[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

Spectrophotometric and Solvent-extraction Studies of Uranyl Phosphate Complexes[1]

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RECEIVED SEPTEMBER 21, 1956

A study of uranyl phosphate complexes has been made at an ionic strength of 1.06 to 1.07 and a temperature of 24 to 25°. The spectrophotometric study yielded a formation constant of 15.5 for the complex $UO_2H_2PO_4^+$. The solvent-extraction data showed that the further complexes $UO_2(H_2PO_4)_2$ and $UO_2(H_2PO_4)_2{\cdot}H_3PO_4$ have the formation constants 21.8 and 10.2, respectively. No statistically significant evidence was obtained for the existence of a still higher complex.

Introduction

One of the first revealing clues concerning the nature of uranyl phosphate complexes was the observation by G. R. Leader[2] that the solubility behavior of $UO_2HPO_4{\cdot}4H_2O$ in nitric acid solutions suggested the presence of a complex ion such as $UO_2H_2PO_4^+$. His data also led him to postulate higher complexes in the presence of excess phosphate. Similar, more comprehensive, studies were pursued by Baes and Schreyer, but their interpretation of the results in terms of the formation of complexes was conditioned in part by the effects of inconstant ionic strength.[3,4] Findings from the original spectrophotometric study of the first complex,[5] which they and J. M. Lesser had made, recently have been revised to take into account the effect of the second complex.[6] These results as well as those of this article will be discussed in some detail later.

1. Spectrophotometric Studies.—Spectrophotometry is one of the more experimentally suitable techniques with which to study complex ions of uranium. The ease and rigor with which spectrophotometric data on complex ions have been interpreted have depended largely upon the complexity of the system and the degree of overlap of the ranges of stability of the complex ions. In his study of chromate–phosphate complexes, Holloway was able to separate largely the two operative equilibria, and thus simplify the problem, by altering the *p*H.[7] The method was based on successive approximations. The slope-intercept method of Benesi and Hildebrand[8] for a single complex has been modified and extended by McConnell and Davidson for the case of two overlapping chlorocupric complexes.[9] Apart from approximations needed in correcting for light absorption by the uncomplexed metal ion, the latter method is subject to the uncertainties usually introduced in a graphical handling of the data. A logarithmic method of graphical analysis similar to that for single complexes by Bent and French[10] has been applied by Kingery and Hume to a study of bismuth thiocyanate complexes.[11] The analysis was made less difficult by the fact that most extinction coefficients apparently were directly estimable or zero. The method of "corresponding solutions" of Bjerrum involves the construction of a graph and interpolations between points.[12] It is applicable to systems of strong complexes. All but the last of the above methods that are applicable in the formation of two complex ions become appreciably less accurate or more time consuming if the two complexes have overlapping ranges of stability. The following algebraic treatment is rigorously applicable to the case of two complexes no matter what their degree of overlap. (Even if appreciable amounts of other complexes are present, a proper use of the data will yield better information concerning one of the two principal complexes than would be obtained otherwise.) A minimum amount of data is required. No extinction coefficients need be directly estimated. The method is most suitable for systems of other than strong complexes. As in all of the above methods except that of Bjerrum, the concentration of unbound complexing agent must be calculated with corrections for its equilibrium as an acid or base and for what is bound in complexes, the latter possibly requiring a few successive approximations. In the present application no more than 20% of the complexing agent was bound to the uranium in any solution.

This treatment is designed for the case of a light-absorbing species A (UO_2^{++}) forming two complexes with a non-light-absorbing, *s*-basic acid H_sB (H_3PO_4).

$$A + XH_sB = AH_{sX-x}B_X + xH^+ \tag{1}$$

$$k_y = \frac{[AH_{sX-x}B_X][H^+]^x}{[A][H_sB]^X} \tag{2}$$

The equilibria are expressed in terms of undissociated acid as the complexing agent because this is its predominant form at the acidities (0.5 and 1.0

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[1] Work done under the auspices of the Atomic Energy Commission. Based on the report of the same title, LA-1996, February 23, 1956, available from the Office of Technical Services, Department of Commerce.

[2] G. R. Leader, University of Chicago Metallurgical Laboratory Report CN-2195, December 26, 1944.

[3] J. M. Schreyer and C. F. Baes, Jr., "The Chemistry of Uranium (VI) Orthophosphate Solutions: Part II, The Solubility of Uranium (VI) Orthophosphates in Phosphoric Acid Solutions," Oak Ridge National Laboratory Report ORNL-1578, June 30, 1953.

[4] C. F. Baes, Jr., and J. M. Schreyer, "The Chemistry of Uranium(VI) Orthophosphate Solutions: Part III, The Solubility Behavior of $UO_2HPO_4{\cdot}4H_2O$ in Perchloric Acid Solutions," Oak Ridge National Laboratory Report ORNL-1579, July 1, 1953; J. M. Schreyer and C. F. Baes, Jr., *J. Phys. Chem.*, **59**, 1179 (1955).

[5] C. F. Baes, Jr., J. M. Schreyer, and J. M. Lesser, "The Chemistry of Uranium(VI) Orthophosphate Solutions: Part I, A Spectrophotometric Investigation of Uranyl Phosphate Complex Formation in Perchloric Acid Solution," Oak Ridge National Laboratory Report AECD-3596, October 20, 1953.

[6] C. F. Baes, Jr., paper entitled "A Spectrophotometric Investigation of Uranyl Phosphate Complex Formation in Perchloric Acid Solution" presented at the Nuclear Engineering and Science Congress, Cleveland, Ohio, December 12–16, 1955; *J. Phys. Chem.*, **60**, 878 (1956).

[7] F. Holloway, THIS JOURNAL, **74**, 224 (1952).

[8] H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949).

[9] H. McConnell and N. Davidson, *ibid.*, **72**, 3164 (1950).

[10] H. E. Bent and C. L. French, *ibid.*, **63**, 568 (1941).

[11] W. D. Kingery and D. N. Hume, *ibid.*, **71**, 2393 (1949).

[12] J. Bjerrum, *Kgl. Danske Videnskab. Selskab., Mat.-fys. Medd.*, **21**, No. 4, 22 (1944).

M H$^+$) that are employed in this investigation. Ionic charges are neglected for the sake of simplicity in these and subsequent equations that are written in general form. The designations to be used are $y = 1, X = M, x = m$ for the first complex, and $y = 2, X = N, x = n$ for the second. Measurements of optical density are made *versus* the concentration of the complexing agent H_sB at a wave length at which the species A, $AH_{sM-m}B_M$ and $AH_{sN-n}B_N$ have markedly different absorption coefficients. The length of the absorption cell is kept constant, as is also c, the total concentration of A in all forms. In addition the temperature and ionic strength are maintained at fixed values. Under these conditions the following equation, analogous to that derived by Holloway,[7] relates the optical density D to D_1, the optical density obtained in the absence of complexing agent.

$$D - D_1 = \frac{\frac{k_1}{[H^+]^m}[H_sB]^M(LcE_2 - D_1) + \frac{k_2}{[H^+]^n}[H_sB]^N(D_3 - D_1)}{1 + \frac{k_1}{[H^+]^m}[H_sB]^M + \frac{k_2}{[H^+]^n}[H_sB]^N} \qquad (3)$$

The quantity LcE_2 is the optical density that would be obtained if $AH_{sM\cdot m}B_M = c$, and D_3 is that corresponding to $AH_{sN-n}B_N = c$. Neither LcE_2 nor D_3 need be directly measured.

A rearrangement of equation 3 gives the following for each i-th solution

$$\Phi_i(D_i - D_1)[k_1] + (D_i - D_1)[k_2] - [k_2(D_3 - D_1)] - \Phi_i[k_1(LcE_2 - D_1)] = -\theta_i\Phi_i(D_i - D_1) \qquad (4)$$

where

$$\theta_i = \frac{[H^+]_i{}^m}{[H_sB]_i{}^M} \text{ and } \Phi_i = \frac{[H^+]_i{}^{n-m}}{[H_sB]_i{}^{N-M}} \qquad (5)$$

A knowledge of the values of m and n is not required at this point. Leaving m and n unspecified, all other quantities in equation 4 are directly measurable except those that are enclosed in brackets. The four constants within brackets can be evaluated in terms of m and n by the determinantal solution of four equations of the form of equation 4. Hence measurements on four aqueous solutions having different phosphate concentrations and designated as α, β, γ and δ provide the following for k_1 and k_2

$$\frac{k_1}{[H^+]^m} = \frac{\left(\frac{\lambda_1}{[H_sB]_\alpha{}^M} - \frac{\lambda_2}{[H_sB]_\beta{}^M} + \frac{\lambda_3}{[H_sB]_\gamma{}^M} - \frac{\lambda_4}{[H_sB]_\delta{}^M}\right)}{\lambda_4 - \lambda_3 + \lambda_2 - \lambda_1} \qquad (6)$$

$$\frac{k_2}{[H^+]^n} = \left(\frac{1}{[H_sB]_\alpha[H_sB]_\beta[H_sB]_\gamma[H_sB]_\delta}\right)^{N-M} \times \left(\frac{\lambda_5 - \lambda_6 + \lambda_7 - \lambda_8}{\lambda_4 - \lambda_3 + \lambda_2 - \lambda_1}\right) \qquad (7)$$

where it is assumed that the hydrogen ion concentration is the same among these four solutions, and

$$\lambda_1 = \frac{(D_\alpha - D_1)}{[H_sB]_\alpha{}^{N-M}}\left[\frac{(D_\delta - D_\gamma)}{[H_sB]_\beta{}^{N-M}} - \frac{(D_\delta - D_\beta)}{[H_sB]_\gamma{}^{N-M}} + \frac{(D_\gamma - D_\beta)}{[H_sB]_\delta{}^{N-M}}\right] \qquad (8)$$

$$\lambda_2 = \frac{(D_\beta - D_1)}{[H_sB]_\beta{}^{N-M}}\left[\frac{(D_\delta - D_\gamma)}{[H_sB]_\alpha{}^{N-M}} - \frac{(D_\delta - D_\alpha)}{[H_sB]_\gamma{}^{N-M}} + \frac{(D_\gamma - D_\alpha)}{[H_sB]_\delta{}^{N-M}}\right] \qquad (9)$$

$$\lambda_3 = \frac{(D_\gamma - D_1)}{[H_sB]_\gamma{}^{N-M}}\left[\frac{(D_\delta - D_\beta)}{[H_sB]\alpha^{N-M}} - \frac{(D_\delta - D_\alpha)}{[H_sB]_\beta{}^{N-M}} + \frac{(D_\beta - D_\alpha)}{[H_sB]_\delta{}^{N-M}}\right] \qquad (10)$$

$$\lambda_4 = \frac{(D_\delta - D_1)}{[H_sB]_\delta{}^{N-M}}\left[\frac{(D_\gamma - D_\beta)}{[H_sB]_\alpha{}^{N-M}} - \frac{(D_\gamma - D_\alpha)}{[H_sB]_\beta{}^{N-M}} + \frac{(D_\beta - D_\alpha)}{[H_sB]_\gamma{}^{N-M}}\right] \qquad (11)$$

$$\lambda_5 = \frac{(D_\alpha - D_1)}{[H_sB]_\alpha{}^M}\Big[[H_sB]_\beta{}^{N-M}(D_\delta - D_\gamma) - [H_sB]_\gamma{}^{N-M}(D_\delta - D_\beta) + [H_sB]_\delta{}^{N-M}(D\gamma - D_\beta)\Big] \qquad (12)$$

$$\lambda_6 = \frac{(D_\beta - D_1)}{[H_sB]_\beta{}^M}\Big[[H_sB]_\alpha{}^{N-M}(D_\delta - D_\gamma) - [H_sB]_\gamma{}^{N-M}(D_\delta - D_\alpha) + [H_sB]_\delta{}^{N-M}(D_\gamma - D_\alpha)\Big] \qquad (13)$$

$$\lambda_7 = \frac{(D_\gamma - D_1)}{[H_sB]_\gamma{}^M}\Big[[H_sB]_\alpha{}^{N-M}(D_\delta - D_\beta) - [H_sB]_\beta{}^{N-M}(D_\delta - D_\alpha) + [H_sB]_\delta{}^{N-M}(D_\beta - D_\alpha)\Big] \qquad (14)$$

$$\lambda_8 = \frac{(D_\delta - D_1)}{[H_sB]_\delta{}^M}\Big[[H_sB]_\alpha{}^{N-M}(D_\gamma - D_\beta) - [H_sB]_\beta{}^{N-M}(D_\gamma - D_\alpha) + [H_sB]_\gamma{}^{N-M}(D_\beta - D_\alpha)\Big] \qquad (15)$$

A combination of four aqueous solutions will give values for $k_1/[H^+]^m$ and $k_2/[H^+]^n$ that are the same within experimental error as those from another combination of four aqueous solutions at the same hydrogen ion concentration only if the correct values for M and N have been used.

It should be noted that in equations 6 to 15 the only spectrophotometric quantities required are *differences* in optical densities. Hence one need not measure directly the optical density D_1, for example, but can obtain instead all of the necessary spectrophotometric data by measuring each of the four solutions *versus* the solution with pure A in it to give the quantities $D_\alpha - D_1$, $D_\beta - D_1$, $D_\gamma - D_1$ and $D_\delta - D_1$. This use of the technique of differential spectrophotometry should also give improved accuracy.[13]

All of the spectrophotometric data were obtained with a Beckman Model DU spectrophotometer. The cell compartment was thermostated at 25.0 ± 0.1° and the solutions were left in a 25.0 ± 0.1° constant-temperature bath for at least 10 hours before measurement. Solutions of hexavalent uranium are known to re-emit absorbed light in the form of fluorescent light with a wave length of 490 mμ and higher.[14,15] Since such fluorescence could have destroyed the Beer's law relation implicit in equation 3, all uranium solutions were measured with a light filter in the light path between the sample compartment and the phototube compartment. The wave lengths at which optical density measurements were made were below 400 mμ. Hence the filter that was used was a Corning No. 5970 Color Filter, which cut out light above 425 mμ.

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(13) For example, see R. Bastian, R. Weberling and F. Palilla, *Anal. Chem.*, **22**, 160 (1950).

(14) S. I. Weissman and R. B. Duffield, "Estimation of Small Quantities of Uranium in Thorium," Los Alamos Scientific Laboratory Report LA-15, July 26, 1943.

(15) C. J. Rodden and J. C. Warf, Part 1. Ch. 1, p. 131, in C. J. Rodden, ed., "Analytical Chemistry of the Manhattan Project," NNES, McGraw-Hill Book Co., Inc., New York, N. Y., 1950.

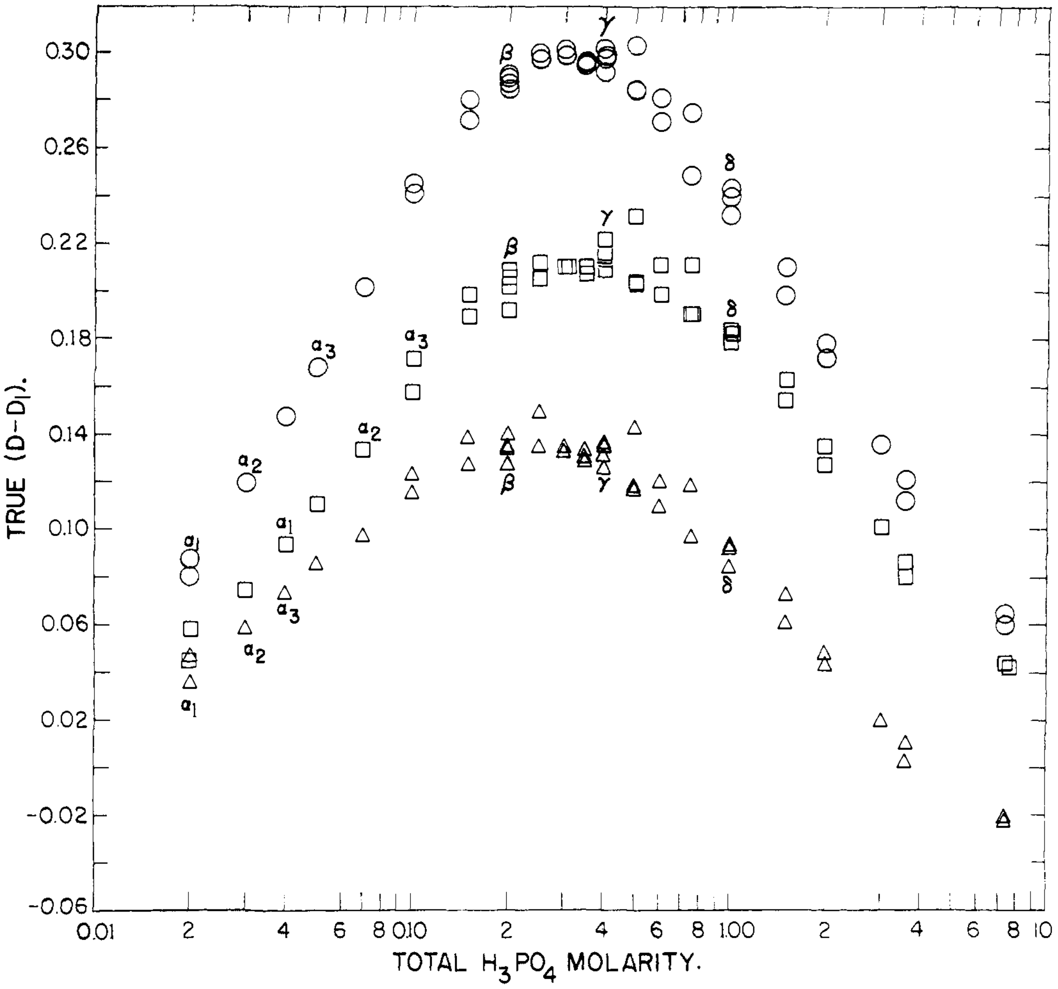

Fig. 1.—Spectrophotometric data at three wave lengths in $UO_2(ClO_4)_2$–H_3PO_4 solutions at 1.004 M H^+ and an ionic strength of 1.06: ○, at 393 mμ; □, at 388 mμ; △, at 383 mμ.

Four different wave lengths were found at which UO_2^{++} and the first two complexes had absorption coefficients favorable to the study of these two complexes. The four different wave lengths—393, 388, 383 and 376 mμ—were located in a region where the extinction coefficients varied rapidly with wave length. The solutions were measured in matched 10.00-cm. silica absorption cells and the appropriate blank corrections always were made. Exactly the same slit width was reproduced for each measurement at a given wave length. The band width was about 4 mμ. It was found that Beer's law was obeyed in the absence or presence of phosphoric acid. The fact that Beer's law was obeyed in 3.7 M phosphoric acid indicated that no significant amounts of polynuclear complexes were formed in the more concentrated phosphoric acid solutions. The concentration of uranium used in the subsequent spectrophotometric measurements was 0.01885 M, in the mid-section of the plots of Beer's law.

All of the spectrophotometric and solvent-extraction studies of the complex-ion equilibria were made in $HClO_4$–$NaClO_4$ solutions having a calculated ionic strength of 1.06 or 1.07. The contribution to the ionic strength of the 0.01885 M $UO_2(ClO_4)_2$ used in the spectrophotometric measurements was assumed to be 3 × 0.01885 = 0.057, but in many solutions the actual contribution to the ionic strength probably was as much as 0.019 less than that because of the effect of phosphate complexing.

The contribution to the ionic strength and to the hydrogen-ion concentration that was made by the dissociation of the phosphoric acid was calculated from a value of k_{1a} = 0.019 ± 0.001 for the first concentration dissociation constant for this acid. This figure was determined at an ionic strength of 1.07 in $NaClO_4$ solutions having no uranium. The method was that of v. Halban and Brüll,[16] in which, for the present application, $HClO_4$ was the source of the known hydrogen-ion concentration and the indicator was thymolsulfonphthalein at a chemically negligible concentration. This value of k_{1a} agrees well with a value of 0.020 (30°, μ = 1.0 to 1.1) by Cher and Davidson[17] and a value of 0.021 (*ca.* 25°, μ = *ca.* 1) estimated by Baes, Jr.[6] (The second and third dissociations of phosphoric acid were ignored because their effect on the complex ion equilibria was negligible.)

The spectrophotometric data on the complexes were obtained at two different values of the hydrogen-ion concentration. Figure 1 represents the data at 1.004 M hydrogen ion and an ionic strength of 1.06. Similar data also were obtained with 0.510 M hydrogen ion and an ionic strength of 1.07. The values of "true ($D - D_1$)" were obtained by measuring the solution with phosphoric acid *versus* a solution having the same uranium concentration, hydrogen-ion molarity and ionic strength, but no phosphoric acid. The blank corrections were determined and applied for each solution. The values of corrected or true H_3PO_4 molarity were consistent within ±3% in every case with the final constants for the complexes as summarized at the end of the paper.

The data at the higher acidity were examined in order to determine M of equations 1 and 2 by plotting log ($D - D_1$) *versus* log (true H_3PO_4 molarity) in a manner similar to that of Bent and French.[10] The slope was found to be +0.82 at about 0.020 M true H_3PO_4 molarity. This H_3PO_4 concen-

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(16) H. v. Halban and J. Brüll, *Helv. Chim. Acta*, **27**, 1719 (1944).

(17) M. Cher and N. Davidson, This Journal, **77**, 793 (1955).

tration is a little too high to allow more than an approximate identification of M with the slope. A better approximation is to take $M = +0.82\ (1 + k_1[H_3PO_4]^M/[H^+]^m)$. Anticipating the values of $k_1 = 15.5$, $M = 1$ and $m = 1$, one calculates $M = 1.07$ which is 1 within experimental error. Hence a value of unity was taken for M. The data at both acidities were tested for the most consistent value for N by a method derived from a treatment for dibasic acids.[18] The best value by far for N was 2. However, the resulting values for $k_2/[H^+]^n$ varied considerably more than the values for $k_1/[H^+]^m$, thus indicating the probable presence of a still higher complex.

Because of the presence of the third complex it was decided not to estimate values of $k_2/[H^+]^n$ from the spectrophotometric data. Only values of $k_1/[H^+]^m$ were calculated by the method of equations 6 to 15, which automatically corrected for the presence of the second complex. Rules of thumb concerning the optimum spectrophotometric relations as summarized in an analogous treatment of dibasic acids[19] were modified to minimize the effect of the third complex. The data that were used were confined to solutions for which it was later estimated that the one with the highest phosphoric acid concentration (solution δ) had about 21% of the uranium in the form of the third complex. (The resulting percentage of error produced in $k_1/[H^+]^m$ should be much smaller than this, however.) Figure 1 and Table I indicate the points that were used at 1.004 M H^+. Likewise, Table II shows the data that were used at 0.510 M H^+. Equations 6, 8, 9, 10 and 11 were used in calculating the values of $k_1/[H^+]^m$ given in the last column of Tables I and II. The constancy within experimental error of these values within each table further confirms that $M = 1$ and $N = 2$. The average value of $k_1/[H^+]^m$ obtained from Table I is $k_1/1.004^m = 15.9 \pm 1.9$.

TABLE I

CALCULATION OF $k_1/[H^+]^m$ AT 1.004 M H^+ FROM EQUATION 6 ($\mu = 1.06$, $[H_3PO_4]_\beta = 0.180$ M, $[H_3PO_4]_\gamma = 0.373$ M, $[H_3PO_4]_\delta = 0.956$ M)

Wave length, mμ	$[H_3PO_4]\alpha$, M	$D\alpha - D_1$	$D_\beta - D_1$ (av)	$D\gamma - D_1$ (av)	$D_\delta - D_1$ (av)	$\frac{k_1}{[H^+]^m}$
393.0	0.0159	0.084(av)	0.2884	0.2981	0.2388	15.3
393.0	.0242	.1195	.2884	.2981	.2388	16.6
393.0	.0415	.168	.2884	.2981	.2388	16.3
388.0	.0328	.094	.2026	.2155	.1823	13.4
388.0	.0592	.1335	.2026	.2155	.1823	12.7
388.0	.0866	.1648(av)	.2026	.2155	.1823	16.1
383.0	.0159	.0415(av)	.1341	.1321	.0893	16.1
383.0	.0242	.059	.1341	.1321	.0893	17.7
383.0	.0328	.0735	.1341	.1321	.0893	19.1

Similarly, the average and standard deviation obtained from Table II is $k_1/0.510^m = 28.2 \pm 5.2$. Solving for the value of m one obtains $m = 0.85 \pm 0.32$. In view of the magnitude of the standard deviation, there is little justification for assuming m to be other than unity. Hence the value of m is taken to be exactly 1. Use of $m = 1$ gives $k_1 = 16.0 \pm 1.9$ and $k_1 = 14.4 \pm 2.7$, respectively, the grand mean of which is $k_1 = 15.5 \pm 1.6$.

TABLE II

CALCULATION OF $k_1/[H^+]^m$ AT 0.510 M H^+ FROM EQUATION 6 ($\mu = 1.07$, $[H_3PO_4]_\beta = 0.0819$ M, $[H_3PO_4]_\gamma = 0.1185$ M, $[H_3PO_4]_\delta = 0.4114$ M)

Wave length, mμ	$[H_3PO_4]\alpha$, M	$D\alpha - D_1$	$D\beta - D_1$ (av)	$D\gamma - D_1$ (av)	$D_\delta - D_1$ (av)	$\frac{k_1}{[H^+]^m}$
393.0	0.0138	0.1275	0.3093	0.3298	0.3108	25.9
393.0	.0215	.174	.3093	.3298	.3108	26.9
393.0	.0296	.2145	.3093	.3298	.3108	31.4
388.0	.0138	.089	.2253	.2445	.2378	24.2
388.0	.0215	.1215	.2253	.2445	.2378	24.6
388.0	.0379	.165(av)	.2253	.2445	.2378	21.3
383.0	.0138	.0675	.1535	.1618	.1388	29.6
383.0	.0215	.0905	.1535	.1618	.1388	30.4
383.0	.0296	.112	.1535	.1618	.1388	39.7

It might be mentioned that in principle one could rigorously extend the method of this section as embodied in equations 4 to 15 to the case of the formation of three complexes instead of two. However, the solution of the sixth-order determinants that would be involved is thought to necessitate such a prohibitive amount of work as to be impractical.

2. Solvent-extraction Studies.—Although the spectrophotometric data had allowed an evaluation of the formula and stability of the first complex, they had not done so reliably for the second complex, and they had only shown the probable existence of a third complex species. However, experiments with solvent extraction were found to yield data that more readily delineated the nature of the second and third complexes.

The equilibria are expressed in terms of equations 1 and 2 with $y = 1$, $X = M = 1$, $x = m = 1$ and $k_1 = 15.5$ for the first complex; $y = 2$, $X = N$, $x = n$ for the second; and $y = 3$, $X = P$, $x = p$ for the third. The algebraic handling of Leden's method[20] by Sullivan and Hindman[21] can be extended to allow the implicit evaluation of the extraction equilibrium constant k, as well as the determination of k_2 and k_3 by means of the equations

$$k_2 = \frac{\left(1 - \frac{f_\alpha}{f_r} - \mu_\alpha k_1\right)\pi_\beta - \left(1 - \frac{f_\beta}{f_r} - \mu_\beta k_1\right)\pi_\alpha}{\nu_\alpha\pi_\beta - \nu_\beta\pi_\alpha} \quad (16)$$

$$k_3 = \frac{\left(1 - \frac{f_\beta}{f_r} - \mu_\beta k_1\right)\nu_\alpha - \left(1 - \frac{f_\alpha}{f_r} - \mu_\alpha k_1\right)\nu_\beta}{\nu_\alpha\pi_\beta - \nu_\beta\pi_\alpha} \quad (17)$$

where

$$\mu_i,\ \nu_i \text{ or } \pi_i = \frac{f_i[H_sB]_i{}^X}{f_r[H^+]_i{}^x} - \frac{[H_sB]_r{}^X}{[H^+]_i{}^x} \quad (18)$$

and $X = M, x = m$ for μ; $X = N, x = n$ for ν; and $X = P$, $x = p$ for π. The quantities f_α, f_β and f_r represent the fractions of aqueous uranium that are complexed at three different complexing agent concentrations none of which is zero. The quantities f_α/f_r and f_β/f_r are determined experimentally. The determination of N and P rests upon the fact that at the same acidity various pairs of solutions serving as α and β will give values of k_2 and k_3 that are constant within experimental error only if the right values have been chosen for N and P. Similarly, the obtaining of the same values of k_2 and k_3 at different acidities gives evidence of the proper choice for n and p.

Dibutyl phosphate dissolved in kerosene was used as the extracting agent. A purified grade of dibutyl phosphate, obtained from the Victor Chemical Works, was used without further purification. A sample of it was titrated with sodium hydroxide to determine its dibutyl phosphate content and the content of the likely contaminant monobutyl phosphate.[22] Its composition by weight corresponded to 96.0% dibutyl phosphate, 0.35% monobutyl phosphate and 3.65% of non-acidic material. This small amount of monobutyl phosphate would not appreciably extract uranium[23] nor

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(18) B. J. Thamer and A. F. Voigt, *J. Phys. Chem.*, **56**, 225 (1952).

(19) B. J. Thamer, *ibid.*, **59**, 450 (1955).

(20) I. Leden, *Z. physik. Chem.*, **A188**, 160 (1941).

(21) J. C. Sullivan and J. C. Hindman, THIS JOURNAL, **74**, 6091 (1952).

(22) R. M. Wagner, "The Hydrolysis Products of Tributyl Phosphate and Their Effect on the Tributyl Phosphate Process for Uranium Recovery," Hanford Works Report HW-19959, April 15, 1951.

(23) D. C. Stewart and T. E. Hicks, "Alkyl Phosphoric Acid Extractions," University of California Radiation Laboratory Report UCRL-861, August 9, 1950.

would it form a precipitate with it.[22] If the non-acidic material were tributyl phosphate, this component by itself should have no extracting action because no nitrate was present in these solvent-extraction experiments.[24] In any case the non-acidic material was considered to act only as a diluent. All concentrations reported herein for dibutyl phosphate have been corrected for these impurities. Kerosene was used as the organic solvent because it gave good phase separations. The dibutyl phosphate solutions always were prepared from the same stock of kerosene.

Studies by Wagner[22] have indicated that with 0.005 to 0.01 *M* dibutyl phosphate in a paraffinic hydrocarbon mixture (AMSCO 125-90 W) the extraction equilibrium conforms to the equation

$$UO_2^{++}(aq) + 2HD(org) = UO_2D_2(org) + 2H^+(aq) \quad (19)$$

$$k = \frac{(U)}{[UO_2^{++}]} \times \frac{[H^+]^2}{(HD)^2} \quad (20)$$

where (HD) is the molarity of free dibutyl phosphate in the organic phase and (U) is the molarity of UO_2D_2 in the organic phase. Equations 19 and 20 also have been verified for extractions with di-(2-ethylhexyl)-phosphoric acid in *n*-hexane over the range of 10^{-5} to 0.2 *M* initial uranium, 0.001 to 2 *M* extractant, and 0.1 to 2 *M* perchloric acid in the aqueous phase.[25] However, some results obtained by Stewart and Hicks[23] have indicated that with 0.004 to 0.015 *M* dibutyl phosphate in *n*-hexane and an aqueous phase containing 0.58 or 1.98 *M* HNO_3, the extraction coefficient varies as the third power of the concentration of free dibutyl phosphate. Studies by Burger[26] have indicated that appreciable dimerization of dibutyl phosphate might take place in the organic phase. The data of Table III were obtained in order to determine what dibutyl phosphate dependence was operative under the experimental conditions of this investigation. Since the total phosphoric acid molarity is the same for each solution, so also is the fraction of aqueous uranium that is uncomplexed. Under these conditions the slope of the log-log plot of the fourth *versus* the third column should be equal to the number of dibutyl phosphate molecules reacting with each uranyl ion in equation 19. The slope of the least-squares straight line drawn through these points is 1.99, *i.e.*, a value of 2 within experimental error. Hence these data indicate that equations 19 and 20 as written are the correct relations. (The values calculated for the third column of Table III were calculated on the assumption of two dibutyl phosphate groups per uranium atom in the extracted species. However, the value of this assumed figure would influence the slope only slightly.) If the non-acidic impurity in the dibutyl phosphate were tributyl phosphate, the molarity of the latter would be 3% of the initial dibutyl phosphate molarity. Although the data of Table III provide support for the use of equations 19 and 20, it is possible that this small amount of tributyl phosphate might exert some synergistic influence on the extraction such as it has been found to do with di-(2-ethylhexyl)-phosphoric acid.[25] Of the data to be presented shortly in Table IV, the equilibration that would be affected the most by such an effect would be the one with a total phosphate molarity of 3.76, because the uranium loading in the organic phase would be the least in that equilibration. That equilibration was repeated in a separate experiment with the organic phase containing an amount of added Eastman tributyl phosphate equal to 3% of the dibutyl phosphate molarity. Thus this equilibration involved twice the tributyl phosphate concentration that those of Table IV might have. The extraction coefficient in this equilibration was 4% less than that of the otherwise identical one in Table IV. The difference probably was within experimental error and, in any event, no increased synergistic effect was observed. Hence, it is concluded that no such measurable effect is operative in the equilibrations presented in Table IV. The hydrogen-ion dependence as given in equations 19 and 20 receives approximate corroboration in the acid range 0.5 to 1.0 *M* H^+ of the present experiments from data obtained by Stewart and Hicks[23] with dibutyl phosphate dissolved in dibutyl ether.

TABLE III

THE DIBUTYL PHOSPHATE DEPENDENCE OF THE URANIUM EXTRACTION COEFFICIENT *E* AT 1.004 *M* TOTAL H_3PO_4

$V_{aq}/V_{org} = 1$, 0.510 *M* H^+

Initial (HD)	(U) at equilibrium	(HD) at equilibrium	*E*
0.0817	0.00733	0.0592	1.64
.0817	.00719	.0594	1.62
.1441	.01035	.1090	6.51
.192	.01682	.1399	8.29

TABLE IV

THE SOLVENT EXTRACTION OF URANIUM AT VARIOUS PHOSPHORIC ACID CONCENTRATIONS

H^+, *M*	Total phos-phate, *M*	True $[H_3PO_4]$	(U)	*E*	$\frac{V_{aq}}{V_{org}}$	(HD) from eq. 21	$\frac{f}{f_{.35}}$ from eq. 22
0.510	0.3514	0.323	0.01035	8.70	1	0.0539	0.989
.510	.3514	.323	.01037	8.85	1	.0538	1.010
.510	.6024	.562	.00912	3.82	1	.0560	.402
.510	1.004	.947	.00733	1.64	1	.0592	.1546
.510	1.004	.947	.00719	1.62	1	.0594	.1516
.510	1.505	1.427	.00520	0.713	1.167	.0617	.0618
.510	2.545	2.427	.00247	.269	1	.0678	.01933
.510	2.545	2.427	.00228	.263	1	.0681	.01873
1.036	2.545	2.473	.00224	.240	1	.0684	.0699
1.036	2.545	2.473	.00220	.232	1	.0685	.0673
0.510	3.76	3.597	.000931	.0897	1	.0705	.00596

If one equilibrates V_{org} milliliters of organic phase containing originally a dibutyl phosphate molarity of $(HD)_{in}$ with V_{aq} milliliters of aqueous phase containing uranium, the following relation holds at equilibrium

$$(HD) = \frac{(HD)_{in} - 2(U)}{1 + \frac{1}{k_{HD}}\left(1 + \frac{k_a}{[H^+]}\right)\frac{V_{aq}}{V_{org}}} \quad (21)$$

where k_{HD}, the distribution coefficient for undissociated dibutyl phosphate, has been determined to be 8.0 ± 0.4, and k_a, the aqueous ionization constant for dibutyl phosphate, is estimated to be 0.031 by means of Wagner's data[22] and the Debye–Hückel equation. Equation 21 is used in all of the solvent-extraction equilibrations reported here for calculating the molarity of free dibutyl phosphate in the organic phase at equilibrium. The equation

$$\frac{f_i}{f_r} = \left(\frac{[H^+]_i}{[H^+]_r}\right)^2\left(\frac{(HD)_r}{(HD)_i}\right)^2\left(\frac{E_i}{E_r}\right) \quad (22)$$

relates the desired quantity f_i/f_r for an i-th solution to the uranium extraction coefficients, E_i and E_r, of the i-th solution and the r-th, or reference, solution, respectively. In the present application the reference solution is the average of the two at the lowest complexing agent concentration in Table IV. The r-th solution had as its principal uranium species the first complex, the stability of which was known from the spectrophotometric studies. Thus the r-th solution, in effect, represents the evaluation of *k* in equation 20. This experimental arrangement allowed all extraction coefficients to be within a factor of about 10 of unity in order to minimize errors due to imperfect phase separations, and it allowed (HD) of Table IV to be within 13% of a constant value in order to minimize errors due to any slight deviation from equation 19.

The solvent-extraction equilibrations were conducted in separatory funnels shaken at maximum pitch on a Burrell Model BB Wrist-Action Shaker. The temperature was 24.0 ± 0.5°. The shaking time was 1 hour, which was proven by tests to give complete equilibration. At the end of this period the separatory funnels were allowed to stand for one more hour in order to allow complete phase separation before the phases were analyzed. Observations under a strong light at this time showed the aqueous phase to be completely free of suspended material, but the organic phase sometimes had a fine mist of aqueous droplets in it. Tests indicated that although longer standing caused the mist to

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(24) R. L. Moore, "Mechanism of Extraction of Uranium by Tributyl Phosphate," Atomic Energy Commission Report AECD-3196, June 11, 1951.

(25) K. B. Brown, *et al.*, "Narrative Status Report, Raw Materials Chemistry Section," Oak Ridge National Laboratory Report ORNL-2002, November 11, 1955.

(26) L. L. Burger, "Partition of Dibutyl Phosphate," General Electric Company Report HW-33682, November 8, 1954.

disperse, the analyses of the two phases remained unchanged. The data have been summarized in Table IV. The initial concentration of uranium in the aqueous phase was 0.0115 *M*. The initial concentration of dibutyl phosphate in the organic phase was 0.0817 *M*. If the equilibrated phases were allowed to stand several hours before analysis, a pale yellow precipitate would form. The precipitate may have been the uranyl dibutyl phosphate salt, judging from solubility figures that have been given for it by Wagner.[22] However, the data of Table IV were obtained in the absence of any precipitate, and presumably they should be explainable within the scope of equilibria that have already been formulated. The uranium concentration in the aqueous phase was determined by analyzing an aliquot by the procedure of Schreyer and Baes,[27] using smaller quantities of reagents and applying an indicator correction. The uranium concentration in the organic phase was determined on a 20-ml. aliquot by diluting it fourfold with kerosene, re-extracting with three successive 20-ml. portions of 1:3 85% H_3PO_4, and then using the same analytical procedure. Experiments indicated that the re-extraction procedure was quantitative. The values of true $[H_3PO_4]$ given in Table IV were calculated from the values of total phosphate molarity as in the spectrophotometric studies. They are consistent within ±1% with the final constants for the complexes as summarized at the end of the paper.

The values of $f/f_{0.35}$ in the last column of Table IV have been plotted *versus* phosphate molarity in Fig. 2. The values $N = 2$, $n = 2$, $P = 3$, $p = 2$ have been assumed in calculating the results given in Table V, which includes calculations from all of the data at 0.510 M H^+. The standard deviations given for k_2 and k_3 at the bottom of the table indicate good consistency among the assumed values of $N = 2$, $P = 3$, and the experimental data. The same type of calculation has been repeated in Table VI, with the same assumptions but with point β at 1.036 M H^+. The results confirm that, in equations 1 and 2, $N = 2$, $n = 2$ for the second complex and $P = 3$, $p = 2$ for the third. In Tables V and VI all available combinations of points were used for α and β except those involving adjacent points, *i.e.*, those immediately to the left and right of one another in Fig. 2. Such combinations were omitted in order to keep the effect of experimental error to a minimum. The grand means of the results of Tables V and VI give $k_2 = 21.8 \pm 2.0$ and $k_3 = 10.2 \pm 0.5$ for these equilibria in equations 1 and 2. The curves that have been drawn in Fig. 2 have been calculated with the aid of these values.

TABLE V

CALCULATIONS OF k_2 AND k_3 FROM DATA AT 0.510 M H^+ BASED ON THE ASSUMPTION $N = 2$, $n = 2$, $P = 3$, $p = 2$

Point α		Point β			
True $[H_3PO_4]\alpha$	$\frac{f\alpha}{f_{0.35}}$	True $[H_3PO_4]\beta$	$\frac{f\beta}{f_{0.35}}$	k_2 from eq. 16	k_3 from eq. 17
0.562	0.402	1.427	0.0618	22.3	11.1
.562	.402	2.427	.01933	25.7	9.0
.562	.402	2.427	.01873	24.4	9.8
.562	.402	3.597	.00596	19.2	13.0
.947	.1531(av)	2.427	.01933	22.6	9.2
.947	.1531(av)	2.427	.01873	20.3	9.9
.947	.1531(av)	3.597	.00596	13.3	12.3
				k_2 = 21.1 ± 3.8	k_3 = 10.6 ± 1.4

TABLE VI

CALCULATIONS OF k_2 AND k_3 WITH POINT α AT 0.510 M H^+ AND POINT β AT 1.036 M H^+ BASED ON THE ASSUMPTION $N = 2$, $n = 2$, $P = 3$, $p = 2$

Point α		Point β			
True $[H_3PO_4]\alpha$	$\frac{f\alpha}{f_{0.35}}$	True $]H_3PO_4]\beta$	$\frac{f\beta}{f_{0.35}}$	k_2 from eq. 16	k_3 from eq. 17
0.562	0.402	2.473	0.0699	24.8	9.6
.562	.402	2.473	.0673	23.2	10.6
.947	.1531(av)	2.473	.0699	21.3	9.6
.947	.1531(av)	2.473	.0673	18.7	10.5
				k_2 = 22.0 ± 2.3	k_3 = 10.1 ± 0.5

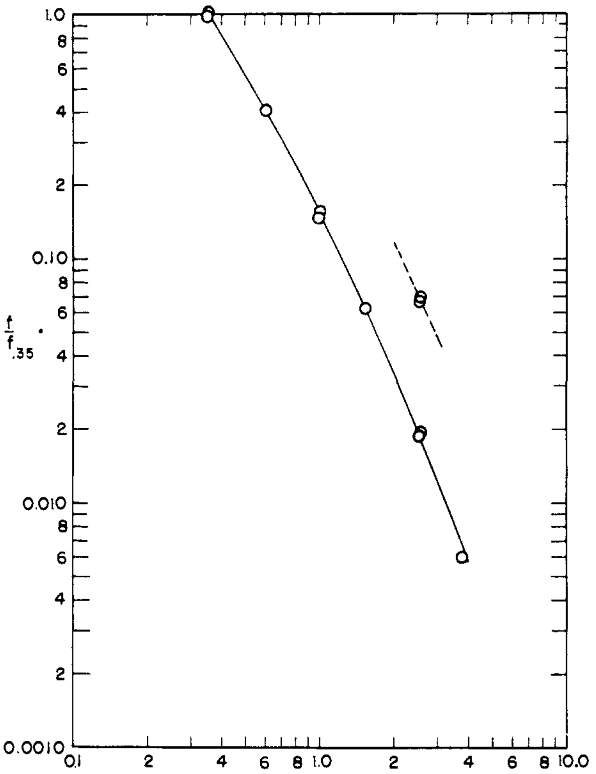

Fig. 2.—Values of $f/f_{0.35}$ *vs.* total phosphate molarity from Table IV and curves calculated from the three complex ion equilibria: solid curve, 0.510 M H^+; dotted curve, 1.036 M H^+.

Other assumed combinations of n and p fit the data much more poorly. An extension of the method of equations 16, 17 and 18 can be used to include a 1:4 uranyl phosphate complex. Since the value of k_4 thus found is 1 ± 2, it is concluded that no fourth complex is present.

Discussion

It is thought that nearly the best experimentally feasible conditions were obtained for the attainment of constancy of activity coefficients and concentration constants. Biedermann and Sillén have obtained evidence in $HClO_4$–$NaClO_4$ solutions of ionic strength 3 tending to indicate that the activity coefficients of cations remain constant from 0.0 M to at least 0.6 M $HClO_4$.[28] It has been assumed that a constancy of activity coefficients held for cations and neutral species in the present experiments. Appreciable concentrations of phosphoric acid had to be used in studying the uranyl phosphate complexes. The value of k_1 was determined entirely from points of 1 M H_3PO_4 or less. Most of the data used in calculating the values of k_2 and k_3 were obtained at phosphoric acid concentrations of 2.5 M or less. The one exception, the point at 3.76 M H_3PO_4, was used in less than 20% of these calculations. It departed more from the

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[27] J. M. Schreyer and C. F. Baes, Jr., "The Volumetric Determination of Uranium (VI) in Phosphate Solutions," Oak Ridge National Laboratory Report ORNL-1292, May 4, 1952; *Anal. Chem.*, **25**, 644 (1953).

[28] G. Biedermann and L. Sillén, *Arkiv Kemi*, **5**, 425 (1953); *C. A.* **47**, 11938^g (1953).

other data than any other point, as may be seen in Fig. 2. This departure may have been simply experimental error, or it may have been a result of appreciable alteration in the dielectric constant of the solvent or change in the specific nature of the ionic field due to the higher phosphoric acid concentration. Both of these effects could alter the activity coefficients,[29] but they probably would not affect the determined values of k_2 and k_3 drastically, because the second and third complexes were found to be neutral in charge and they were the most important species to be affected in the more concentrated phosphoric acid solutions. If an effect of appreciable concentrations of phosphoric acid on the activity coefficients was tolerated as being largely unavoidable, nevertheless there was avoided the additional larger effect that could be caused by a varying ionic strength.

Inasmuch as 0.5 to 1.0 *M* $HClO_4$ was present in all of the experiments, the hydrolysis of the 0.001 to 0.02 formal uranium present was negligible.[30,31] Insignificant error is introduced into the present studies by assuming that $HClO_4$ is completely ionized in mixtures with $NaClO_4$ having a total concentration of 1 *M*. The data of Hood, Redlich and Reilly[32] indicate $HClO_4$ to be so strong an acid that it probably would be ionized to an extent greater than 97% in all of the present solutions. It also might be mentioned that in both the spectrophotometric and solvent-extraction studies the acid liberated by the formation of the uranyl phosphate complexes was considered not to alter appreciably the hydrogen-ion concentration of the solution. The maximum variation in the hydrogen ion so liberated was 0.027 *M* in the spectrophotometric data that were used. However, the resultant effect was negligible in the calculations pertaining to the first complex. The maximum variation of the concentration of hydrogen ion liberated in the solvent-extraction experiments was only 0.006 *M*; the effect probably was less than experimental error.

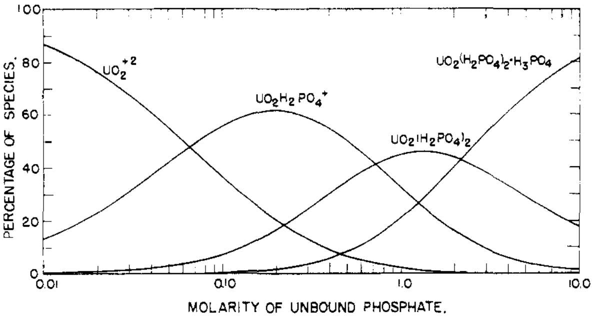
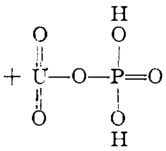


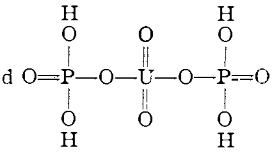
Fig. 3.—Relative amounts of species as a function of unbound phosphate concentration; 1.00 *M* H^+; μ = 1.06 to 1.07.

The structure of the first two complexes (exclusive of hydration) could be represented by



$\mathrm{{}^{+}O{=}U({=}O){-}O{-}P({=}O)(OH)_2}$

and



$\mathrm{(HO)_2P({=}O){-}O{-}U({=}O)_2{-}O{-}P({=}O)(OH)_2}$

where the double bonds would be understood to have some ionic character. The third complex might owe its existence to hydrogen bonding as in one of the following structures or a combination of the two:

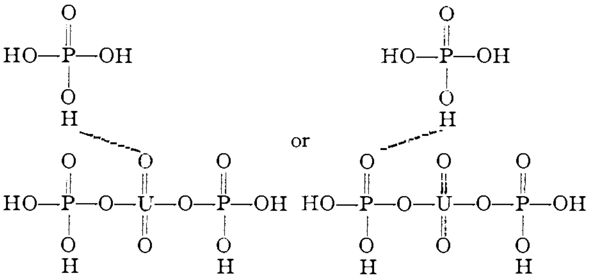


Figure 3 shows the percentage of each uranium species that is calculated from the above results to be present at any phosphoric acid concentration. It may be noted that the results recently obtained by Baes from spectrophotometric measurements in 1 *M* $HClO_4$ agree substantially with the above conclusions concerning the first and second complexes.[6] His formation quotient for the first complex would appear to be reliable, but the value for the second would be less so because the use of as much as 0.6 *M* H_3PO_4 would introduce appreciable amounts of a third complex, as may be seen from Fig. 3. His repetition of the spectrophotometric measurements with 0.1 *M* $HClO_4$–0.9 *M* $NaClO_4$ led him to consider the first complex to be a mixture of $UO_2H_2PO_4^+$ and $UO_2H_3PO_4^{++}$ and the second complex to be a mixture of $UO_2(H_2PO_4)_2$ and $UO_2(H_2PO_4)(H_3PO_4)^+$. Although the results of the present spectrophotometric study could have been interpreted in terms of the presence of a small amount of $UO_2H_3PO_4^{++}$ along with $UO_2H_2PO_4^+$, there was no statistical justification for doing so. It is thought that the solvent-extraction data at 2.545 *M* total phosphate, together with the other values in Table IV, provide striking evidence that the 1:2 and 1:3 uranyl phosphate complexes have the same charge as the uranium species that is extracted into the organic phase, *i.e.*, zero. Hence the species $UO_2(H_2PO_4)(H_3PO_4)^+$ must have been present to a much smaller extent than $UO_2(H_2PO_4)_2$ in the 0.5 to 1.0 *M* hydrogen-ion concentration of these experiments. It is evident that the conclusions based on the measurements of Baes in 0.1 *M* $HClO_4$–0.9 $NaClO_4$ might differ significantly from those of the present data in 0.5 *M* $HClO_4$–0.5 *M* $NaClO_4$, although there is good agreement at 1 *M* $HClO_4$. It is possible that the differences might have been caused by the existence of different activity coefficients in 0.5 and 0.9 *M* $NaClO_4$, even though the ionic strength was the same. The variation in activity coefficients from those in 1 *M* $HClO_4$ probably would be less in the present measurements than in Baes's spectrophotometric study. For example, this generalization would be

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(29) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd edition, Reinhold Publ. Corp., New York, N. Y., 1950, pp. 397–401.

(30) S. Ahrland, *et al.*, *Acta Chem. Scand.*, **8**, 1907 (1954).

(31) J. Sutton, *J. Chem. Soc.*, S275 (1949).

(32) G. C. Hood, O. Redlich and C. A. Reilly, *J. Chem. Phys.*, **22**, No. 12, 2067 (1954).

expected to hold for $\gamma_\pm$ of perchloric acid itself, judging from a study of activity coefficients in analogous 1 M chloride solutions.[33] Also, the corrections due to ionized phosphoric acid would be less at the higher acidity. Nevertheless an elucidation of the charges on the complex ions would require less accuracy from Baes's values for the formation constants.

The data of Schreyer and Baes on the solubility of uranyl phosphates in phosphoric acid[3,4,34] can be interpreted in terms of a 1:3 uranyl phosphate complex in addition to the lower complexes.[4,6] However, the interpretation of such data is futile whenever charged complexes are concerned unless a constant ionic strength is maintained. An interesting, possibly anomalous, phenomenon is the solubility behavior in phosphoric acid at 6.1 M H_3PO_4, the transition point between $UO_2HPO_4 \cdot 4H_2O$ and $UO_2(H_2PO_4)_2 \cdot 3H_2O$.[3,34] If a neutral 1:3 uranyl phosphate complex were the principal dissolved species at that point, the solubility would be expected to continue to increase there instead of sharply decreasing, as it actually does. The reversed solubility trend might be explained by assuming the average complex to be a polynuclear species, *e.g.*, a 3:5 uranyl phosphate complex. However, evidence confuting the existence of appreciable amounts of such polynuclear complexes at the uranium concentration of the present investigation is supplied by conformance of the uranium solutions to Beer's law at 3.7 M H_3PO_4 in the present investigation, the spectrophotometric results of Baes,[6] and the incompatibility of large amounts of polynuclear complexes with the present solvent-extraction data.

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(33) H. S. Harned, THIS JOURNAL, **48**, 326 (1926).

(34) J. M. Schreyer and C. F. Baes, Jr., *ibid.*, **76**, 354 (1954).

[COMMUNICATION NO. 1893 FROM THE KODAK RESEARCH LABORATORIES, EASTMAN KODAK COMPANY]

The Mechanism of Dye Formation in Color Photography. V. The Effect of a Non-ionic Surfactant on the Ionization of Couplers[1]

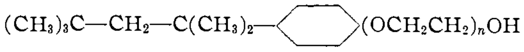
BY L. K. J. TONG AND M. CAROLYN GLESMANN

RECEIVED APRIL 2, 1957

The effect of a non-ionic surfactant on the apparent ionization constant of phenolic and naphtholic hydrogen has been measured by a photometric method. The data have been interpreted by assuming a different solubilization of the acid and salt forms of these compounds. The solubilization constants, defined as distribution coefficients between the micelle and the aqueous phase, were found to be very similar to the corresponding distribution coefficients between *n*-octanol and water. The solubilized salts appear to be completely dissociated.

The dyes in many color photographic systems are products of the oxidative condensation of a developing agent, usually N,N-disubstituted-*p*-phenylenediamines and a coupler, a compound with an active coupling site. In the Kodacolor and Kodak Ektacolor systems, water-insoluble couplers are incorporated in a highly dispersed organic phase, in the aqueous gelatin medium of the photographic emulsion; and the developing agent is supplied to the film from a high-*p*H-bath during processing. The couplers, on contact with the alkaline developer solution, form salts, which presumably are oriented in high concentration at the very large interface. This reaction is probably rapid and reversible; therefore, equilibrium is likely to be established before an appreciable fraction of the coupler reacts with the oxidized developer to form dye.

Dye formation may take place both in the organic phase and at the interface. The relative importance of both sites for color formation depends on many factors, and it was one of our primary objectives in this work to investigate these factors. In this paper and in the next (Part VI) emphasis is placed on the phenomena at the interface. Systems containing micelle-forming colloids are convenient for such studies because of their large surface-to-volume ratio. The colloid used for this investigation was Triton X-100. This material, supplied by Rohm and Haas, is the condensation product of diisobutylphenol and ethylene oxide. From its origin and molecular weight the following formula has been derived



in which n has an average of 9.5 units. This surfactant was chosen because its properties as a micelle-forming agent are well known from the investigations of Marsden, Gonick and McBain.[2]

The equilibria of the molecular species involved in dye formation and their distribution are discussed in the present paper, thus laying the foundation for a study of the dye formation in the subsequent communication.

II. Experimental Method and Treatment of Data

The behavior of couplers in the presence of Triton X-100 was studied by means of light absorption and *p*H measurements of coupler solutions containing different concentrations of this colloid. Most of the experiments were carried out with solutions of constant ionic strength (μ = 0.43 to 0.45) and constant potassium ion concentration (0.25 M). Therefore, in the following equations, the equilibrium constants are expressed in terms of concentrations, and are equal to the products of the thermodynamic constants and of the activity co-

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(1) For Parts III and IV, see L. K. J. Tong and M. Carolyn Glesmann, THIS JOURNAL, **79**, 583 (1957).

(2) (a) S. S. Marsden and J. W. McBain, *J. Phys. Chem.*, **52**, 110 (1948); (b) E. Gonick and J. W. McBain, THIS JOURNAL, **69**, 334 (1947).