorate corresponding curves are displaced about 0.2 pH units in

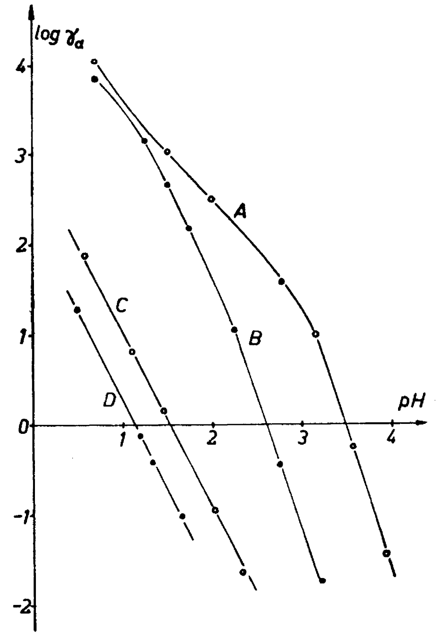

Fig. 3. Extractions with n-butanol from HCl—NaCl solutions.
curve A, phosphomolybdic acid,
» B, » » , water phases 0.6 M in NaCl.
curve C, silicomolybdic acid,
» D, » » , water phases 0.6 M in NaCl.

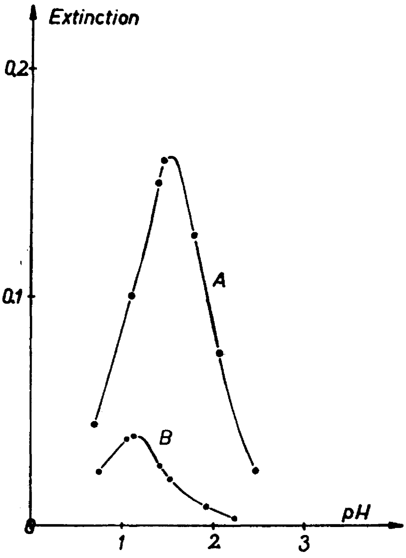

Fig. 4. Extinction as a function of wavelength for n-butanol extracts from blank HCl—NaCl solutions.
curve A, no NaCl added,
» B, water phase 0.6 M in NaCl.

the direction of decreasing pH. In all three cases the slopes of the lines are —1/2 in the case of silicomolybdic acid; phosphomolybdic acid seems to split off two protons of about the same strength in the neighbourhood of pH 3 if no extra salt has been added; below that pH-value only one proton seems to have been split off. However, all conclusions regarding the basicity of these acids, drawn from experiments such as these, must be regarded with some uncertainty.

The effect of salt additions is important. At high pH values the displacement of the phosphomolybdic acid line is greater than that of the silicomolybdic acid line for a given increase in salt concentration. This implies that when separation is to take place at say pH 2.5, it is necessary to keep the amounts of salts present to a minimum. On the other hand, when extractions are made at pH-values around 2, salt additions have about the same effect on both systems.

Another effect of adding salts is to lower the extinctions of extracts from blank solutions. This should be born in mind if phosphorus is to be determined in the organic phase. When silica is determined in the water phase the blanks

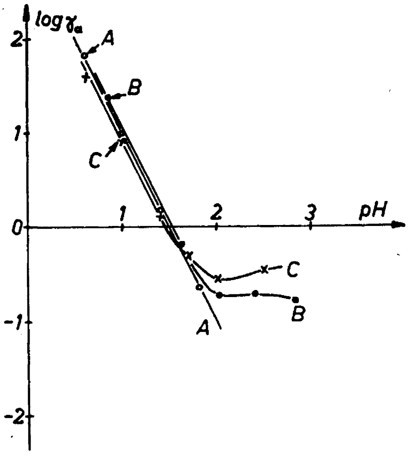

Fig. 5. Extractions with *n*-butanol of $H_2SO_4-Na_2SO_4$ water solutions.
curve A, no Na_2SO_4 added,
» B, $[Na_2SO_4] = 0.2$ M,
» C, » $= 0.4$ M.

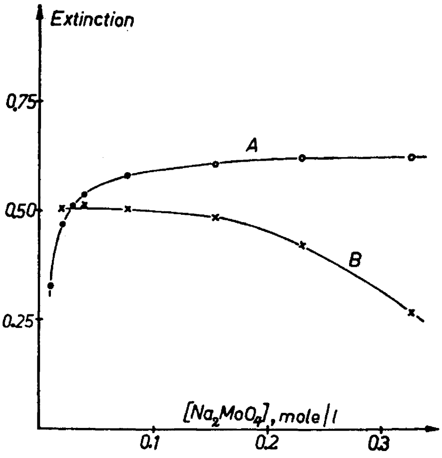

Fig. 6. Extinctions of water solutions (curve A) and extracts (curve B) of phosphomolybdic acid as functions of $[Na_2MoO_4]$.

are very low, being hardly affected if some molybdic acid has been extracted into the organic phase.

The system sulphuric acid-sodium sulphate exhibits a peculiar behaviour when silicomolybdic acid is extracted from these water phases, Fig. 5. The curves change direction when the pH has about the same value as the pK_s for HSO_4^- (2.0), the apparent distribution constants being much larger than expected. This implies that only small amounts of sulphate ions must be present if no silicomolybdic acid is to be extracted.

The results obtained in section 2 seem to show that the formation of phosphomolybdate in the experiments just described is not complete; in spite of this, however, straight lines are obtained in accordance with the simple theory in section 3. In this connection it must be pointed out that increasing the sodium molybdate concentration in the water phase has the effect of lowering the apparent distribution constant in the same way as when e.g. sodium chloride is added. This is demonstrated in the following experiment.

Water solutions, which were 0.8×10^{-3} M in Na_2HPO_4 and had a pH-value of 2.5, contained different amounts of Na_2MoO_4; 20 ml were extracted with 10 ml *n*-butanol in a beaker as described in section 4.1. The extinction of the extracts and of the original water solution were measured at 400 mμ. The results are shown in Fig. 6. Curve A demonstrates a rise in extinction, that could be predicted from the curves in Fig. 1, while on the other hand the decrease of extinction of the organic phase is evident from curve B.

4.3. Extractions with n-butanol — benzene mixtures

4.3.1. *Preliminaries.* To see if there was a composition of the organic mixture in question that was particularly suitable for extracting phosphomolybdic acid, the following experiment was performed.

15 ml water solution, 0.2 × 10^{-3} M in silicon or phosphorus, 0.02 M in Na_2MoO_4 and with the pH adjusted to 1.25 with HCl, was shaken with organic mixture (10 ml) until equilibrium was reached; by varying the composition of this organic mixture, organic phases with different extracting properties could be obtained. Extinctions of the extracts were measured at 400 mμ. Finally the pH of the water phase was checked once to see that it did not differ from the chosen value, 1.25.

In Fig. 7 the extinctions obtained are plotted along the vertical axis and the mole fraction of n-butanol in the organic mixture along the horisontal axis. A maximum extinction value is obtained, when the mole fraction is 0.5. The curves for silicomolybdic acid and for the blanks show that also at a mole fraction of 0.5 a separation between phosphomolybdic and silicomolybdic acids

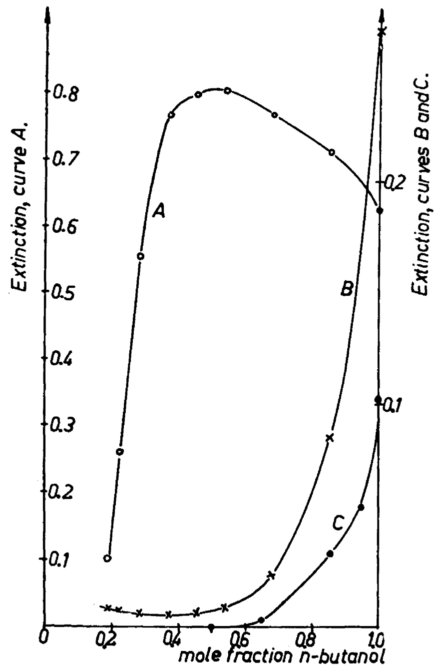

Fig. 7. Extinction of extracts as function of mole fraction n-butanol in the organic mixture.
curve A, phosphomolybdic acid extracted,
» B, blank solution extracted,
» C, silicomolybdic acid extracted.

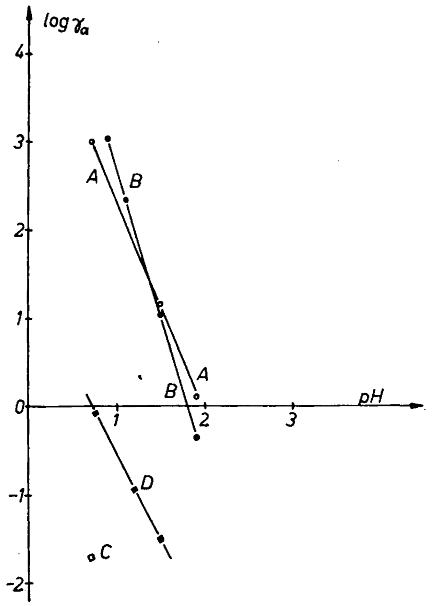

Fig. 8. Exyractions with 0.5 mole fraction n-butanol—benzene mixture from HCl—NaCl and H_2SO_4—Na_2SO_4 solutions.
curve A, phosphomolybdic acid,
» B, » » , water phase 0.3 M in NaCl.
point C, silicomolybdic acid,
curve D, » » , water phase 0.4 M in Na_2SO_4.

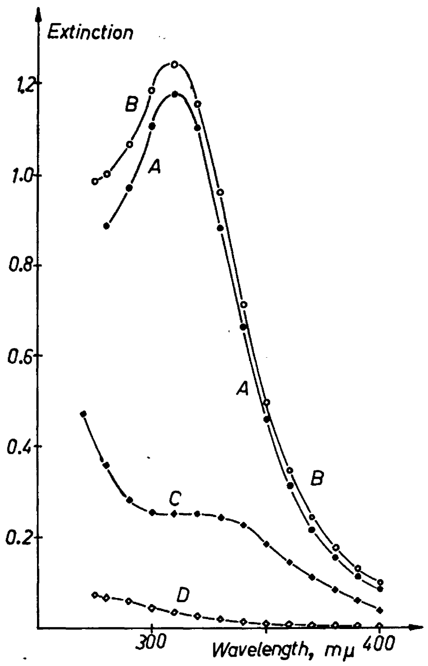

Fig. 9. Extinctions as a function of wavelength for phosphomolybdic acid in organic solvents.
curve A, extract No. 2 from Table 1, curve B, extract No. 6 from Table 1,
» C, corresponding blank, » D, corresponding blank.

is possible; at the same time a low blank is assured for the organic phase, if phosphorus is to be determined spectrophotometrically in that phase.

4.3.2. *Results of experiments.* In Fig. 8 the results of extraction experiments with water phases of the same composition as in 4.2.2 are shown. The systems with hydrochloric acid — sodium chloride and nitric acid — sodium nitrate behave in almost the same way. No extractions with perchloric acid — sodium perchlorate have been made, because at these low pH values and with organic phases containing only small amounts of water there are some risks of explosion. In the case of sulphuric acid — sodium sulphate, phosphomolybdic acid behaves in almost the same way as with hydrochloric acid — sodium chloride but silicomolybdic acid is more easily extracted: here too therefore only small amounts of sulphate should be present.

5. INFLUENCE OF TEMPERATURE

Extraction experiments with *n*-butanol and *n*-butanol — benzene mixtures showed that between 18° and 24°C only very small variations in apparent distribution constants with temperature were obtained, causing practically no changes in the curves of Figs. 3, 5 and 8.

Table 1.

No.	pH of water phase	Initial volume (ml) of		Final volume (ml) org phase	mmole P in initial 15 ml water phase	Extinction of final org. phase
		water phase	org. phase			
Extractions with *n*-butanol						
1	2.25	15	10	25	0.72×10^{-3}	0.050
2	2.25	15	10	25	1.20×10^{-3}	0.084
3	2.25	15	10	25	2.40×10^{-3}	0.170
4	2.25	15	10	25	3.60×10^{-3}	0.255
Extractions with *n*-butanol-benzene mixture, mole fraction *n*-butanol = 0.5						
5	1.25	15	10	25	0.72×10^{-3}	0.060
6	1.25	15	10	25	1.20×10^{-3}	0.098
7	1.25	15	10	25	2.40×10^{-3}	0.196
8	1.25	15	10	25	3.60×10^{-3}	0.301

6. NOTE ON THE DETERMINATION OF PHOSPHORUS AS PHOSPHOMOLYBDIC ACID EXTRACTED INTO ORGANIC SOLVENTS

In connection with the determination of distribution constants for phosphomolybdic acid some experiments with the spectrophotometric determination of phosphorus were made. They are best discussed at this point.

The extractions were here carried out in separatory funnels after the pH-value of the water phase had been adjusted in the way described in section 4.1. When the phases had separated, the water phase (lower layer) was transferred to another funnel and the organic phase to a calibrated measuring flask; the water phase was once more extracted with a new portion of organic solvent. The combined extracts were diluted in the measuring flask to the mark with the corresponding solvent or solvent mixture. The extinctions were measured at 400 mμ; however, especially in the case of the 0.5 mole fraction mixture, a shorter wavelength (310 mμ, the maximum value of the extinction as a function of wavelength) can be chosen.

The results of these experiments can be found in Table 1; in Fig. 9 is also shown the extinctions as functions of wavelength for some typical extracts.

I wish to thank Dr. F. Nydahl, Head of the Department of Analytical Chemistry, for his continued interest in this investigation and for the facilities put at my disposal.

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