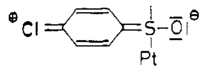
The somewhat greater (twofold) reactivity of 4-chlorophenyl methyl sulfoxide compared to that of the other substituted phenyl methyl sulfoxides might be accounted for by a conjugative displacement of charge that reduces this positive charge on the S and hence increases its nucleophilicity (Elding) or enhances the negative charge on the oxygen and increases its nucleophilicity:



Unfortunately, 4-nitrophenyl methyl sulfoxide is not soluble enough to be used in this study.

The sensitivity of the nucleophilicity of the sulfoxides to the bulk of the substituents is quite considerable and greater than the effect already noticed in the case of the reaction between $[Pt(dien)Br]^+$ and thioethers.[20] This is shown by comparing the sequence of *n*-alkyl sulfoxides. Although the order of reactivity is the same, if the rate constant for $(CH_3)_2S$ is taken as 100, the thioether sequence is $(CH_3)_2S = 100 > (CH_3)(C_2H_5)S = 83 > (C_2H_5)_2S = 53 > (n\text{-}C_4H_9)S = 33$ whereas in the sulfoxide sequence the rate constants are $(CH_3)_2SO = 100 > (CH_3)(C_2H_5)_2SO = 58 > (C_2H_5)_2SO = 12 > (n\text{-}C_3H_7)_2SO = 4$. This is even more strongly indicated by the fact that rate constants could be measured for $(i\text{-}C_3H_7)_2S$ and $(s\text{-}C_4H_9)_2S$ whereas the reaction of $(i\text{-}C_3H_7)_2SO$ was too slow to be measured. Of course, these refer to two different substrates, with different charges and steric properties of the ligands cis to the leaving groups (which are the major contributions to steric hindrance from the complex), but until now we have been unable to find a common substrate for both studies. Reactions of $[PtCl_4]^{2-}$ with thioethers are complicated by subsequent reactions, and the sulfoxides will not react with the cationic dien species under kinetically useful conditions.

Acknowledgment. We thank Mrs. Lucia Gemelli for technical assistance and the Italian Council for Research (CNR-Rome) and the British Council for financial support in a bilateral research project.

Registry No. $PtCl_4^{2-}$, 13965-91-8; MeEtSO, 1669-98-3; Et_2SO, 70-29-1; $(2\text{-}ClC_2H_4)MeSO$, 5331-57-7; PhMeSO, 1193-82-4; $(p\text{-}MeC_6H_4)MeSO$, 934-72-5; $(p\text{-}ClC_6H_4)MeSO$, 934-73-6; $(p\text{-}MeOC_6H_4)MeSO$, 3517-99-5; MePrSO, 14094-08-7; Pr_2SO, 4253-91-2; Cl, 22537-15-1; $(CH_3)_2SO$, 67-68-5; thiophane 1-oxide, 1600-44-8.

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(20) Bonivento, M.; Canovese, L.; Cattalini, L.; Marangoni, G.; Michelon, G.; Tobe, M. L., submitted for publication in *Inorg. Chem.*

(21) Cattalini, L.; Orio, A.; Doni, D. *Inorg. Chem.* **1966**, *5*, 1517.

(22) Cattalini, L. *Prog. Inorg. Chem.* **1970**, *13*, 263.

(23) Annibale, G.; Cattalini, L.; Maresca, L.; Michelon, G.; Natile, G. *Inorg. Chim. Acta* **1974**, *10*, 211.

(24) Pearson, R. G.; Sobel, H.; Songstad, J. *J. Am. Chem. Soc.* **1968**, *90*, 319.

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Solubility and Equilibrium Constants of Uranyl(2+) in Phosphate Solutions

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Precipitation studies of uranyl(2+) in phosphate solutions, performed at 298.15 K and various ionic strengths ($I = (3 \times 10^{-4})\text{–}(4 \times 10^{-2})$ mol dm^{-3}), complete the present knowledge of uranyl(2+) hydrogen phosphate tetrahydrate and uranyl(2+) phosphate octahydrate solubility and uranyl phosphate complex formation, composition, and stability. The concentrations of uranyl, phosphate, and hydrogen ions have been determined in solution equilibrated with the solid phase. From experimental data the values for equilibrium constants of soluble complexes are obtained and corrected to $I = 0$. The following values of homogeneous and heterogeneous equilibria in the uranyl–phosphate system at $I = 0$ have been determined: $\log [a(UO_2H_2PO_4^+)\ a(H^+)\ a^{-1}(UO_2^{2+})\ a^{-1}(H_3PO_4)] = 1.50 \pm 0.05$; $\log [a(UO_2H_3PO_4^{2+})\ a^{-1}(UO_2^{2+})\ a^{-1}(H_3PO_4)] = 1.30 \pm 0.10$; $\log [a(UO_2(H_2PO_4)_2^0)\ a^2(H^+)\ a^{-1}(UO_2^{2+})\ a^{-2}(H_3PO_4)] = 1.30 \pm 0.05$; $\log [a(UO_2(H_3PO_4)(H_2PO_4)_2^0)\ a^2(H^+)\ a^{-1}(UO_2^{2+})\ a^{-3}(H_3PO_4)] = 2.30 \pm 0.05$; $\log [a(UO_2^{2+})\ a(HPO_4^{2-})] = -12.33 \pm 0.06$; $\log [a^3(UO_2^{2+})\ a^2(PO_4^{3-})] = -49.00 \pm 0.80$.

Introduction

The formation of insoluble and slightly soluble uranyl(2+) phosphates is important in the technology of uranium production, especially for low-grade uranium phosphate ores and in fuel reprocessing.[1-3] Previously published papers reported the precipitation conditions,[4] dissolution,[5] composition,[6,7] and stability ranges[8] of the solid phases.

Apart from the general interest in the interaction between uranyl cations and phosphate anions, there is an important practical application of these data in the recovery of uranium from acid phosphate solutions.[9] Many of the authors[10-16] investigated the formation of uranyl phosphato complexes, and they are in disagreement, both in the composition of the complexes and in their stability constants. The values of the solubility products of uranyl(2+) hydrogen phosphate and uranyl(2+) phosphate have also been determined by different authors,[17-21] and they vary with the stability constants of the complexes used in the calculations.

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(1) *Process. Low-Grade Uranium Ores, Proc. Panel* **1967**.

(2) Harrington, D. C.; Ruehle, A. E. "Uranium Production Technology"; Van Nostrand: New York, 1959.

(3) Linstead, R. P.; Burstall, F. M.; Arden, T. V. British Patent 759900, 1956.

(4) Pavkovič, N.; Branica, M.; Težak, B. *Croat. Chem .Acta* **1968**, *40*, 117.

(5) Chretien, A.; Kraft, J. *Bull. Soc. Chim. Fr.* **1938**, *5*, 372.

(6) Kobets, L. V.; Kolevich, T. A.; Umreiko, D. S. *Zh. Neorg. Khim.* **1978**, *23*, 909.

(7) Howe, A. T.; Shilton, M. G. *J. Solid State Chem.* **1979**, *28*, 345; **1980**, *31*, 393.

(8) Schreyer, J. M.; Baes, C. F., Jr. *J. Am. Chem. Soc.* **1954**, *76*, 354.

(9) *Recovery Uranium, Proc. Symp.* **1971**.

(10) Baes, C. F., Jr.; Schreyer, J. M. *Oak Ridge Natl. Lab.* [*Rep.*] *ORNL* (*U.S.*) **1953**, *ORNL-1579*.

(11) Schreyer, J. M.; Baes, C. F., Jr. *J. Phys. Chem.* **1955**, *59*, 1179.

(12) Baes, C. F., Jr. *J. Phys. Chem.* **1956**, *60*, 878.

(13) Thamer, B. J. *J. Am. Chem. Soc.* **1957**, *79*, 4298.

(14) Marcus, Y. *Proc. U.N. Int. Conf. Peaceful Uses At. Energy* **1958**, *3*, 465.

(15) Moskvin, A. I.; Shelikina, A. M.; Perminov, P. S. *Zh. Neorg. Khim.* **1967**, *12*, 3319.

0020-1669/83/1322-0978$01.50/0

In the system $UO_2(NO_3)_2$–H_3PO_4–H_2O (spontaneous precipitation) the stable solid phases were determined[22] to be $UO_2HPO_4 \cdot 4H_2O$ and $(UO_2)_3(PO_4)_2 \cdot 8H_2O$.

In this work the concentrations of all components in equilibrated solutions with these solid phases are determined. The calculations of K_s values, according to earlier published uranyl phosphato complex constants,[10–13] did not give satisfactory results. Therefore, the equilibrium constants of soluble complexes were determined from our solubility data by an iterative procedure described earlier[23] and applied in the calculations of lead(II)[24] and mercury(II)[25] carbonato complexes.

The solubility data at $I = 0.32$ mol dm^{-3} obtained by Vesely, Pekarek, and Abbrent[21] are recalculated and discussed along with equilibrium complex constants determined in this work.

Experimental Section

Solutions were prepared by dissolving analytical grade $UO_2(NO_3)_2$ and H_3PO_4 (Merck, Darmstadt, West Germany) in triply distilled water. The concentration of $UO_2(NO_3)_2$ was determined gravimetrically by precipitating uranium with ammonium hydroxide, igniting the precipitate, and weighing the residue as U_3O_8.[26] Phosphoric acid was standardized by alkalimetric titration with thymolphthalein as indicator.[27]

Solid $UO_2HPO_4 \cdot 4H_2O$ and $(UO_2)_3(PO_4)_2 \cdot 8H_2O$ were precipitated by mixing[28] a solution of uranyl(2+) nitrate and phosphoric acid solution. A 30-day period was allowed for equilibrium. The precipitation systems were centrifuged, and X-ray diffraction patterns, IR spectra, and light microscopy were used to determine the composition of the precipitate. The concentration of soluble uranium was determined by an ac polarographic method[29] in a supporting electrolyte containing $[H_3PO_4] = 2$ mol dm^{-3} and (5×10^{-4})% Triton X-100. Soluble phosphorus was determined spectrophotometrically.[30] The pH was measured with a glass and calomel electrode (GK 2302 C electrode) connected to the Radiometer Mo 26 pH meter. The electrode system was standardized before and after each measurement with the following NBS buffer solutions: 0.01 mol dm^{-3} hydrochloric acid + 0.09 mol dm^{-3} potassium chloride, pH 2.098; 0.05 mol dm^{-3} potassium tetraoxalate, pH 1.679.

The paper electrophoresis was used for the qualitative determination of the charge of the uranyl phosphate complexes. The experimental conditions for paper electrophoresis (Savant Instrument Inc.) were as follows: Whatman 3MM paper strips; voltage 200 V; temperature 298 ± 0.1 K; duration of an experimental run 8 h. The samples for electrophoretic measurements were uranyl(2+) phosphate solutions equilibrated with the solid phase ($UO_2HPO_4 \cdot 4H_2O(s)$ or $(UO_2)_3(PO_4)_2 \cdot 8H_2O(s)$). Phosphoric acid solutions of the same phosphate concentration as in the corresponding sample were taken as the basic electrolytes. Electrophoretic zones were detected in the following way: strips were wetted with hydrochloric acid ($[HCl] = 0.1$ mol dm^{-3}) in order to destroy uranyl phosphate complexes prior to the red-brown color development of free uranyl ions with $K_4Fe(CNS)_6$.

Table I. Experimental Solubility Data and Calculated K_s Values for $UO_2HPO_4 \cdot 4H_2O(s)$

system no.	$10^4 \times [UO_2]_{soln}$/mol dm^{-3}	$10^3 \times [PO_4]_{soln}$/mol dm^{-3}	pH	$10^3 I$/mol dm^{-3}	log K_s	log $K_s(I = 0)$
1	3.19	7.32	2.28	5.5	−11.94	−12.22
2	6.88	14.80	2.10	9.0	−11.83	−12.15
3	5.80	14.60	2.00	10.4	−12.00	−12.35
4	8.36	19.80	1.94	11.9	−11.92	−12.28
5	11.00	15.10	1.83	15.4	−11.81	−12.24
6	12.20	26.20	1.77	18.0	−11.87	−12.33
7	17.60	36.80	1.70	21.0	−11.75	−12.28
8	17.60	44.60	1.66	22.0	−11.87	−12.36
9	16.50	40.20	1.58	28.6	−11.89	−12.43
10	35.40	73.50	1.57	28.4	−11.71	−12.26
11	20.00	52.00	1.49	30.4	−11.89	−12.44
12	33.70	73.40	1.45	36.0	−11.74	−12.34
13	38.70	93.90	1.41	38.9	−11.80	−12.42
14[a]	1.40	4.50	2.49	3.0	−12.14	−12.34
15	2.00	7.00	2.35	5.0	−12.10	−12.36
16	2.80	9.00	2.31	6.0	−11.98	−12.26
17	4.50	15.00	2.20	8.0	−11.93	−12.25
18	6.00	20.00	2.20	9.0	−11.98	−12.32
19	8.00	30.00	2.06	11.0	−11.87	−12.32
20	10.00	35.00	1.91	13.0	−12.00	−12.39
21	14.00	45.00	1.85	16.0	−11.90	−12.33
22	30.00	90.00	1.74	25.0	−11.79	−12.31
23	20.00	70.00	1.72	21.0	−11.95	−12.43
24	40.00	111.00	1.57	30.0	−11.86	−12.41

[a] Equilibrium concentrations in systems 14–24 were determined according to the precipitation boundary.[4]

Results

Precipitation of $UO_2HPO_4 \cdot 4H_2O(s)$ and $(UO_2)_3(PO_4)_2 \cdot 8H_2O(s)$ was studied in a broad concentration region of uranyl nitrate ((5×10^{-4})–(1×10^{-2}) mol dm^{-3}) and phosphoric acid ((4×10^{-4})–(1×10^{-1}) mol dm^{-3}). In all systems phosphates were present in excess. The resulting pH in the equilibrated solutions varied from 3.17 to 1.41.

In Table I are given the experimental values of all components in the solutions equilibrated with $UO_2HPO_4 \cdot 4H_2O(s)$: concentrations of uranyl and phosphate, pH values, and ionic strengths. In systems 1–13 the chemical analysis of equilibrated solutions was performed. The equilibrium concentrations in systems 14–24 are defined according to the precipiation boundary given in a previous paper.[4] The precipitation boundary is the curve that separates the region of spontaneous precipitation from the clear solution region.

The concentration $[UO_2]_{soln}$ is the sum of all uranyl species in solution, and it is given by

$$[UO_2]_{soln} = \sum_{i=0}\sum_{j=0}[UO_2(H_3PO_4)_i(H_2PO_4)_j{}^{(2-j)+}] \quad (1)$$

The concentration $[PO_4]_{soln}$ is the sum of the concentrations of free phosphates (H_3PO_4, $H_2PO_4^-$) and phosphates incorporated in uranyl complexes:

$$[PO_4]_{soln} = [PO_4]_{free} + [PO_4]_{complex} \quad (2)$$

$[PO_4]_{complex}$ is given by

$$[PO_4]_{complex} = \sum_{i=0}\sum_{j=0}(i + j)[UO_2(H_3PO_4)_i(H_2PO_4)_j{}^{(2-j)+}] \quad (3)$$

The equilibrium constants of different complex species are defined as

$$\beta_{ij} = \frac{[UO_2(H_3PO_4)_i(H_2PO_4)_j{}^{(2-j)+}][H^+]^j}{[UO_2{}^{2+}][H_3PO_4]^{i+j}} \quad (4)$$

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(16) Kin, J. *Pr. Wydz. Nauk Tech., Bydgoskie Tow. Nauk, Ser. A* **1975**, *No. 10*, 55; *Chem. Abstr.* **1976**, *84*, 112428*m*.
(17) Chukhlantsev, V. G.; Stepanov, S. I. *Zh. Neorg. Khim.* **1956**, *1*, 478.
(18) Chukhlantsev, V. G.; Alyamovskaya, K. V. *Khim. Khim. Tekhnol.* **1961**, *4*, 359.
(19) Karpov, V. I. *Zh. Neorg. Khim.* **1961**, *6*, 531.
(20) Moskvin, A. I.; Essen, L. N.; Bukhtiyarova, T. N. *Zh. Neorg. Khim.* **1967**, *12*, 3390.
(21) Vesely, V.; Pekarek, V.; Abbrent, M. *J. Inorg. Nucl. Chem.* **1965**, *27*, 1159.
(22) Pavković, N.; Kojić-Prodić, B.; Marković, M., submitted for publication.
(23) Nancollas, G. H. "Interactions in Electrolyte Solutions"; Elsevier: Amsterdam, 1966; Monogr. 8, pp 73–93.
(24) Marković, M. Thesis, University of Zagreb, 1979.
(25) Bilinski, H.; Marković, M.; Gessner, M. *Inorg. Chem.* **1980**, *19*, 3440.
(26) Wilson, C. L.; Wilson, D. W. "Comprehensive Analytical Chemistry"; Elsevier: Amsterdam, 1962; Vol. Ic, p 611.
(27) Vogel, A. I. "A Textbook of Quantitative Inorganic Analysis", 2nd ed.; Longmans, Green and Co.: London, 1951; p 245.
(28) Težak, B.; Matijević, E.; Schulz, K. *J. Phys. Colloid Chem.* **1951**, *55*, 1557.
(29) Heyrovský, J.; Kůta, J. "Principles of Polarography"; Czechoslovak Academy of Sciences: Prague, 1966; p 167.
(30) "Vogel's Textbook of Quantitative Inorganic Analysis", 4th ed.; Longmans, Green and Co.: New York, 1978; p 756.

Table II. Homogeneous and Heterogeneous Equilibria in the Uranyl(2+)-Phosphate System[a]

equilibria	log $K(I = 0)$	ref	log $K(I = 0.32$ mol dm$^{-3})$	ref
1. $H^+ + PO_4^{3-} = HPO_4^{2-}$	12.35 (K_1)	32	11.55	33, 35
2. $H^+ + HPO_4^{2-} = H_2PO_4^-$	7.199 (K_{12})	33	6.62	35, 36
3. $H^+ + H_2PO_4^- = H_3PO_4$	2.148 (K_{13})	34	1.89	35, 36
4. $UO_2^{2+} + H_3PO_4 = UO_2H_2PO_4^+ + H^+$	1.50 ± 0.05	*b*	1.30	*c*
5. $UO_2^{2+} + H_3PO_4 = UO_2H_3PO_4^{2+}$	1.30 ± 0.10	*b*	1.30	*c*
6. $UO_2^{2+} + 2H_3PO_4 = UO_2(H_2PO_4)_2^0 + 2H^+$	1.30 ± 0.05	*b*	1.03	*c*
7. $UO_2^{2+} + 3H_3PO_4 = UO_2(H_3PO_4)(H_2PO_4)_2^0 + 2H^+$	2.30 ± 0.05	*b*	2.03	*c*
8. $UO_2HPO_4(s) = UO_2^{2+} + HPO_4^{2-}$	−12.33 ± 0.06	*b*	−11.05	*d*
9. $(UO_2)_3(PO_4)_2(s) = 3UO_2^{2+} + 2PO_4^{3-}$	−49.00 ± 0.80	*b*	−47.01	*d*

[a] At 298.15 K. [b] This work. [c] Corrected to $I = 0.32$ mol dm^{-3}. [d] Recalculated in this work.

According to eq 1 and 4 the solubility product ($K_s = [UO_2^{2+}][HPO_4^{2-}]$) is expressed as

$$K_s = \frac{[UO_2]_{soln}[H_3PO_4]}{K_{13}K_{12}[H^+]^2}\left(\sum_{i=0}\sum_{j=0}\frac{\beta_{ij}[H_3PO_4]^{i+j}}{[H^+]^j}\right)^{-1} \tag{5}$$

The pH values were directly measured, while the activity coefficients of the other species (at $I < 0.04$ mol dm^{-3}) were calculated by using the Davies equation.[31] The values of β_{ij} were fitted (iterative procedure) according to eq 5 until a constant value of $K_s(I = 0)$ in all systems (Table I, systems 1–13) was obtained. In the initial step of calculation three complex species[10–14] are postulated: $UO_2H_2PO_4^+$, $UO_2H_3PO_4^{2+}$, and $UO_2(H_2PO_4)_2^0$. Calculations of the stability constants of these complex species were performed by an iterative procedure (iterative step 0.05 on the log scale) according to eq 5; this procedure was carried out up to a constant value of $K_s(I = 0)$. The occurrence of these complex species explains the solubility in systems 1–8 (Table I); the $K_s(I = 0)$ values obtained show differences in the range of experimental error. In contrast, higher values of $K_s(I = 0)$ in systems 9–13 (pH <1.58) were obtained. For an explanation of the solubility in systems 9–13 one more uranyl phosphate complex, $UO_2(H_3PO_4)(H_2PO_4)_2^0$, postulated by Baes and Schreyer,[10–12] was introduced. The values of equilibrium constants of four uranyl phosphate complexes were fitted by an iterative procedure as described above. Constant values of log $K_s(I = 0)$ were obtained in all systems (Table I, 1–13); log $K_s(I = 0)$ has an average value of −12.33 with a standard deviation of 0.06 (Table II, equilibrium 8). This procedure indicates that under these experimental conditions the following species predominate in a solution: UO_2^{2+}, $UO_2H_2PO_4^+$, $UO_2H_3PO_4^{2+}$, $UO_2(H_2PO_4)_2^0$, and $UO_2(H_3PO_4)(H_2PO_4)_2^0$. Their values of equilibrium constants are given in Table II (equilibria 4–7). Deviations are of the same order as the iterative step.

The values of log K_s (at corresponding ionic strengths) and of log $K_s(I = 0)$ for each system are listed in Table I.

In Table II are listed the values of association constants of phosphoric acid (K_{13}, K_{12}, K_1)[32,36] and the homogeneous and heterogeneous equilibria in the uranyl–phosphate system including the values of the equilibrium constants and the references.

In Figure 1 are presented experimental results for the precipitation of $UO_2HPO_4 \cdot 4H_2O(s)$ from phosphate solutions. The solubility data are plotted as −log $[UO_2]_{soln}$ vs. −log $[H_3PO_4]_{free}$. Theoretical solubility iso-pH curves were calculated by using equilibria 1–8 in Table II, and their equilibrium constants were corrected to the corresponding ionic strengths.[31] Experimental points close to the corresponding curve have pH values and ionic strengths similar to those of the theoretical curves.

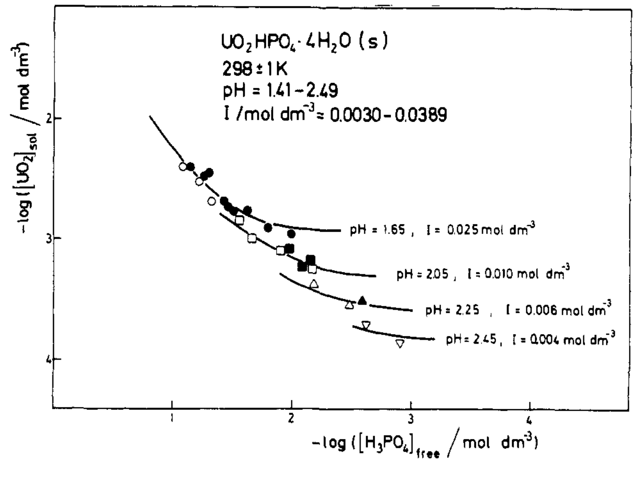

Figure 1. Complex solubility of $UO_2HPO_4 \cdot 4H_2O(s)$ in phosphate solutions explained by iso-pH curves. The values $[H_3PO_4]_{free}$ are calculated from eq 2 and 3 by inserting experimental values of $[PO_4]_{soln}$ (Table I) and phosphoric acid association constants (Table II). The systems 1–13 (Table I) are presented by solid symbols and those from 14 to 24 (Table I) by open symbols. The experimental pH values in the samples (○, ●) deviate from the theoretical iso-pH curve pH 1.65 by ±0.2 pH unit. For the iso-pH curves pH 2.05, 2.25, and 2.45 corresponding experimental points are assigned as (□, ■), (△, ▲), and (▽), respectively. The pH values for these points deviate from the corresponding iso-pH curves by ±0.1 pH unit.

Table III. Experimental Solubility Data and Calculated K_s Values for $(UO_2)_3(PO_4)_2 \cdot 8H_2O(s)$

system no.	$10^5 \times [UO_2]_{soln}$/mol dm^{-3}	$10^4 \times [PO_4]_{soln}$/mol dm^{-3}	pH	$10^3 I$/mol dm^{-3}	log K_s	log $K_s(I = 0)$
1	6.19	7.10	2.93	1.40	−47.71	−48.25
2	9.00	18.90	2.81	2.60	−47.88	−48.50
3	14.30	17.30	2.76	2.10	−47.57	−48.20
4	67.60	3.82	2.72	2.00	−48.47	−49.10
5	92.90	24.00	2.50	3.40	−48.94	−49.74
6	14.30	17.50	2.32	5.00	−48.68	−49.64
7	16.90	27.80	2.27	5.60	−48.78	−49.79
8	57.00	20.30	2.02	10.00	−47.34	−48.66

In Table III are given experimental values of uranyl and phosphate concentrations, pH, and ionic strengths in solutions equilibrated with $(UO_2)_3(PO_4)_2 \cdot 8H_2O(s)$. The values of log $K_s(I = 0)$ of $(UO_2)_3(PO_4)_2 \cdot 8H_2O$ are calculated by inserting equilibrium constants (equilibria 1–7 in Table II) and experimental results into the equation

$$K_s = \frac{[UO_2]_{soln}^3[H_3PO_4]^2}{(K_{13}K_{12}K_1)^2[H^+]^6}\left(\sum_{i=0}\sum_{j=0}\frac{\beta_{ij}[H_3PO_4]^{i+j}}{[H^+]^j}\right)^{-3} \tag{6}$$

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(31) Stumm, W.; Morgan, J. J. "Aquatic Chemistry", 2nd ed.; Wiley-Interscience: New York, 1981; p 135.
(32) Bates, R. G. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1951**, *47*, 127.
(33) Smith, R. M.; Martell, A. E. "Critical Stability Constants"; Plenum Press: New York, 1976; Vol. 4.
(34) Ender, F.; Teltschik, W.; Schäfer, K. *Z. Elektrochem.* **1957**, *61*, 775.
(35) Elliot, J. S.; Sharp, R. F.; Lewis, L. *J. Phys. Chem.* **1958**, *62*, 686.
(36) Galal-Gorchev, H.; Stumm, W. *J. Inorg. Nucl. Chem.* **1963**, *25*, 567.

The values of log K_s (at corresponding ionic strengths) and of log $K_s(I = 0)$ for each system are listed in Table III. log $K_s(I = 0)$ has an average value of −49.00 with a standard deviation of 0.80 (Table II, equilibrium 9).

The electrophoretic measurements were performed in the solutions equilibrated with $UO_2HPO_4{\cdot}4H_2O$ (Table I, systems 4 and 16) and also with $(UO_2)_3(PO_4)_2{\cdot}8H_2O$ (Table III, systems 5 and 8). In all the experiments uranyl(2+) species were detected in the cationic zone near the starting point, which indicates that the uranyl phosphato complexes present in the system either are neutral or are positively charged. These results support our selection of the complex species used in this work.

Discussion

The results of our investigations can be compared with those of studies on the composition of complex species given by other authors.[10-14] Marcus[14] and Baes and Schreyer[10-12] presumed the existence of $UO_2H_2PO_4^+$, $UO_2H_3PO_4^{2+}$, $UO_2(H_2PO_4)_2^0$, and $UO_2(H_3PO_4)(H_2PO_4)_2^0$ while Thamer[13] did not find the last complex mentioned. Marcus presumed the existence of uranyl complex species with three phosphate groups corresponding to the general formula $UO_2(H_3PO_4)_i(H_2PO_4)_{3-i}$ (i varied from 0 to 3). In our investigations only one complex with three phosphate groups, $UO_2(H_3PO_4)(H_2PO_4)_2^0$, was determined. According to Moskvin et al.[15] only $UO_2HPO_4^0$ and $UO_2(HPO_4)_2^{2-}$ complex species exist in equilibria with solid $UO_2HPO_4{\cdot}4H_2O$. However, our electrophoretic measurements show that uranyl complexes in equilibrated solutions are neutral or positive; thus, the hypothesis of Moskvin et al. has to be eliminated.

The values of the equilibrium constants of the complex species determined in this work (Table II, equilibria 4–7, $I = 0$) are corrected to ionic strength $I = 1$ mol dm^{-3} according to the activity coefficients of uranyl ions:[37,38] log $\beta_{01} = 1.39$, log $\beta_{10} = 1.30$, log $(\beta_{01} + \beta_{10}) = 1.65$, log $\beta_{02} = 1.16$, log $\beta_{12} = 2.16$. These recalculated values are in very good agreement with the constants determined by Baes and Schreyer directly at $I = 1$ mol dm^{-3}: log $(\beta_{01} + \beta_{10}) = 1.57$, log $\beta_{02} = 1.18$, log $\beta_{12} = 2.30$.

According to eq 5, by the use of equilibrium constants listed in Table II (equilibria 4–8, $I = 0$) the detailed analysis of uranyl phosphate species distribution in equilibria with $UO_2HPO_4{\cdot}4H_2O(s)$ can be performed. The calculations are performed at two phosphate concentrations, $[PO_4]_{soln} = 5 \times 10^{-3}$ and 5×10^{-2} mol dm^{-3}, and $1 < pH < 2.5$ (the stability region of $UO_2HPO_4{\cdot}4H_2O(s)$). The results are presented in Figure 2. The analysis shows major differences in the complex composition of the solution in equilibria with $UO_2HPO_4{\cdot}4H_2O(s)$ depending on phosphoric acid concentration and pH:

(i) The $UO_2H_2PO_4^+$ complex prevails at low $[PO_4]_{soln}$ ($1 < pH < 2.5$). The increase in pH results in the reduction of UO_2^{2+} and the increase of $UO_2(H_2PO_4)_2^0$ (Figure 2a).

(ii) $UO_2H_2PO_4^+$, $UO_2(H_2PO_4)_2^0$, and $UO_2(H_3PO_4)(H_2PO_4)_2^0$ complex species dominate at high $[PO_4]_{soln}$ and determine the solubility of $UO_2HPO_4{\cdot}4H_2O(s)$. The concentrations of UO_2^{2+} and $UO_2H_3PO_4^{2+}$ are negligible under these conditions (Figure 2b).

Vesely, Pekarek, and Abbrent[21] determined the solubility products for uranyl(2+) hydrogen phosphate and uranyl(2+) phosphate at $I = 0.32$ mol dm^{-3} (an excess of phosphates). In the calculation of K_s at $I = 0.32$ mol dm^{-3} the authors[21] included literature constants[10] of uranyl complexes determined at $I = 1$ mol dm^{-3} and literature association constants of H_3PO_4 determined at $I = 0$. The final results (values of K_s) are included in ref 33. So that Vesely, Pekarek, and Abbrent's solubility data (performed at $I = 0.32$ mol dm^{-3}) could be recalculated, the values of the equilibrium constants for complex species determined in this work (at $I = 0$) have been corrected to $I = 0.32$ mol dm^{-3} (Table II, equilibria 4–7). These values and the original values of the association constants of H_3PO_4 at I = 0.32 mol dm^{-3} (Table II, equilibria 1–3) were used in the recalculation. The recalculated values of Vesely, Pekarek, and Abbrent's experimental solubility data for $UO_2HPO_4{\cdot}4H_2O$ are presented in Figure 3 (open circles), for which the intercept of the straight line with the ordinate gives directly the mean value of log $K_s = -11.05$.

The same figure contains also our solubility data (solid and open squares). The theoretical straight line (corresponding to $I = 0$) intercepts the ordinate at the value of log $K_s(I = 0)$

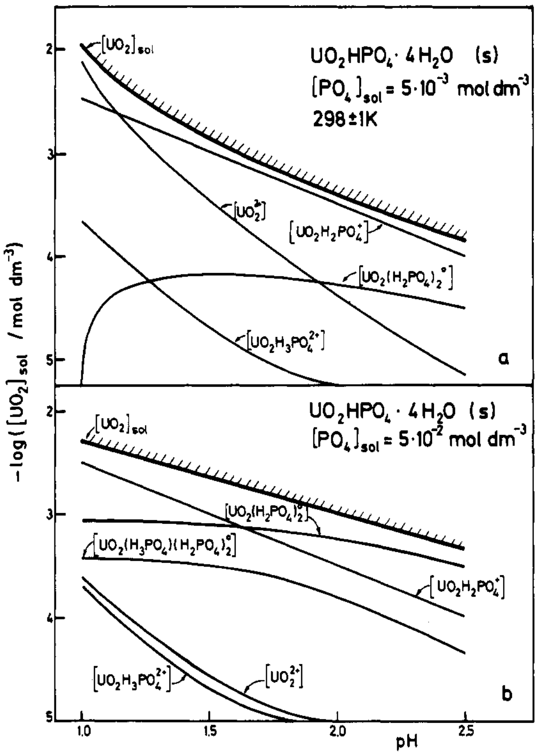

Figure 2. Calculated solubilities of $UO_2HPO_4{\cdot}4H_2O(s)$ and the distribution of uranyl phosphate species at constant phosphate concentration, represented as −log $[UO_2]_{soln}$ vs. pH curves: (a) $[PO_4]_{soln} = 5 \times 10^{-3}$ mol dm^{-3}; (b) $[PO_4]_{soln} = 5 \times 10^{-2}$ mol dm^{-3}.

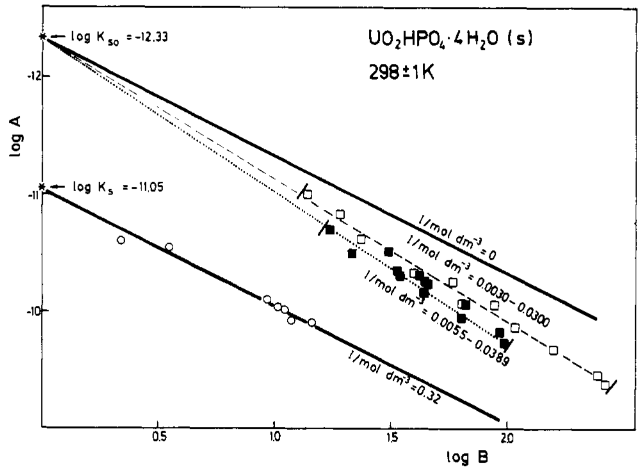

Figure 3. Determination of log K_s for $UO_2HPO_4{\cdot}4H_2O(s)$ at low ionic strengths (our data) and at $I = 0.32$ mol dm^{-3} (reinterpreted literature data[21]). The values of K_s are determined according to eq 5: $A = [UO_2]_{soln}[H_3PO_4]K_{13}^{-1}K_{12}^{-1}[H^+]^{-2}$; $B = \sum_{i=0}\sum_{j=0}\beta_{ij}[H_3PO_4]^{i+j}[H^+]^{j-}$; log K_s = log A − log B. The systems 1–13 and 14–24 (Table III) are represented by solid and open squares, respectively.

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(37) MacKay, H. A. C. *Trans. Faraday Soc.* **1951**, *47*, 436.
(38) Brusilovsky, S. A. *Dokl. Akad. Nauk SSSR* **1958**, *120*, 305.

while both lines through our experimental points (assigned intervals, corresponding to $I > 0$) tend to meet at the same point on the y axis (where $I = 0$).

The value of log $K_s(I = 0)$ for $(UO_2)_3(PO_4)_2\cdot 8H_2O$ determined in this work (Table II, equilibrium 9) is in very good agreement with the value of log $K_s(I = 0) = -49.1$ for $(UO_2)_3(PO_4)_2\cdot 6H_2O$ determined by Chukhlantsev and Alyamovskaya.[18] The value of K_s for $(UO_2)_3(PO_4)_2\cdot 6H_2O$ at $I = 0.32$ mol dm^{-3} determined by Pekarek, Vesely, and Abbrent[21] was recalculated, and the result is presented in Table II, equilibrium 9.

Baes and Schreyer's data[10-12] on the composition and stability of uranyl phosphato complexes (at $I = 1$ mol dm^{-3}), Vesely, Pekarek, and Abbrent's solubility data (at $I = 0.32$ mol dm^{-3}), and the constants of the homogeneous and heterogeneous equilibria determined in this work (at $I = 0$) give a detailed and complete picture of the uranyl-phosphate system at $1.4 < \text{pH} < 3.2$.

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Registry No. UO_2HPO_4, 61156-01-2; $(UO_2)_3(PO_4)_2$, 12037-44-4; U, 7440-61-1; UO_2^{2+}, 16637-16-4.

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Mixing of States and the Determination of Ligand Field Parameters for High-Spin Octahedral Complexes of Nickel(II). Electronic Spectrum and Structure of Bis(1,7-diaza-4-thiaheptane)nickel(II) Perchlorate

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The mixing of the ^1E_g and $^3T_{2g}$ excited states in six-coordinate nickel(II) complexes via spin-orbit coupling is discussed. The effect of the mixing of states is that in the above Ni(II) complexes, when the ligand field splitting parameter, $10Dq$, is close to 12 000 cm^{-1}, two bands at approximately 12 500 and 11 500 cm^{-1} are observed, which cannot be assigned to pure $^3A_{2g} \rightarrow {}^3T_{2g}$ or $^3A_{2g} \rightarrow {}^1E_g$ transitions. As $10Dq$ increases from 11 000 to 13 000 cm^{-1}, the positions of these bands remain relatively constant. What does change is their relative intensities. A method is proposed whereby the relative intensities of the two bands in the 12 000-cm^{-1} region can be used to obtain in a simple manner the positions of the two bands corrected for mixing of states. It is shown that these corrections lead to more rational values of $10Dq$ and the Racah parameters. The split bands in the complex $[Ni(daes)_2]^{2+}$ (daes = 1,7-diaza-4-thiaheptane) are assigned to mixing of $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^1E_g$, rather than trans positioning of the sulfur donors. The crystal structure determination supporting this assignment is reported for $[Ni(daes)_2](ClO_4)_2$. A conventional R factor of 0.08 was achieved. Cis coordination of the sulfurs is found, with a mean Ni-S bond length of 2.459 Å and a mean Ni-N of 2.11 Å.

The electronic spectrum of six-coordinate nickel has been particularly useful in coordination chemistry. The position of the lowest energy band gives a direct measure of $10Dq$, and making such simplifying assumptions as using the rule of average environment, and neglecting distortion to lower than O_h symmetry, gives one some insight into factors influencing bonding to the Ni(II) ion. However, the problem of mixing of spin-allowed with spin-forbidden bands has been discussed only briefly[1,2] in relation to such simple determinations of the ligand field (LF) parameters. This mixing is particularly important for the spin-forbidden $^3A_{2g} \rightarrow {}^1E_g$ and spin-allowed $^3A_2 \rightarrow {}^3T_2$ transitions at values of the LF splitting parameter, $10Dq$, of about 12 000 cm^{-1}. In Figure 1 we have plotted the energies of the $^3A_{2g} \rightarrow {}^1E_g$ and $^3A_{2g} \rightarrow {}^3T_{2g}$ transitions against those of $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, for a variety of Ni(II) complexes containing six nitrogen and/or fluorine donor atoms. For this set there appears to be an inverse relationship between $10Dq$ and B; e.g., these parameters are[1] as follows for the sets of ligands: 6F$^-$, 7300 and 950; 6 H_2O, 8600 and 930; 3 glycine, 10 100 and 926; 6 NH_3, 10 700 and 890; 3 en, 11 500 and 860; 3 bpy, 12 300 and 845 cm^{-1}. If we examine the expressions[3] for the $^3A_{2g}$, $^3T_{2g}$, $^3T_{1g}(F)$, and ^1E_g states, we see that a direct relationship between the energies of $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and an inverse relationship between $^3A_{2g} \rightarrow {}^1E_g$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, is expected. (The relationship will break down if ligands with second-row donors such as S or Cl are included, since the relation between $10Dq$ and B is different.) The relationships between $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and between $^3A_{2g} \rightarrow {}^1E_g$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ are found to hold very well in Figure 1, except where the transitions to the ^1E_g and $^3T_{2g}$ states approach each other in energy. This is the cause of the difficulty when the energies of these bands are used to calculate the LF parameters in a simple manner for complexes in aqueous solution.

The explanation for the fact that the two bands appear to repel each other, and never have the same energy, as indicated by the broken lines, is that the Russell-Saunders coupling scheme is breaking down as the separation, δ, between the two excited states becomes smaller, due to coupling between the spin- and orbital-angular momenta. In the simple LF approach such mixing is generally ignored, although, as pointed out by a reviewer, it can be corrected for. One cannot neglect the mixing and assign either of the two band maxima as being the energy of the pure $^3A_{2g} \rightarrow {}^3T_{2g}$ or $^3A_{2g} \rightarrow {}^1E_g$ transition. Doing so has led, for example, to the calculation[4] of anomalously low B values for complexes such as $[Ni(bpy)_3]^{2+}$. The problem of calculating LF parameters arose in our own case with the electronic spectra of the complexes $[Ni(daes)_2]^{2+}$ and [Ni(9-

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[1] Jørgensen, C. K. *Struct. Bonding (Berlin)* **1966**, *1*, 1-31.

[2] Hancock, R. D.; McDougall, G. J. *J. Chem. Soc., Dalton Trans.* **1977**, 67-70.

[3] Hare, C. R. In "Spectroscopy and Structure of Metal Chelate Compounds"; Nakamoto, K, McCarthy, P. J., Eds.; Wiley: New York, 1968; pp 73-149.

[4] Palmer, R. A. ; Piper, T. S. *Inorg. Chem.* **1966**, *5*, 864-879.