[CONTRIBUTION FROM CLARKSON COLLEGE OF TECHNOLOGY]

Heteropoly Compounds. IV.[1-3] The Basicities of Some Heteropoly Tungstic and Molybdic Acids and the Charge of Their Anions[4,5]

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The basicities of a number of heteropoly acids were determined by a spectrophotometric technique. The acids studied were 12-tungstosilicic, 12-tungstophosphoric, 9-tungstophosphoric, 6-molybdocobaltic(III), 6-molybdochromic(III) and 12-molybdoceric(IV). The method is based on the influence of the heteropoly acid upon the ionization of methyl orange, taking ionic strength effects into account. It gives conclusive results only if the state of agglomeration is known. This latter information was obtained by determining the charges on the heteropoly ions in solution using a coagulation technique. The following formulations are proposed: $H_4SiW_{12}O_{40}$, $H_7PW_{12}O_{42}$, $H_6P_2W_{18}O_{62}$, $H_3CoMo_6O_{21}$, $H_3CrMo_6O_{21}$ and $H_8CeMo_{12}O_{42}$. The solubility product of silver 12-molybdocerate(IV) has been determined.

Introduction

Although much has been written on the composition and strucutre of heteropoly compounds[6] there is still a great deal of confusion in the literature on this subject. Various authors ascribe different formulas to the same compound. For example, for 12-tungstosilicic acid either $H_4SiW_{12}O_{40}$ or $H_8SiW_{12}O_{42}$, and for 12-tungstophosphoric acid, $H_3PW_{12}O_{40}$ or $H_7PW_{12}O_{42}$ are given. This is true for almost any heteropoly acid or salt.

The main reason for the discrepancies has to be sought in the rather complicated structure of the large heteropoly ion. Neither of the methods usually employed for such a structure determination, quantitative chemical and X-ray analysis, give unambiguous results. Therefore, additional independent methods such as diffusion, basicity determinations, vapor pressure measurements, coagulation activity, light scattering, etc., have to be used in order to solve the structural problems of heteropoly compounds.

The experiments have to be carried out in two directions: (a) to elucidate the state of aggregation, *i.e.*, whether the ion is a monomer, dimer or possibly a polymer and (b) to determine the valency of the ion.

In earlier papers we have employed light scattering[1,3] to determine the state of aggregation and coagulation[2] to determine the charges of some heteropolytungstate ions. In the present paper we have extended the coagulation measurements to a number of heteropolymolybdate ions and in addition have determined the basicities of the corresponding heteropoly acids using a spectrophotometric method. The heteropoly ions investigated were: (a) 12-tungstosilicate, (b) 12-tungstophosphate, (c) 9-tungstophosphate, (d) 6-molybdocobaltate(III), (e) 6-molybdochromate(III), (f) 12-molybdocerate(IV). In the case of 12-molybdocerate(IV) the solubility product of its silver salt was also determined. Our results are consistent with the following molecular formulas for the heteropoly acids: (a) $H_4SiW_{12}O_{40}$, (b) $H_7PW_{12}O_{42}$, (c) $H_6P_2W_{18}O_{62}$, (d) $H_3CoMo_6O_{21}$, (e) $H_3CrMo_6O_{21}$ and (f) $H_8CeMo_{12}O_{42}$.

Methods

1. Spectrophotometric Determination of Basicity.—A spectrophotometric method was used in order to determine the basicities of the heteropoly acids. It is a modification of a procedure originally described by Klotz[7] and applied by Singleterry,[8] consisting essentially in measuring the optical density of a methyl orange solution in the presence of various amounts of added acid. Klotz has derived the following equation for the indicator ratio

$$R = \frac{[A^-]}{[HA]} = \frac{\alpha}{1-\alpha} = \frac{\log (I_0/I)_a - \log (I_0/I)_x}{\log (I_0/I)_x - \log (I_0/I)_b} \quad (1)$$

where for a given concentration of indicator, $[A^-]$ and $[HA]$ are the equilibrium concentrations of the basic and the acid forms, $\log (I_0/I)_b$ and $\log (I_0/I)_a$ are the optical densities of the basic and the acid forms and $\log (I_0/I)_x$ is the optical density of the indicator at an intermediate acidity. α is the degree of ionization.

The dissociation of the indicator proceeds in the manner

$$HA \rightleftarrows H^+ + A^- \quad (2)$$

The ionization constant can be written

$$K = \frac{[H^+][A^-]}{[HA]} \frac{\gamma_{H^+} \cdot \gamma_{A^-}}{\gamma_{HA}} \quad (3)$$

so that combining with (1), and taking $\gamma_{H^+}\gamma_{A^-}/\gamma_{HA} = f$

$$K = [H^+]Rf \quad (4)$$

The concentration of indicator must be sufficiently low compared to that of the added acid so that $[H^+]$ is furnished almost entirely by the latter.

For a reference solution of known hydrogen ion concentration, $[H^+]_0$

$$K = [H^+]_0 R_0 f_0 \quad (5)$$

At comparable ionic strengths, the ratios of activity coefficients are essentially the same, *i.e.*, $f = f_0$, and combination of equations 4 and 5 gives

$$[H^+] = \frac{R_0}{R} [H^+]_0 \quad (6)$$

From the measured values of R and R_0 and the known value of $[H^+]_0$, $[H^+]$ for a given concentration of acid whose basicity is unknown can be determined. In the case of the heteropoly acids, the alternative formulas have weights which differ only slightly, *e.g.*, $H_3PW_{12}O_{40}$ and $H_7PW_{12}O_{42}$, so that the molarities are known quite precisely. From $[H^+]$ and the molarity, the basicity is obtained directly, as long as the acid is nearly completely ionized. It should be noted that the data on basicity are not unambiguous, if the state of aggregation of the heteropoly ion is not known. A tribasic monomeric acid and the corresponding hexabasic dimer

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[1] M. Kerker, D. Lee and A. Chou, THIS JOURNAL, **79**, 3355 (1957).

[2] E. Matijević and M. Kerker, *J. Phys. Chem.*, **62**, 1271 (1958).

[3] E. Matijević and M. Kerker, THIS JOURNAL, **81**, 1307 (1959).

[4] Supported by the U. S. Atomic Energy Commission Contract No. AT(30-1)-1801.

[5] Presented in part at the 134th meeting of the American Chemical Society, Chicago, Ill., September 1958.

[6] *Cf.* Recent reviews in W. Hückel, "Structural Chemistry of Inorganic Compounds," Elsevier, New York, N. Y., 1950; A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, New York, N. Y., 1950; J. C. Bailar, "Chemistry of the Coördination Compounds," Reinhold Pub. Corp., New York, N. Y., 1956; J. R. Van Wazer, "Phosphorus and its Compounds," Interscience Publ., New York. N. Y., 1958.

[7] I. M. Klotz, Thesis, The University of Chicago, 1940; see also R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths Sci. Publ., London, 1955.

[8] C. R. Singleterry, Thesis, The University of Chicago, 1940.

would give the same number of hydrogen ions per unit weight and could not be distinguished by this method. Therefore, independent methods must be used in order to establish the state of aggregation. We have employed two methods, *viz.*, light scattering[1,3] and coagulation.[2]

2. **Determination of Ionic Charges by Coagulation.**—According to the Schulze–Hardy rule, the coagulation concentration of an electrolyte depends in a sensitive way on the charge of the counterions in solution. The higher the charge, the lower is the coagulation concentration. Thus, determination of the coagulation concentration of a compound whose ionic state is unknown and comparison with data for known species can reveal the charge of the counterion. This becomes useful for the heteropoly compounds where the stoichiometric ratio of the principal atomic consituents (P/W, P/Mo, etc.) can be determined from chemical analysis, but where the basicity and the state of aggregation (*e.g.*, dimerization) are in doubt.

The method is especially convenient for a number of reasons. First, any decomposition of heteropoly ion into species of lower valency would considerably decrease the coagulation power of the solution, giving much higher coagulation concentrations. Therefore, the low coagulation concentrations which we have obtained, *e.g.*, for 12-tungstophosphate, indicating high valency, cannot be attributed to decomposition. On the other hand, in determination of basicities, decomposition of the heteropoly ions could result in the erroneous conclusion of higher valency of the ions in question.

Secondly, coagulation effects of heteropoly ions eliminate the ambiguity of basicity measurements as to possible alternative formulas, such as H_3X or H_6X_2. Half the molar concentration of ions of double charge would give a much lower coagulation concentration than the corresponding lower charged species. Also, owing to the high charge of these ions, the coagulation effects are observed at very high dilutions (10^{-6} to 10^{-8} *M*) where most of the salts or acids are fully ionized. Therefore, the coagulation values indicate directly the charge of the ion in solution.

The experimental technique and interpretation of the data have been described in detail previously[9] and have been employed recently in a slightly modified form for the determination of the charges of the 12-tungstosilicate, 12-tungstophosphate and 9-tungstophosphate ions in solution.[2] In this paper, the same method has been extended to the heteropoly molybdates.

3. **Solubility Determination.**—Solubility determinations were made following a procedure described by Kratohvil, Težak and Vouk.[10] Solutions of the two precipitation components, *viz.*, $AgNO_3$ and 12-molybdoceric(IV) acid, were mixed in different concentration ratios keeping one component constant. Above the solubility limit, precipitate is formed and the sols scatter light. At the solubility limit the solutions remain optically clear and this can be followed in a very sensitive way by light scattering. The solubility product was calculated from the ionic concentrations at the solubility limit.

Experimental

Materials.—1. **12-tungstophosphoric acid**, $H_7PW_{12}O_{42}$, was the Baker analyzed reagent, purified as described previously.[3]

2.—**9-tungstophosphoric acid**, $H_6P_2W_{18}O_{62}$, and **ammonium 9-tungstophosphate**, $(NH_4)_6P_2W_{18}O_{62}$, were prepared and purified as described previously.[3] **Sodium 9-tungstophosphate**, $Na_6P_2W_{18}O_{62}$, was obtained from the free acid by using the ion-exchange resin Dowex 50W-8X in Na^+ form.

3.—**12-tungstosilicic acid**, $H_4SiW_{12}O_{40}$, was the Baker analyzed reagent, purified as follows. The commercial, free acid was dissolved in as little water as possible; to this, a solution of HCl (1:1) was added and the 12-tungstosilicic acid extracted with ether. The ether was removed from the ether–acid complex by evaporation *in vacuo* and the acid so obtained dissolved in water, recrystallized and then dried *in vacuo* over P_2O_5. **Sodium 12-tungstosilicate**, $Na_4SiW_{12}O_{40}$, was obtained from the free acid using the ion-exchange resin Dowex 50W-8X in Na^+ form.

4.—**12-molybdoceric(IV) acid**, $H_8CeMo_{12}O_{42}$, was prepared in solution either from the neutral or from the acid ammonium 12-molybdocerate(IV) using the ion-exchange resin Amberlite IR-120.[11] The salts of the 12-molybdoceric(IV) acid were soluble enough to prepare a solution of the free acid in concentration required for our experiments. The **ammonium 12-molybdocerate(IV)**, $(NH_4)_8CeMo_{12}O_{42}\cdot 8H_2O$, and the **ammonium hydrogen 12-molybdocerate(IV)**, $(NH_4)_6H_2CeMo_{12}O_{42}\cdot 10H_2O$, were synthesized following the procedure given by Barbieri[12] and improved by Baker.[13] Sixty grams of ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Fisher Reagent), was dissolved in 200 ml. of boiling water to which 100 ml. of a 5% solution of ammonium ceric nitrate, $(NH_4)_2Ce(NO_3)_6$ (Fisher, purified), was added drop by drop from a separatory funnel under constant mixing and heating. The yellow precipitate was filtered and washed with a saturated NH_4NO_3 solution, then with methanol and finally dried. To prepare the acid salt 10 g. of the neutral salt was dissolved in 500 ml. of 2% sulfuric acid, warmed up slightly (30–40°) and filtered. Clear yellow solution was poured into a saturated solution of NH_4NO_3. The yellow precipitate was filtered, thoroughly washed with a saturated solution of NH_4NO_3, then with methanol and dried.

A sample of $(NH_4)_8CeMo_{12}O_{42}\cdot 8H_2O$ prepared independently in another laboratory[14] was compared with ours. Identical absorption spectra in ultraviolet were obtained.

5.—**6-molybdochromic(III) acid**, $H_3CrMo_6O_{21}$, and **6-molybdocobaltic(III) acid**, $H_3CoMo_6O_{21}$, were prepared from their ammonium salts using the ion-exchange resin Amberlite IR-120. **Ammonium 6-molybdochromate(III)**, $(NH_4)_3CrMo_6O_{21}\cdot$aq, and **ammonium 6-molybdocobaltate(III)**, $(NH_4)_3CoMo_6O_{21}\cdot$aq. were given to us by L. C. W. Baker, who prepared the salts according to a procedure described previously.[15]

In all cases where the ion-exchange technique was used for preparation of free heteropoly acids from corresponding ammonium salts, the effluent was carefully checked for the absence of ammonia. In the case of conversion of acids into sodium salts, the completion of the reaction was checked by constancy of the *p*H of the effluent. No loss in concentration of heteropoly ions could be detected during the ion-exchange process. The concentration tests were made spectrophotometrically using a Beckman DU spectrophotometer and choosing an appropriate wave length for each compound.

6.—All other salts used in the experiments were commercial chemicals of highest purity grade purified by recrystallization before use. Redistilled constant boiling **hydrochloric acid** was used in the spectrophotometric determinations of basicity. Methyl orange (Fisher Reagent) was twice recrystallized and dried *in vacuo*.

All solutions were prepared with doubly distilled water, the second distillation being carried out in an all-Pyrex still. The glassware was thoroughly cleaned with cleaning solution and well steamed before use.

Instruments.—Optical densities in spectrophotometric measurements were determined using the Beckman DU spectrophotometer at a wave length of 520 mμ. The cell chamber of the instrument was provided with a thermostat jacket which was connected with the water pump of a constant temperature bath (25°), in which all solutions were kept prior to taking readings. Calibrated Corex cells of approximately 1 cm. width were used. For each sample at least four readings were taken in two different cells and with two fillings of each cell. The precision of reading was ± 0.001 in optical density.

The coagulation process was followed with an Aminco light scattering microphotometer, using the mercury lamp and a filter giving incident light of 546 mμ. The changes in light scattering of the solutions during the coagulation were read over a period of two hours and expressed in turbidities (τ, cm.$^{-1}$). All readings were taken at an angle of 45°.

A Beckman Model G glass electrode *p*H meter was used for *p*H measurements. The scale of the *p*H meter was calibrated with appropriate buffer solutions.

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(9) P. Težak, E. Matijević and K. Schulz, *J. Phys. Chem.*, **55**, 1557 (1951).

(10) J. Kratohvil, B. Težak and V. B. Vouk, *Arhiv kem.*, **26**, 191 (1954)

(11) L. C. W. Baker, G. A. Gallagher and T. P. McCutcheon, THIS JOURNAL, **75**, 2493 (1953).

(12) A. G. Barbieri, *Atti Accad. Lincei*, [5] **23**, 1, 805 (1914).

(13) L. C. W. Baker, private communication.

(14) We are indebted to Professor D. P. Shoemaker, Massachusetts Institute of Technology, for a sample of $(NH_4)_8CeMo_{12}O_{42}\cdot 8H_2O$.

(15) L. C. W. Baker, B. Loev and T. P. McCutcheon, THIS JOURNAL, **72**, 2374 (1950).

Results and Discussion

Basicities.—In order to obtain correct basicities for heteropoly acids by the method described above, two preliminary sets of experiments were found to be necessary. First, we established that equation 6 applies well only if the reference solution has a hydrogen ion concentration which is close to that of the investigated solution. For this reason, we determined the R_0 values for a range of HCl concentrations which covered the methyl orange transition region. In calculating $[H^+]$, the R_0 value closest to the value of R was used so that solutions of comparable acidity were being compared.

Accurate values of R are obtained only when appreciable quantities of both the acid and basic forms of the indicator are present. This means that the working range of $[H^+]$ is limited by the nature of the indicator. To investigate the $[H^+]$ at a higher concentration of heteropoly acid, it is necessary to use an indicator with lower pK and conversely for the low concentration range.

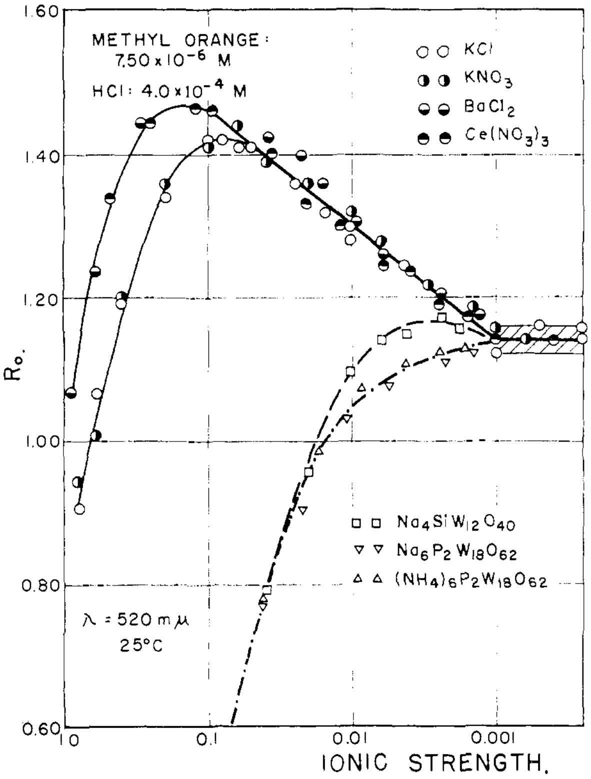

Fig. 1.—The influence of the ionic strength of added neutral electrolytes on the indicator ratio R_0 of methyl orange (7.50×10^{-6} M) in HCl (4×10^{-4} N).

It is possible to extend the method to somewhat lower heteropoly acid concentrations by addition of known amount of HCl to the heteropoly acid solution. Accordingly, some of the experiments were performed both in the presence and absence of HCl. In the former case, the added concentration of HCl was taken into account when the basicities of the heteropoly acids were calculated.

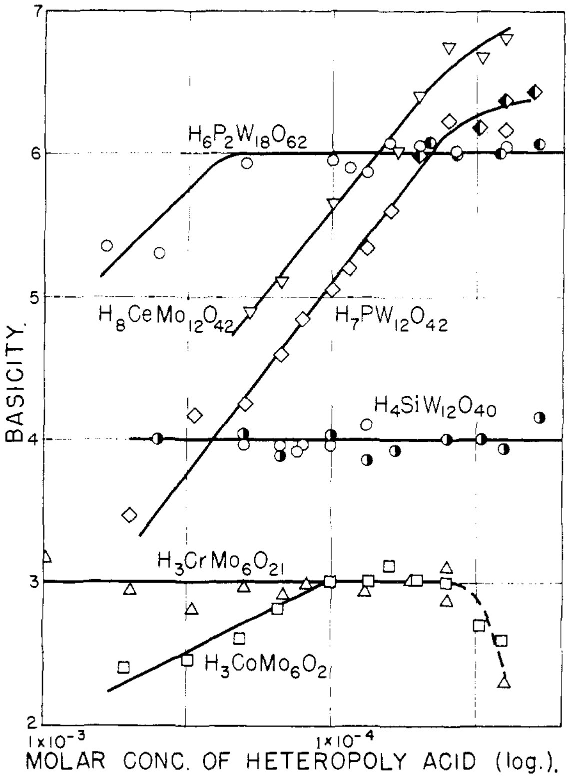

Fig. 2.—Basicities of 12-tungstosilicic acid, 12-tungstophosphoric acid, 9-tungstophosphoric acid, 6-molybdocobaltic(III) acid, 6-molybdochromic(III) acid and 12-molybdoceric(IV) acid plotted against the concentration of investigated solutions.

Secondly, we investigated the influence of neutral electrolytes upon the ionization of methyl orange and hence the value of R_0. Klotz[7] and Singleterry[8] have reported such data for neutral electrolytes of the 1-1 and 2-1_2 types. Since we were working with species of higher charge types, we have extended this investigation both to a wider range of electrolyte concentration and to additional types of electrolytes including the following: KCl, KNO_3, $BaCl_2$, $Ce(NO_3)_3$, $Na_4SiW_{12}O_{40}$, $(NH_4)_6P_2W_{18}O_{62}$ and $Na_6P_2W_{18}O_{62}$.

In order to disentangle the ionic strength effect on R_0 from that due to pH changes, we were limited to electrolytes which do not undergo hydrolysis at the concentrations employed. For example, $La(NO_3)_3$ and $Th(NO_3)_4$ give acid solutions as a result of cationic hydrolysis and could not be used. Similarly, anionic hydrolysis of $Na_3CrMo_6O_{21}$ gave slightly basic solutions and this compound was, therefore, eliminated.

In Fig. 1, the value of R_0 for 4×10^{-4} N HCl and 7.5×10^{-6} M methyl orange is plotted against the ionic strength in the presence of the above neutral electrolytes. We also performed a similar experiment with KCl using a higher concentration of HCl (1×10^{-3} N) and obtained a constant ratio for R_0 at lower and higher HCl concentrations over the whole region of μ as required by equation 5.

Up to an ionic strength of 0.1 M, which is considerably higher than the range in which we worked (<0.01 M), there is no difference in the influence of 1-1, 2-1_2 and 3-1_3 electrolytes on R_0. However the neutral salt effects of sodium 12-tungstosilicate and sodium 9-tungstophosphate are strikingly different giving much lower R_0 values than the salts of lower

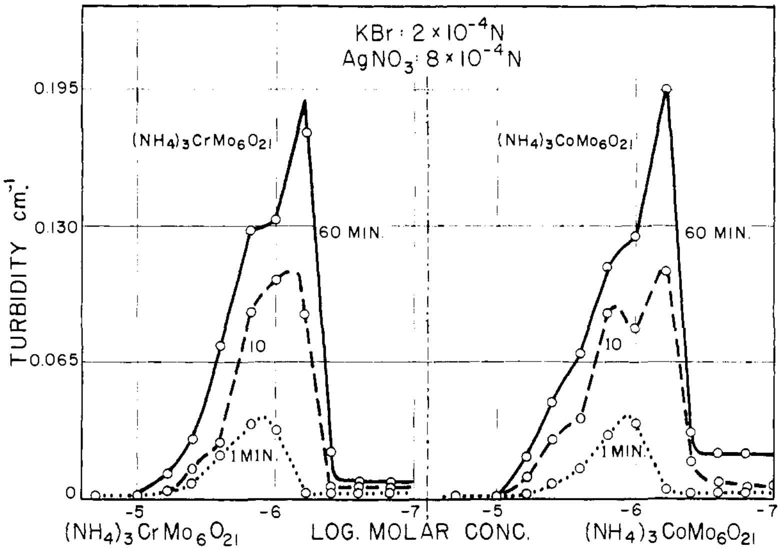

Fig. 3.—Coagulation curves of ammonium 6-molybdochromate(III) and ammonium 6-molybdocobaltate(III) for a positive silver bromide sol *in statu nascendi*, 1, 10 and 60 minutes after mixing the reacting components.

charge type. Whereas at moderate concentrations, the salts of the lower charge types enhance the ionization of the methyl orange, the sodium 12-tungstosilicate and sodium 9-tungstophosphate repress it. This effect is electrostatic and not due to anion hydrolysis since such hydrolysis would actually increase R_0 by virtue of the corresponding increase in pH. The ammonium 9-tungstophosphate gave results similar to the sodium salt which shows that at low concentration the effect of ammonium hydrolysis is not significant compared to the tremendous electrostatic effects.

Upon applying equation 6 to the calculation of $[H^+]$, R and R_0 must be compared both at the same acidity and the same ionic strength. However, the influence of ionic strength on R_0 must be evaluated from the curve in Fig. 1 corresponding to the charge type of the acid being investigated. In practice, a first approximation of the basicity is obtained by utilizing values of R_0 in the absence of added salt. Using the approximate basicity so obtained, it is then possible, by successive approximations, to correct this result for the ionic strength effects. Figure 2 gives the basicities of the 12-tungstosilicic, 12 - tungstophosphoric, 9 - tungstophosphoric, 6-molybdocobaltic(III), 6-molybdochromic(III) and 12-molybdoceric(IV) acids as obtained at different molarities of mentioned acids.

Data obtained in the presence of HCl are denoted with half blackened signs. The consistency of the method is brought out by the fact that although in the presence of HCl one is working at a different part of the R curve, the same basicities are obtained. Since the results in Fig. 2 show that identical basicities are obtained in the presence and absence of HCl, this is an additional indication that no decomposition has taken place at higher pH's. We had previously shown that in the region up to pH 6 these compounds are stable if carefully purified.[3] The fact that addition of HCl does not lower the calculated basicity shows that the heteropoly acids are nearly completely ionized since the mass action effect on the added $[H^+]$ is not appreciable.

According to the results presented in Fig. 2, the 6-molybdochromic(III) and 6-molybdocobaltic(III) acids are tribasic, the latter being incompletely ionized at concentrations greater than 1×10^{-4} M. The possibility of a hexabasic dimer is excluded on the basis of our coagulation results to be discussed below. The 12-tungstosilicic acid is tetrabasic and completely ionized over the concentration range studied. The 9-tungstophosphoric acid is hexabasic and also completely ionized below 3×10^{-4} M. The basicity of the 12-tungstophosphoric acid and 12-molybdoceric acids is definitely higher than six, but at the lowest concentrations used in these experiments they are obviously not fully ionized and therefore the expected basicities of 7 and 8, respectively, have not been obtained.

The downturn of the basicity curves for the tribasic acids (dashed part of the curve) at low acid concentrations illustrates the failure of the method when the indicator is almost completely in the basic form. Under these circumstances, the determination of the indicator ratio R is inaccurate. As pointed out above, in order to extend the results to lower heteropoly acid concentrations, it would be necessary to use an indicator of higher pK. It is very probable, in such a case, that higher basicities for the 12-tungstophosphoric and 12-molybdoceric acids would be obtained, since the degree of ionization would increase with dilution, as indicated by the trend of the relevant curves in Fig. 2.

Charge of Heteropoly Ions.—Figure 3 represents the coagulation curves of ammonium 6-molybdochromate(III) and ammonium 6-molybdocobaltate(III) for positive silver bromide sols 1, 10 and 60 minutes after mixing the components. The shape of the coagulation curve is typical for either large or highly charged counterions. At low concentration of coagulating ion, we have the coagulation limit and at a higher concentration, the stability limit which is due to the reversal of charge. Above the stability limit, the turbidity is low because of the low scattering power of the very small, uncoagulated, recharged, primary particles.[16] The coagulation concentration is obtained by extrapolating the tangent of the steepest part of the coagulation curve to zero turbidity. We note that there is no difference between the 10 and 60 minute limits and that the 1 minute curve gives only a slightly higher coagulation concentration. This small time dependence of the coagulation concentration is also characteristic for negative counterions with charge up to four.

The coagulation concentrations are usually expressed in normalities, but we prefer to use the

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(16) E. Matijević, D. Broadhurst and M. Kerker, *J. Phys. Chem.*, **63**, 1552 (1959).

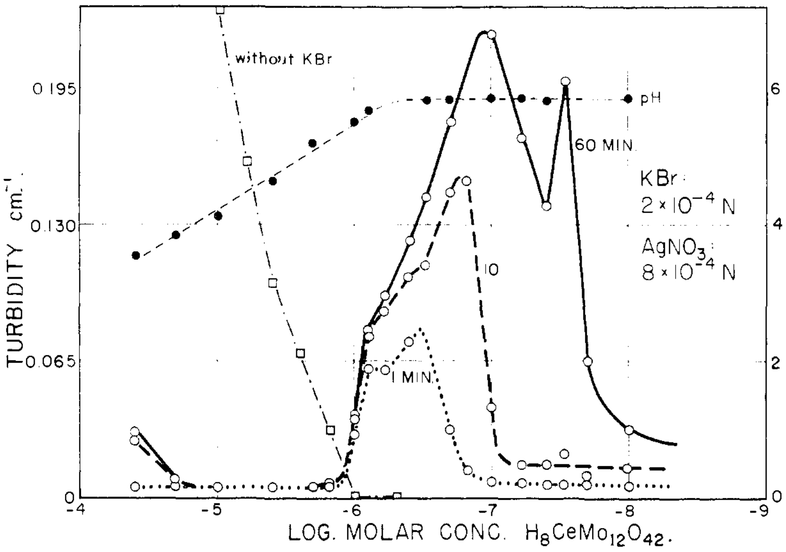

Fig. 4.—Coagulation curves of 12-molybdoceric(IV) acid for a positive silver bromide sol., 1, 10 and 60 minutes after mixing the reacting components. The precipitation curve for the system $AgNO_3$ (8×10^{-4} *N*) + $H_8CeMo_{12}O_{42}$ (varied) is denoted with squares.

molarity scale in this work since the charge of the ions was not known with certainty. When the values obtained in Fig. 3 are compared with coagulation concentrations of other trivalent anions, such as citrate, they show a somewhat lower coagulation concentration. This is explained by the large size of the heteropoly ion. It is known that increase in size causes a decrease in coagulation concentration, this effect being more pronounced with ions of lower valencies.[17] The coagulation values obtained are still higher than those for four valent counterions of similar size, such as 12-tungstosilicate.[2] For all these reasons, we conclude that 6-molybdochromate(III) and 6-molybdocobaltate(III) ions are trivalent in solution.

Figure 4 represents the coagulation curves of silver bromide sols using 12-molybdoceric(IV) acid as the coagulating agent. In this case, the coagulation values decrease markedly with time, a behavior which is typical of highly charged counterions. The critical coagulation time is 60 minutes. The coagulation concentration is very low (1.5×10^{-8} *M*), comparable to that for 12-tungstophosphate but definitely lower than 9-tungstophosphate.[2] This would indicate a charge of about seven, in agreement with the basicity measurements.

The silver salt of the 12-molybdocerate(IV) is known to be sparingly soluble,[16] but no data on solubility are reported. Since we were coagulating positive silver bromide sol using excess of $AgNO_3$ it was necessary to establish whether the solubility of silver 12-molybdocerate(IV) was sufficiently high to avoid the formation of two insoluble salts simultaneously, *viz.*, AgBr and silver 12-molybdocerate(IV). We determined the solubility of the latter and found the values given in Table I, where the solubility product is calculated for four different pairs of $[Ag^+]$ and $[CeMo_{12}O_{42}^{8-}]$.

It is obvious that in the critical coagulation region, the concentrations of molybdocerate(IV) and silver ions are below the limit necessary to form silver 12-molybdocerate(IV).

In Fig. 4, we have plotted the precipitation curve (denoted with squares) obtained using only 8×10^{-4} *N* $AgNO_3$ and a gradient of concentrations of 12-molybdoceric(IV) acid (without adding KBr). This precipitation curve does not interfere with the coagulation curve. However, in the stability region of AgBr ($>10^{-6}$ *M* $H_8CeMo_{12}O_{42}$), the turbidity in the presence of KBr is much lower than when it is absent. This is because, in the presence of KBr, a great part of the Ag^+ is used up in forming very small primary particles of AgBr and also for adsorption as stabilizing ions. This amount of Ag^+ is therefore not available for formation of silver molybdocerate. Furthermore, the concentration of molybdocerate ions is also reduced because of their adsorption on the primary particles. It is this adsorption, with the accompanying reversal of charge, which accounts for the stability region in the first place.

TABLE I

SOLUBILITY PRODUCT, K_{sp}, OF $Ag_8CeMo_{12}O_{42}$

Molar concn. of Ag^+	Molar concn. of $CeMo_{12}O_{42}^{8-}$	Ksp $[Ag^+]^8 \times [CeMo_{12}O_{42}^{8-}]$
1.5×10^{-4}	3.0×10^{-5}	7.7×10^{-36}
1.6×10^{-4}	2.0×10^{-5}	8.6×10^{-36}
1.7×10^{-4}	1.0×10^{-5}	7.0×10^{-36}
2.0×10^{-4}	4.0×10^{-6}	10.2×10^{-36}
	Mean	8.4×10^{-36}

Finally, Fig. 5 shows the comparison of the coagulation limits of all six heteropoly ions investigated. The sequence of these curves, which depends on the ionic charge of the coagulation anions, justifies the formulas used in the diagram. Only in the case of 12-molybdoceric(IV) acid is the order somewhat distorted. Two reasons might account for this. Either the acid is not fully ionized, even in as low concentration as used in the critical coagulation region, or for very highly charged ions, factors other than charge become important and the coagulation process ceases to follow the simple form of the Schulze–Hardy rule.

Structural Considerations and Conclusions

The Heteropoly Tungstic Acids.—Our earlier coagulation work,[2] reinforced by the studies presented in this paper, shows that the basicity of 12-tungstophosphoric acid is seven and that of 9-tungstophosphoric acid is six. Qualitative results based upon *p*H,[18] as well as earlier analytical work[19] also support this view. Similarly, the basicity of

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[17] B. Težak, E. Matijević and K. F. Schulz, THIS JOURNAL, **59**, 769 (1955); E. Matijević, K. F. Schulz and B. Težak, *Croat. Chem. Acta* **28**, 81 (1956).

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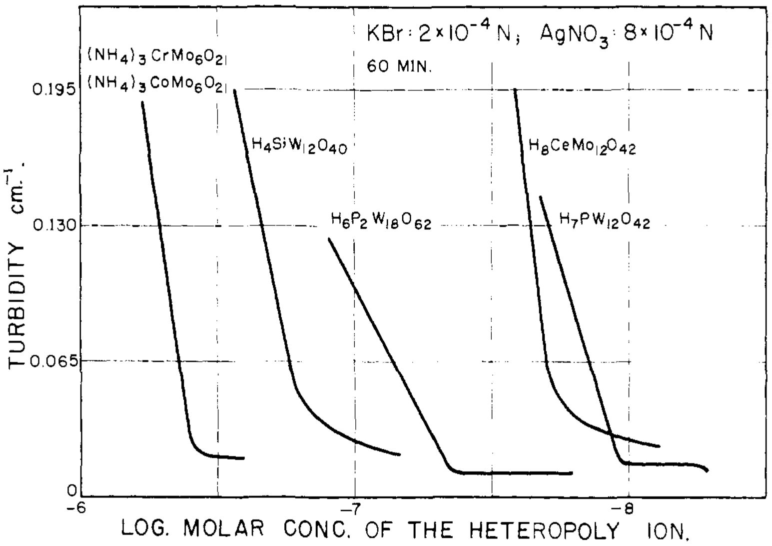

Fig. 5.—A comparison of the coagulation limits of ammonium 6-molybdochromate(III), ammonium 6-molybdocobaltate(III), 12-tungstosilicic acid, 9-tungstophosphoric acid, 12-molybdoceric(IV) acid and 12-tungstophosphoric acid as obtained for a positive silver bromide sol *in statu nascendi*.

12-tungstosilicic acid was found to be four. The state of aggregation of each of these compounds (*i.e.*, monomer, dimer, etc.) was established by light scattering.[1,3,20]

Much of the current literature assumes a tribasicity for 12-tungstophosphoric acid. This was first proposed by Pauling[21] based upon structural considerations and further elucidated by Keggin,[22] based on X-ray studies.

The basicity of such a compound is dependent upon two structural factors, *viz.*, the coördination of the central phosphorus and the extent of the condensation between the parent acids—phosphoric and tungstic acids.

Although it is almost impossible to fix the oxygens directly by X-ray work, the presently available evidence indicates tetrahedral coördination for the central phosphorus. However, this alone does not determine the basicity which is also dependent upon the number of condensations among the parent acids, with the formation of oxygen bridges. Thus, although 9-tungstophosphoric acid probably has tetrahedral coördination of the central phosphorous atoms similar to tetrabasic pyrophosphoric acid, its basicity is six rather than four. In the same way, the basicity of 12-tungstophosphoric acid (seven) need not be the same as the parent phosphoric acid (three). It is not yet possible, then, to decide this question from purely structural considerations and physicochemical experiments of the type described above must be carried out.

For the 12-tungstophosphoric acid, the apparent discrepancy between the tribasicity found in the solid state by X-ray analysis and the heptabasicity which we find in dilute solution can be reconciled by considering that in solution, the trivalent ion takes up two oxygen ions (hydrolysis of two oxygen bridges). Since our spectrophotometric results at $10^{-4.5}$ M (see Fig. 2) and our coagulation results at 10^{-8} M (see Fig. 5) both indicate heptabasicity, we have formulated the acid as heptabasic. We are planning to extend our spectrophotometric experiments to lower concentrations, using an indicator of higher pK, in order to see whether the spectrophotometric curve (Fig. 2), which appears to be approaching a limit of seven, actually does so. There is the possibility of a continued uptake of oxygen ions, leading to even higher basicities. However, in view of the coagulation results, we believe this is unlikely.

The Heteropoly Molybdic Acids.—Baker, *et al.*,[23,24] have recently discussed the structural problem of the 6-heteropoly molybdic acids, including 6-molybdochromic(III) and 6-molybdocobaltic(III) acids. They present a detailed argument, based on chemical evidence, to show that the formula of such acids may be represented by $(H_3XMo_6O_{21})_n$, where X represents the octahedrally coördinated, tervalent, central atom. Our basicity results agree with this formulation, *i.e.*, three ionizable hydrogens per central atom, but as pointed out earlier, basicity determination alone cannot define the state of aggregation, n.

We attempted to determine the molecular weight of these acids by light scattering, but were not successful for two reasons. First, the solubility was too low to obtain solutions of high enough concentration to get appreciable scattering. Secondly, the compounds are highly absorbing so that whatever light was scattered was strongly attenuated before leaving the solution.

However, our coagulation studies definitely indicate an ionic charge of minus three, so that we have proposed the monomeric formulations, $H_3CoMo_6O_{21}$ and $H_3CrMo_6O_{21}$. Rosenheim[25] and Pauling[21] had assumed these were monomers. Baker, Foster, Scholnick and McCutcheon had argued on structural grounds for a dimeric formulation but Tsigdines, Pope and Baker[26] have recently reported cryoscopic measurements in sodium sulfate decahydrate which indicate the monomeric structures.

Our results for the 12-molybdoceric(IV) acid, $H_8CeMo_{12}O_{42}$, are consistent with octahedral coordination of the central atom, and this agrees with the early formulation by Barbieri[12] and the later confirmation by Baker.[11]

Acknowledgment.—We are indebted to Professor L. C. W. Baker of Boston University for a supply of ammonium 6-molybdocobaltate(III) and am-

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monium 6-molybdochromate(III) as well as his refined directions for preparation of ammonium 12-molybdocerate(IV). We are also indebted to Mr. William A. Light for assistance in obtaining some of the preliminary basicity data and Mr. Donald Broadhurst for obtaining some of the coagulation data.

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Mixed Tetra-(chlorobromo)-platinates(II). Equilibrium Constants for Formation in Aqueous Solution[1]

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A radiochemical procedure, combined with a least squares treatment, has been used to obtain the four equilibrium constants for the stepwise replacement by bromide of the ligands in $[PtCl_4]^=$. The equilibrium constants for the single ligand replacement reactions at 25° are 14.5, 8.3, 2.0 and 1.65. The ΔH^0 for each step is estimated to be -1.8 ± 0.3 kcal. The results fail to show that the higher stability of the bromide ligand bond results primarily from π-bonding. Upper limits for the acid hydrolysis equilibrium constants in the system were also obtained.

Introduction

A radiochemical procedure has been used to evaluate the set of four equilibrium constants for the successive substitution reactions indicated by eq. 1

$$[PtCl_{4-n}Br_n]^= + Br^- \rightleftarrows [PtCl_{3-n}Br_{n+1}]^= + Cl^-, K_n \quad (1)$$

where $n = 0, 1, 2, 3$. Platinum(II) belongs to the rather limited group of ions for which the order of stability for halide ligand bonds is reversed from the normal, *i.e.*, Br^- is bonded more strongly than Cl^-.[2] Latimer[3] has estimated that for the overall reaction

$$[PtCl_4]^= + 4Br^- \longrightarrow [PtBr_4]^= + 4Cl^- \quad (2)$$

ΔF° is -6.7 kcal. In addition, Leden and Chatt[4] found an equilibrium constant of 3.4 ($\Delta F^0 = -0.72$ kcal.) for the replacement by bromide of labile chloride *trans* to ethylene in trichloro-(ethylene)-platinate(II).

The higher stability of the bromide bond, compared to chloride, may result from additional π-bonding for the bromide. Bromide has a stronger *trans*-directing effect than chloride, and Chatt, *et al.*,[5] and Orgel[6] have attributed the *trans*-directing property of a ligand to its π-bonding character.

In addition, bromide ligands in platinum(II) complexes are more labile than chloride toward exchange with the free ion.[7] Banerjea, Basolo and Pearson[8] have presented evidence that the substitutions for ligands in platinum(II) complexes are rapid for entering groups which are generally considered to provide a high degree of π-bonding. Electron pairs of the platinum ion, normally considered as non-bonding, are utilized in the π-bonds which therefore give multiple bond character for the complexes. Chatt and Wilkins[9] have found that ΔH^0 for the isomerization of *cis*- to *trans*-dichlorobis-(triethylphosphine)-platinum-(II) is nearly +2.5 kcal./mole. They suggested that the stability of the *cis*-isomer was possibly due to the π-bonding, since the two π-bonds to phosphorus could utilize both the d_{zx} and d_{zy} orbitals of platinum, whereas in the *trans*-isomer only one of these orbitals is suitable for forming π-bonds to the phosphorus atoms. Therefore, a π-bonding ligand is expected to detract from the π-bond *trans* to itself.

It appeared worthwhile to attempt an evaluation of the successive bromide substitution equilibrium constants for $[PtCl_4]^=$. If the stability of the platinum-bromide bond does result from its π-bond character, it is expected that $[PtCl_3Br]^=$ and *cis*-$[PtCl_2Br_2]^=$, which have no bromides *trans* to other bromides, will be especially stable. If the equilibrium constants could be determined with sufficient accuracy, it was expected that high values for K_0 and possibly K_1 would lend support to the π-bonding hypothesis.

Platinum(II) forms the well-known square complexes which are inert. Consequently, halide complexes with coördination number greater than 4 have not been considered. Ample time must be provided to attain equilibrium in the systems. At moderate halide concentration, the acid hydrolysis (or aquation) can yield the trihalide complexes according to reaction 3

$$[PtCl_{4-n}Br_n]^= + H_2O \rightleftarrows [PtCl_{3-n}Br_n(H_2O)]^- + Cl^-, K_{an} \quad (3)$$

where $n = 0, 1, 2, 3$.

Grantham, Elleman and Martin[10] reported 0.018 mole/l. at 25° for K_{a0}, the equilibrium constant for the aquation of $[PtCl_4]^=$. An evaluation of the acid hydrolysis equilibria of the mixed complexes is interdependent upon the determi-

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