results calculated for K_9 and K_{10} by the two methods, while in poor agreement, are of the same order of magnitude. The value of K_{10} calculated from *p*H titration may be in error because of formation of colloidal ferric hydroxide, since at points slightly beyond those used for calculation it was apparent that precipitation was taking place. The polarographic results depend upon the value of K_5, which may be in error.

Bobtelsky and Jordan[2] titrated an iron(III) solution with sodium citrate and found an increase in conductivity as the citrate was first added. In this titration the reactions represented by equations 8 and 9 would be expected to occur. The hydrogen ion produced by the second of these reactions would cause the *p*H to decrease. A check at the beginning of this titration showed that the *p*H did decrease, thus causing a conductivity increase as reported by Bobtelsky and Jordan. As the *p*H decreases one would expect relatively more of the material reacting to follow equation 8 and also the competitive reaction

$$\mathrm{Cit}^{\equiv} + \mathrm{H}^{+} \longrightarrow \mathrm{HCit}^{=} \qquad (15)$$

The hydrogen ion concentration would then decrease, resulting in a conductivity decrease, which would continue even after all of the iron was complexed because of 15. Finally the conductivity would start to increase because of the addition of sodium citrate. The breaks in the conductivity curve would, according to this explanation, bear no direct relationship to the complex ion composition.

Definite points of difference exist with Lingane[5] and Meites[6] with regard to the polarographic measurements. Lingane has claimed that the half-wave potential may be represented by an equation linear in *p*H from 4 to 12. The slope given by this equation is intermediate between the slopes of the two portions of our plot, and may have resulted from Lingane's larger but less detailed range of study. The differences with Meites are harder to explain since we have found only a single wave at all *p*H values. Meites suggested that his differences from Lingane might be the result of the fact that Lingane had used 0.005% gelatin. We did not use gelatin, but have results corresponding more closely with those of Lingane.

Acknowledgment.—We would like to express our thanks to Dr. S. R. Dickman who originally suggested the study of the citrate complexes of iron(II) and assisted by giving summer support to one of us (C.M.S.) from U.S. Public Health funds under his direction, as the investigation first started.

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Spectrophotometric Studies of the Uranyl–Lactate, –Malate and –Tartrate Systems in Acid Solution[1]

BY ISAAC FELDMAN AND JEAN R. HAVILL

RECEIVED NOVEMBER 19, 1953

Absorption spectra and Job's method of continuous variations have been employed to determine the stoichiometry of the possible complexes in the uranyl–lactate, –malate and –tartrate systems in acid solution. Only a combining ratio of unity is evident in the uranyl–lactate system at *p*H 3.5. In the uranyl–malate system at *p*H 3.5 complexes having uranyl/malate combining ratios of one and two exist. The former ratio predominates in equimolar uranyl–malate mixtures and in excess malate up to at least *p*H 4.8. In the uranyl–tartrate systems, it is probable that there exist complexes having combining ratios of one, two and three. Although only 1:1 stoichiometry prevails in excess tartrate up to at least *p*H 4.6, it is probable that in the *p*H range 3.6–5 an equimolar uranyl–tartrate mixture contains a small fraction of a species having a combining ratio greater than one.

As part of a program of investigation of the reactions of uranyl ions with carboxylic acids, spectrophotometric studies were carried out to determine the stoichiometry of the possible complexes in the uranyl–lactate, –malate and –tartrate systems. The uranyl–citrate system has been studied previously.[2]

Experimental

The experimental procedure followed was as described in the earlier paper[2] with one modification: the solutions were prepared in semi-darkness and stored in the dark. The spectral absorbences, $A = \log_{10} I_0/I$, of the uranyl–lactate solutions were measured two hours after the solutions were prepared, since apparently decomposition occurs on standing overnight. Absorbences of the uranyl–lactate mixtures remained constant from two to six hours. Below about *p*H 5 uranyl–malate and uranyl–tartrate solutions, if stored in the dark, gave constant absorbences from less than one hour to at least 24 hours. Therefore, all spectral measurements on uranyl–malate and uranyl–tartrate solutions were made after 18–24 hours.

Results and Discussion

Absorption Spectra at *p*H 3.5.—The absorption spectra of various uranyl nitrate–lactic acid mixtures, uranyl nitrate–malic acid mixtures and uranyl nitrate–tartaric acid mixtures raised to *p*H 3.5 are presented in Figs. 1A, 1B and 1C, respectively. The portions below 400 mμ are omitted to save space. In each curve there is a relatively broad minimum near 380 mμ followed by rapidly increasing general absorption with decreasing wave length.

In each of these graphs the 1:1 and 1:9 curves seem sufficiently similar to indicate that in none of these systems does there exist appreciable concentration of a complex with a combining ratio of less than unity at *p*H 3.5.

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[1] This paper is based on work performed under contract with the United States Atomic Energy Commission at the University of Rochester Atomic Energy Project, Rochester, N. Y.

[2] I. Feldman and W. F. Neuman, THIS JOURNAL, **73**, 2312 (1951).

The curves in Fig. 1A suggest further that for the uranyl–lactate system at *p*H 3.5 the 1:1 complex is also the predominating form when uranium is in excess. If mixtures having a uranium/lactate ratio greater than unity contain only the 1:1 complex plus uncomplexed uranium, one would expect a gradual transition from the 1:1 spectrum to the 1:0 curve similar to that seen in Fig. 1A.

In Fig. 1B it is seen that when the uranium/malate ratio was increased from 1:1 to 2:1 the contour of the spectrum changed abruptly, the maximum being shifted from 435 to 428 mμ and a shoulder appearing near 416 mμ. Further increase in the uranium/malate ratio produced the gradual transition toward the 1:0 curve which would be expected if the 3:1 and 5:1 mixtures contained only the 2:1 complex and uncomplexed uranium. It appears, therefore, that no complex with a higher uranium/malate ratio than 2:1 exists to an appreciable extent at *p*H 3.5.

In Fig. 1C the spectra of the 2:1 and 3:1 uranyl–tartrate mixtures have their maxima at the same wave length, 428 mμ. This fact could indicate that the 3:1 mixture contained only the 2:1 complex and excess uranyl ion or that the 2:1 mixture contained 1:1 and 3:1 complexes principally. However, in either case, the 2:1 and the 3:1 curves would not coincide from 395 mμ to 415 mμ. It seems likely, then, that 2:1 and 3:1 uranyl–tartrate complexes, as well as the 1:1 form, exist to a significant extent at *p*H 3.5.

Method of Continuous Variations.—The above conclusions were confirmed by the application of Job's well-known method of continuous variations.[2–4]

For the uranyl–lactate system, maxima in the continuous-variations curves, shown in Fig. 2A, were obtained only near $X = 0.5$ indicating a 1:1 uranyl–lactate complex. Curves for 400, 420 and 440 mμ also have maxima near $X = 0.5$, but are omitted from Fig. 2A. No significance should be attributed to the lack of symmetry of these curves, since the relatively large *p*H effect (Fig. 3A) leads to considerable experimental error.

In Fig. 2B maxima are seen at $X = 0.5$, 0.65 and and 0.70, confirming the existence of 1:1 and 2:1 uranyl–malate complexes at *p*H 3.5. The linearity of the curves below $X = 0.5$ indicates that the 1:1 complex is very stable, whereas the broad maxima at 428 and 400 mμ show that the 2:1 complex is dissociated to some extent at this *p*H.

The peaks at $X = 0.5$ and 0.75 in Fig. 2C confirm the existence of 1:1 and 3:1 uranyl–tartrate complexes at *p*H 3.5. The peaks at intermediate X values for 440 mμ and for 450 mμ could be due to a mixture of 1:1 and 3:1 complexes, but in view of the absorption spectra it is believed that a 2:1 complex is probable.

***p*H Effect on Spectra.**—The large effect of *p*H (Fig. 3A) on the spectrum of the 1:1 uranyl–lactate system and the lack of uniqueness in its spectral contour precludes a productive spectrophotometric study at a *p*H much above *p*H 3.5.

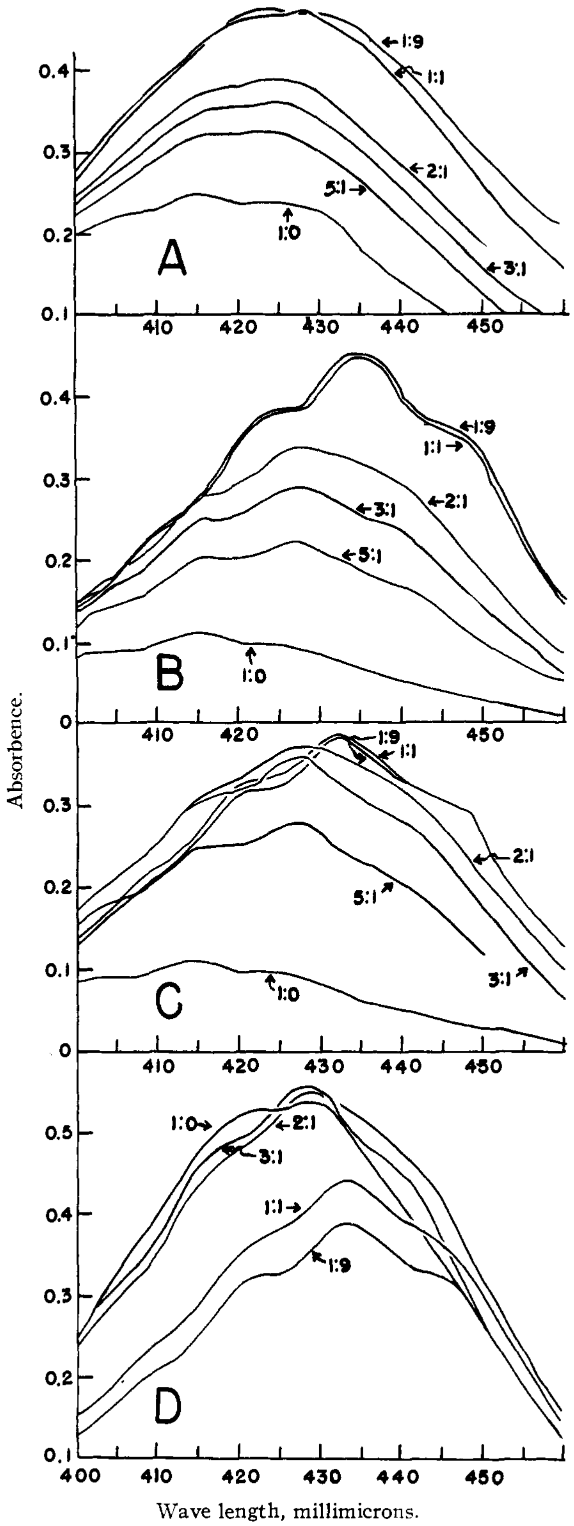

Fig. 1.—Absorption spectra of: (A) uranyl–lactate mixtures, *each* containing 0.02 *M* uranyl nitrate initially, at *p*H 3.5; (B) uranyl–malate mixtures, *each* containing 0.01 *M* uranyl nitrate initially, at *p*H 3.5; (C) and (D) uranyl–tartrate mixtures, *each* containing 0.01 *M* uranyl nitrate initially, at *p*H 3.5 and 4.6, respectively. The numerical ratio associated with each spectrum represents the initial uranium/organic acid molar ratio of the solution studied. Each solution, except the 1:9, contained 0.1 *M* sodium perchlorate.

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(3) P. Job, *Ann. Chem.*, **11**, 97 (1936).

(4) W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 436 (1941).

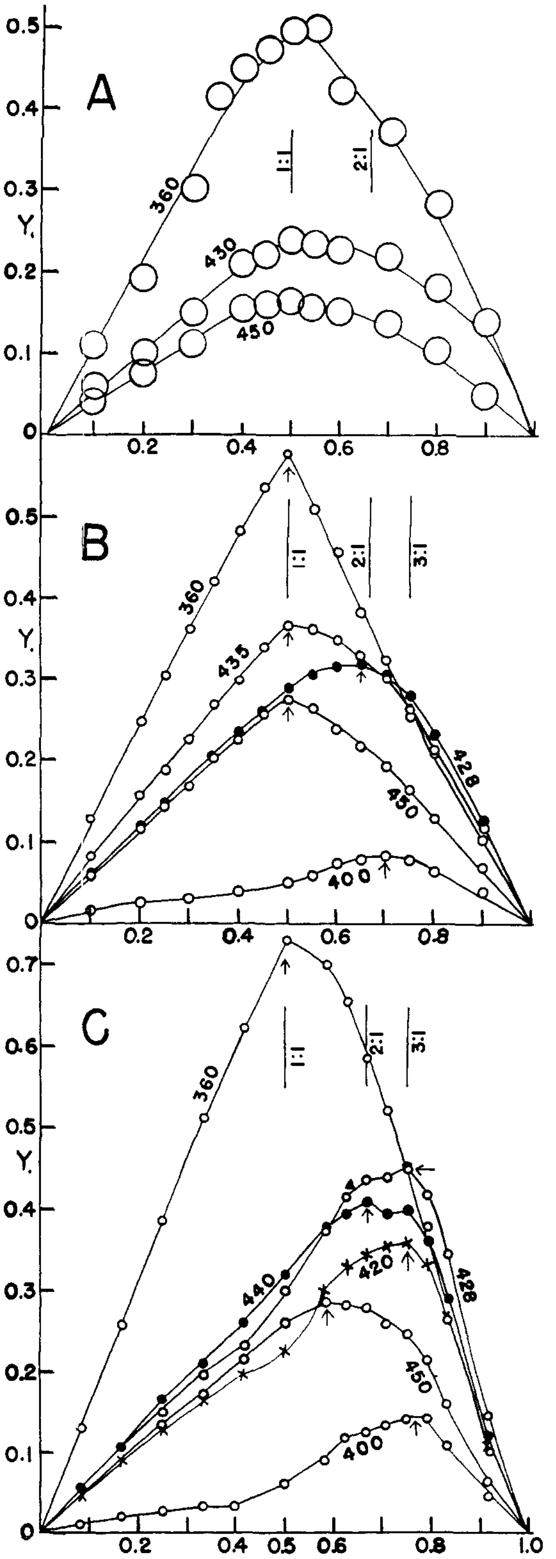

Fig. 2.—Method of continuous variations applied to: (A) uranyl-lactate system, the initial (UO_2^{++} + lactic acid) being 0.04 *M* in each solution; (B) uranyl-malate system, the initial (UO_2^{++} + malic acid) being 0.02 *M* in each solution; (C) uranyl-tartrate system, the initial (UO_2^{++} + tartaric acid) being 0.024 *M* in each solution. Each solution contained 0.1 *M* sodium perchlorate and had a *p*H of 3.5. Abscissa X represents the initial molar ratio UO_2^{++}/UO_2^{++} + organic acid). Ordinate Y is the difference between the observed absorbence and that which would be given by uranium if no complexing occurred. The number associated with each curve is the wave length in millimicrons at which absorbence was measured.

The effect of *p*H on the spectra of 1:1 and 1:9 uranyl-malate mixtures, represented by Fig. 3B, is very similar to the *p*H effect on the spectra of 1:1 and 1:9 uranyl-citrate mixtures.[2] The relative heights of the two curves in Fig. 3B show that there is significant dissociation of the 1:1 complex in a 1:1 mixture until slightly less than *p*H 3.5. The only significant change in the spectra of the 1:1

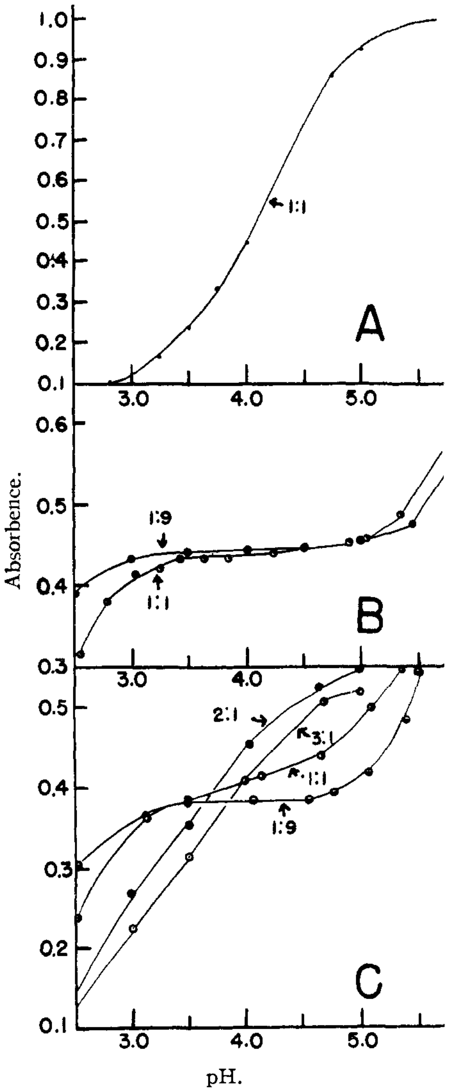

Fig. 3.—Effect of *p*H on spectral absorbence at 434 mμ of (A) uranyl-lactate, (B) uranyl-malate and (C) uranyl-tartrate systems. Number associated with each curve represents the initial uranium/organic acid molar ratio. Each solution, except the 1:9, contained 0.1 *M* sodium perchlorate. The initial uranyl nitrate concentration was 0.012 *M* in the uranyl-lactate mixture and 0.010 *M* in each of the uranyl-malate and uranyl-tartrate mixtures.

and 1:9 mixtures from *p*H 3.5 to 4.8 is a 3% increase in height, indicating that there is very little change in either the 1:1 or 1:9 system in this *p*H range.

In Fig. 3C it is seen that from *p*H 3.5 to 4.5 the absorbence at 434 mμ of the 1:1 uranyl–tartrate mixture increases 10%, whereas that of the 1:9 uranyl-tartrate mixture increases only 2%. The explanation for the larger slope in the 1:1 curve appears to be that there is present in the 1:1 mixture above *p*H 3.5 a small amount of a species with a combining ratio greater than unity. The absorbence of the 1:9 solution at 434 mμ is exceeded by the 2:1 and 3:1 absorbences at about *p*H 3.6, respectively, and the *p*H effect on the 2:1 and 3:1 spectra is very large.

The existence of all three uranyl–tartrate complexes near *p*H 4.6 is evident from the 1:1, 2:1 and 3:1 spectra in Fig. 1D. The spectrum of each of these solutions has the same contour as at *p*H 3.5 (compare Fig. 1D with 1C), the wave lengths of peaks and shoulders being unchanged.

The spectrophotometric results which have been obtained above *p*H 5 will be reported in a subsequent paper along with potentiometric titration data, because of the very close link between the interpretation of these two studies.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Absorption Spectra and Electrical Conductivities of UO_2–ThO_2 Solid Solutions[1]

BY DIETER M. GRUEN

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The absorption spectra of UO_2–ThO_2 solid solutions between 4500 and 7000 Å. show four discrete bands with maxima at 5100, 5400, 6000 and 6500 Å. which are attributed to electronic transitions between various states of the U^{+4} ion. In addition, an intense, continuous absorption band is found whose long wave length edge shifts to shorter wave lengths with decreasing uranium concentration. This band is attributed to resonance of uranium ions between different oxidation states. Electrical conductivities of pressed UO_2–ThO_2 discs were measured for the temperature interval 300–450°K. and were found to decrease by a factor of 10^6 in the concentration range 100–10% uranium. The activation energy for conductivity changed from 0.20 e.v. for pure UO_2 to 0.37 e.v. for 10% UO_2–90% ThO_2 solid solution. An attempt has been made to correlate changes in the optical and electrical properties with nearest neighbor interactions involving uranium ions in different oxidation states.

Although progress in the field of oxidic semiconductors has been rapid,[2] there is as yet no comprehensive theory concerning the mechanism of electronic conduction in these materials. As an aid to the development of such a theory, the "dilution" technique may play an important role since it allows one to introduce the concentration of the semiconducting species as a parameter which can be varied over a wide range at will. The procedure consists of forming solid solutions between a semiconductor (UO_2) and an insulator (ThO_2) and studying relevant properties as a function of the concentration of the semiconducting ingredient. In the present investigation, the absorption spectra and electrical conductivities of a series of UO_2–ThO_2 solid solutions ranging from pure UO_2 to 2.5% UO_2 were measured. These compounds are isomorphous and form a continuous range of solid solutions with the fluorite structure.[3]

Experimental

Preparation of Solid Solutions.—Two methods were used for the preparation of solid solutions, both leading to the same results. The first method was essentially identical with that of Trzebiatowski and Selwood.[3] The dried hydroxides were pressed into discs (0.5" diameter and 1" long) in a stainless steel mold at a pressure of 10 tons/in.^{2} and then fired at 1500° for 8 hours in a hydrogen atmosphere. The second method consisted of intimately mixing UO_2 and ThO_2 in a ball mill, pressing the mixture into discs and firing at 1750° in hydrogen for 8 hours. This procedure was repeated to ensure the formation of solid solution. In all cases, the samples were cooled to room temperature in hydrogen. The X-ray parameters determined on both sets of samples were in good agreement with the previous measurements[3] and showed that true solid solutions were formed. Since the samples fired at 1750° possessed greater mechanical rigidity, they were used in all of the measurements. Spectroscopic analysis of the starting materials showed them to be free (<0.01%) of transition and rare earth metal impurities.

Measurements of Absorption Spectra.—Two techniques were employed for measuring the absorption spectra of the oxides. The first was to incorporate approximately 10 mg. of the oxide into 200 mg. of KBr by grinding in an agate mortar and then pressing the mixture into a 0.5" diameter disc. A modification of this technique has been described in detail in the literature[4,5] where it has been applied to infrared spectra of organic materials. It promises to be a useful tool for the investigation of the spectra of inorganic solids as well. The second technique was to affix a disc of the fired oxide to a thin 0.5" diameter quartz plate by means of Canada balsam and, using optical grinding methods, to reduce the thickness of the oxide disc to the point of light transmission. The final thickness of the oxide film turned out to be 0.001" for pure UO_2 and ≈0.005" for 10% UO_2–90% ThO_2. A Cary spectrophotometer was used for obtaining the spectra. Both methods of obtaining the spectra gave identical results. Discs of ThO_2 were used as blanks.

Spectra were obtained at liquid nitrogen temperatures by mounting the samples in a dewar of a design similar to one described in the literature.[6]

Measurement of Electrical Conductivities.—Resistances were measured with a Leeds and Northrup Type S Test Set. The samples were 0.5" × 0.25" discs cut from the original oxide bodies with a carborundum wheel. They were ground flat on an optical block. The samples were held between platinum plates by means of two 0.5" diameter aluminum rods of equal length. Surrounding the sample and the aluminum rods was a nichrome wound furnace 5"

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[1] Presented in part at the Fall, 1953, Meeting of the American Chemical Society, Chicago, Ill.

[2] J. L. Snoek, "New Developments in Ferromagnetic Materials," Elsevier Pub. Co., New York, N. Y., 1947.

[3] W. Trzebiatowski and P. W. Selwood, THIS JOURNAL, **72**, 4504 (1950).

[4] M. M. Stimson, *ibid.*, **74**, 1805 (1952).

[5] U. Schiedt, *Z. Naturforsch.*, **76**, 270 (1952).

[6] R. Casler, P. Pringsheim and P. Yuster, *J. Chem. Phys.*, **18**, 887 (1950).