$$\bar{V}_{KCl} = 26.50 + 4.89\sqrt{m} - 2.24m$$

with which the values for these constants in the last column of Table I were computed.

For sodium and potassium iodides in water, a good approximation to the experimental results is given by

$$\phi_{NaI} = 35.37 + 0.80\sqrt{m}$$
$$\phi_{KI} = 45.55 + 0.87\sqrt{m}$$

Using Eq. 6 we obtain

$$\bar{V}_{NaI} = 35.37 + 1.20\sqrt{m}$$
$$\bar{V}_{KI} = 45.44 + 1.30\sqrt{m}$$

Similarly, for potassium iodide in 1.46% iodine as solvent

$$\phi_{KI} = 45.26 + 1.48\sqrt{m}$$

and

$$\bar{V}_{KI} = 45.26 + 2.22\sqrt{m}$$

where m is the number of equivalents of potassium iodide in 1,000 g. of iodine and water.

By comparing the values of $\bar{V}_{KI}$, shown in Tables I and III, it will be seen that the presence of dissolved iodine has a very small effect on that constant.

In Table II it will be observed that the values of the apparent equivalent volumes, ϕ_I, at different concentrations of iodine are nearly constant. For iodine in approximately 0.2 N potassium iodide solution

$$\phi_I = 29.98 + 0.73m$$

and from Eq. 6

$$\bar{V}_I = 29.98 + 1.46m$$

where m is the number of equivalents of iodine in 1000 g. of potassium iodide and water. Similarly, for iodine in sodium iodide solution

$$\phi_I = \bar{V}_I = 29.96$$

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[CONTRIBUTION FROM THE VITRO CORPORATION OF AMERICA, FORMERLY THE KELLEX CORPORATION, JERSEY CITY, N. J.]

The Constitution of the Uranates of Sodium[1]

BY C. A. WAMSER, J. BELLE, E. BERNSOHN AND B. WILLIAMSON

Chemical and X-ray diffraction analyses, and the interpretation of pH and conductance data, indicate that two sodium uranates, $Na_2U_7O_{22}$ and $Na_6U_7O_{24}$ (or mixtures thereof) are obtained when uranium is precipitated from uranyl nitrate solution by sodium hydroxide. When sodium hydroxide is added to the point of incipient precipitation (requiring 1 or more moles of NaOH per mole of U), basic uranyl ions of the type $UO_3UO_2^{++}$ and $(UO_3)_2UO_2^{++}$ are formed. The further addition of sodium hydroxide (to NaOH/U = 2.29) effects the quantitative precipitation of uranium as $Na_2U_7O_{22}$. This primary uranate reacts with further sodium hydroxide (to NaOH/U = 2.86) to produce $Na_6U_7O_{24}$, which is the species stable in the presence of excess alkali.

Until the work of Flatt and Hess[2] it had been generally accepted that the addition of alkali hydroxide to solutions of uranyl salts resulted in the precipitation of uranyl hydroxide which then reacted with alkali to form the diuranate $Na_2U_2O_7$. Other investigators[3-5] postulated the uranates $2Na_2O·5UO_3$, $2Na_2O·7UO_3$ and $Na_2O·8UO_3$, respectively, on the basis of chemical analysis or pH data.

Flatt and Hess[2] established, on the basis of a phase rule study, that only two uranates, most closely represented by $K_2O·7UO_3$ and $2K_2O·5UO_3$ (or mixtures thereof), are formed when uranyl nitrate is treated with potassium hydroxide.

Because of the amorphous character of the uranates obtained by precipitation, most of the evidence for their composition has been obtained indirectly.

Most of the previous investigations have not recognized the pronounced effect of aging of the precipitate. Unless equilibrium conditions are closely approached, erroneous conclusions may be deduced from analyses of the precipitates or from measurements on the supernatant liquors.

By preparing the precipitates under carefully controlled conditions approaching equilibrium, and by thorough washing according to a definite experimentally established pattern, it was found possible to obtain analytical and X-ray diffraction data capable of consistent interpretation in terms of definite compounds of sodium and uranium.

Experimental

In the present investigation a series of mixtures was prepared each of which contained a measured volume of an aqueous solution of uranyl nitrate of definite concentration treated with measured volumes of standard carbonate-free sodium hydroxide (added dropwise with continual stirring). Each mixture was diluted to the same final volume with water and allowed to stand in a sealed container at room temperature for five days with occasional agitation. All precipitations were carried out at 25 ± 5°. Under these conditions (which approximate equilibrium conditions) the character of the precipitates obtained facilitated separation and effective washing by centrifugation.

The mother liquors were analyzed for free alkali and uranium content and their pH and conductance determined.

The precipitates were washed by repeated dispersion in water and separation by centrifugation. The method of washing uniformly employed was established by the observed behavior of those precipitates which had been formed at the higher pH values. It was observed that the concentration of free alkali in the water washings decreased to a constant (low) value on repeated application of water and that this alkalinity was maintained on exhaustive washing. On this basis, the precipitates were washed only to the point at which the alkalinity of the filtrate first reached its minimum value. It was demonstrated that this alkali actually resulted from the hydrolysis of the sodium uranate and not by desorption

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(1) Presented before the Division of Physical and Inorganic Chemistry at the 119th Meeting of the American Chemical Society, Cleveland, Ohio, April 11, 1951.

(2) R. Flatt and W. Hess, *Helv. Chim. Acta*, **21**, 1506 (1938).

(3) J. Metzger and M. Heidelberger, THIS JOURNAL, **31**, 1040 (1909).

(4) H. Guiter, *Bull. soc. chim.*, 403 (1946).

(5) H. Guiter, *ibid.*, 275 (1947).

from the precipitate. The precipitates were then washed with acetone and air dried. Sodium was determined gravimetrically as sodium zinc uranyl acetate and uranium spectrophotometrically as the peroxyuranate in NaOH–Na_2CO_3 at 400 mμ. The analytical data are assembled in Table I.

TABLE I

ANALYTICAL DATA: PRECIPITATES FROM $UO_2(NO_3)_2$–NaOH

UO_2 concn. mole/liter	Alkali added moles NaOH/moles U	Mole ratio Na/U in ppt.	X-Ray diffraction pattern
0.08	1.50	0.289	A-1
	2.00	.281	A-1
	2.50	.372	A-1,B
	3.00	.856	B
	4.00	.865	B
	5.00	.855	B
.51	1.50	0.272	A-1
	1.75	.282	A-1
	2.00	.279	A-1
	2.29	.291	A-1
	2.50	.371	A-1,B
	2.75	.717	A-1,B
	2.86	.859	B
	3.00	.867	B
	4.00	.871	B
	5.00	.858	B
	8.00	.868	B
	50		B

Discussion of Results

Uranyl nitrate solutions of concentrations 0.08 and 0.51 mole per liter were employed. The *p*H values of these solutions are 2.68 and 1.94, respectively. The precipitate formed by treatment of these solutions with sodium hydroxide continued to redissolve until the *p*H values of the solutions were 4.4 and 3.6, respectively (corresponding to 1.44 and 0.98 mole NaOH per mole U, resp.). In both cases, uranium precipitation increased from this point until the alkali addition corresponding to a NaOH/U mole ratio of 2.3 (*p*H approx. 6) was reached, when the precipitation of uranium was practically complete. Up to this point, all the precipitates had a Na/U mole ratio of 0.282 ± 0.005. On further addition of alkali the precipitates underwent a change in color from yellow to orange; and up to the point where free alkali first appeared in the system (*p*H approx. 10; mole NaOH per mole U = 2.86), the mole ratio of Na/U in the precipitates increased continually from 0.282 to 0.862. The addition of NaOH beyond 2.86 moles NaOH per mole U did not cause any further change in the Na/U ratio in the precipitate. The Na/U mole ratio of all precipitates obtained from this system when the added NaOH was sufficient to provide free alkali in the mother liquor, was found to be 0.862 ± 0.006.

X-Ray diffraction patterns of the precipitates indicate that: (1) the first permanent precipitates which appear and all those obtained up to a *p*H of approx. 6 (yellow) have the same characteristic pattern (A-1), resembling but not identical with the uranyl hydroxide pattern (A); (2) all the (orange) precipitates obtained when an excess of alkali was present (beyond *p*H 10) had a characteristic pattern (B) different from that corresponding to the precipitates obtained at *p*H values below 6; and (3) the precipitates obtained in the *p*H range of 6–10 (NaOH/U from 2.3–2.86) exhibited the patterns of both A-1 and B.

The analytical and X-ray data can all be interpreted by postulating two uranates $Na_2O \cdot 7UO_3$ and $3Na_2O \cdot 7UO_3$ which precipitate from the system $UO_2(NO_3)_2$–NaOH as indicated in the following equations:

I. Addition of NaOH to the first permanent precipitation:

$$2UO_2^{++} + 2NaOH = UO_3UO_2^{++} + 2Na^+ + H_2O$$

$$3UO_3UO_2^{++} + 2NaOH = 2(UO_3)_2UO_2^{++} + 2Na^+ + H_2O$$

(The basic uranyl ion is discussed by Sutton[6])

II. NaOH addition to the complete precipitation of uranium:

$$7UO_3UO_2^{++} + 18NaOH = 2Na_2U_7O_{22}\downarrow + 14Na^+ + 9H_2O$$

III. Further addition of NaOH to the point where free NaOH first appears in the system:

$$Na_2U_7O_{22}(s) + 4NaOH = Na_6U_7O_{24}(s) + 2H_2O$$

From these equations, the alkali requirement for the first uranate $Na_2U_7O_{22}$, is 2.29; and for the second $Na_6U_7O_{24}$, 2.86. These values are consistent with the observations that uranium precipitation is first essentially complete at NaOH/U = 2.29 and that free alkali first appears in the system beyond NaOH/U = 2.86 (a graphical plot of free alkali, from analyses of the mother liquors, against total alkali added, extrapolates to NaOH/U = 2.86 at the zero free alkali line.) Further, breaks in these regions are indicated in the *p*H and conductance curves presented in Fig. 1. Finally, all the precipitates having NaOH/U mole ratios of 2.29 were of the same light yellow color; between 2.29 and 2.86 the solid phase changed progressively to orange.

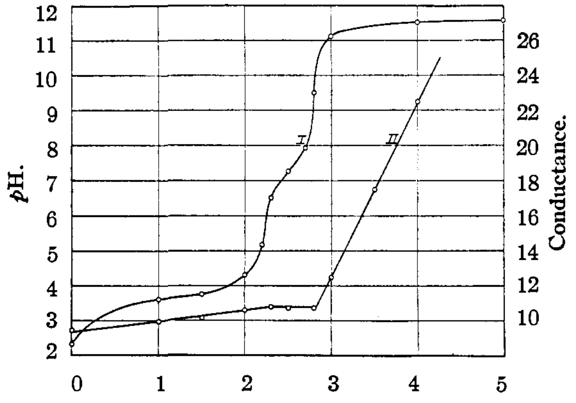

Fig. 1.—*p*H and conductance titrations (equilibrium conditions at each point) – 0.08*M* $UO_2(NO_3)_2$ + NaOH.

The pronounced effect of the condition of the precipitation system with respect to equilibrium was demonstrated by comparison of *p*H data. 0.08 *M* uranyl nitrate was titrated directly with sodium hydroxide, the only aging corresponding to the time required to make the necessary *p*H measurements. The two points of inflection corresponded to 2.22 and 2.48 moles NaOH/U, while

[6] J. Sutton, *J. Chem. Soc.*, (Suppl. Issue No. 2), S275 (1949).

*p*H measurements on the corresponding mixtures which had been aged for five days indicated 2.29 and 2.86, respectively. It is interesting that the values of NaOH/U which correspond to the uranates postulated by some previous investigators[3,4] fall between the extreme cases of equilibrium and non-equilibrium.

The uranate $Na_2U_7O_{22}$ is identical in composition to the analogous compound $K_2U_7O_{22}$ established by Flatt and Hess[2] by an indirect method but their secondary uranate $K_4U_5O_{17}$ (based on K/U = 0.788 ± 0.044) differs appreciably from $Na_6U_7O_{24}$ (based on Na/U = 0.862 ± 0.006). However, the precision of their extrapolated K/U values was only 5.6% whereas in the present investigation, the degree of precision attained for Na/U was 0.7%.

It has been demonstrated that the transformation of $Na_2U_7O_{22}$ into $Na_6U_7O_{24}$ by alkali, is not instantaneous, since treatment of uranyl nitrate with sodium hydroxide to an alkaline reaction followed by rapid separation of the precipitate gave uranates having Na/U values less than 6/7 due to the presence of unconverted $Na_2U_7O_{22}$. However, the addition of uranyl nitrate to sodium hydroxide, gave, as the initial precipitate, the para-uranate $Na_6U_7O_{24}$ which represented the only solid phase as long as the *p*H remained above 10. Reduction of the *p*H below 10 by the addition of uranyl nitrate solution (*p*H 2) resulted in the conversion of $Na_6U_7O_{24}$ to $Na_2U_7O_{22}$. The extent of this conversion was dependent upon the final *p*H of the mixture. This transformation was also accomplished with acid

$$Na_6U_7O_{24}(s) + 4H^+ = Na_2U_7O_{22}(s) + 2H_2O + 4Na^+$$

It was found that the diuranate ($Na_2U_2O_7$) could not be obtained from uranyl nitrate and sodium hydroxide even in the presence of great excesses of the latter. Precipitates prepared under such conditions gave patterns identical with $Na_6U_7O_{24}$. (Because of the difficulties attending the washing of uranates precipitated from large excesses of alkali, high Na/U ratios may be erroneously inferred from direct chemical analyses of such precipitates.)

Treatment of uranyl nitrate with sodium hydroxide in no instance yielded a precipitate which could be identified as uranyl hydroxide, either on the basis of chemical or X-ray analysis. Even the first precipitate obtained on treatment of uranyl nitrate with ammonia was a uranate containing ammonium. However, it was found that uranium could be precipitated as the hydroxide ($UO_2(OH)_2$ or $UO_3 \cdot H_2O$) by treatment of uranyl nitrate solutions with certain weak bases such as pyridine or aniline.

TABLE II

X-RAY DIFFRACTION DATA

Target, Cu–Ni; KV–ma, 30–15; camera rad. 5.716 cm.; 11 hr. exposure; VS, very strong; S, strong; M, moderately strong; W, weak.

Pattern $UO_3\cdot H_2O$ A		$Na_2O\cdot 7UO_3$ A-1		$3Na_2O\cdot 7UO_3$ B	
d	I	d	I	d	I
..	...	7.50	VS	..	...
7.38	VS	..	...	..	...
..	...	..	...	6.06	S
5.08	M	..	...	..	...
4.49	M	..	...	..	...
3.73	M	..	...	..	...
..	...	3.70	W	..	...
3.64	S	..	...	..	...
3.55	M	..	...	..	...
..	...	3.53	M	..	...
3.45	W	..	...	..	...
..	...	..	...	3.42	VS
3.36	W	..	...	..	...
3.25	VS	3.25	S	3.25	VS
3.20	S	..	...	..	...
..	...	3.18	M	..	...
..	...	..	...	3.02	W
..	...	..	...	2.74	W
2.58	W	..	...	..	...
..	...	2.54	M	..	...
..	...	2.10	W	..	...
..	...	2.06	M	..	...
2.03	W	2.03	W	..	...
..	...	..	...	2.01	S
1.99	W	..	...	..	...
..	...	1.98	M	..	...
..	...	..	...	1.91	M
1.80	W	..	...	..	...
..	...	1.79	W	..	...
1.76	W	..	...	..	...
..	...	1.75	W	..	...
..	...	..	...	1.72	W
..	...	..	...	1.66	W

The analyses of air-dried precipitates from uranyl nitrate–sodium hydroxide correspond closely to the hexadecahydrates, *e.g.*

$$Na_2U_7O_{22} \cdot 16H_2O \text{ and } Na_6U_7O_{24} \cdot 16H_2O$$

On desiccation over sulfuric acid the stable hydrate appears to be the dodecahydrate, *e.g.*

$$Na_2U_7O_{22} \cdot 12H_2O \text{ and } Na_6U_7O_{24} \cdot 12H_2O$$

The latter compound may be dehydrated completely at 130°. The resulting anhydrous uranate has the same X-ray diffraction pattern as the 12 and 16 hydrate.

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