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SOME OPTICAL AND CRYSTALLOGRAPHICAL PROPERTIES OF THE ALKALI ZINC URANYL ACETATES

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ABSTRACT

The optical properties and crystal form of the zinc uranyl acetates of sodium, lithium, and potassium were determined. The lithium and sodium zinc uranyl acetates belong to the monoclinic system and are isomorphous. They are capable of forming a series of solid solutions, as is evidenced by the homogeneity and the intermediate optical properties and X-ray pattern of a mixed sodium and lithium zinc uranyl acetate. The potassium zinc uranyl acetate belongs to the tetragonal system and differs from the lithium and sodium zinc uranyl acetates in optical properties and crystal form.

In studying the application of the Barber and Kolthoff method [1] for the quantitative determination of sodium to the analysis of glass,[2] a casual examination of the crystalline precipitate showed that the crystals were, in general, very well formed and were characterized by twinning. Barber and Kolthoff stated that part of the potassium and most of the lithium are precipitated with the sodium salt when they are present. Glaze has recently substantiated Barber and Kolthoff's statement that lithium cannot be separated from sodium, but has shown that potassium can be separated from sodium if proper precautions are taken.[3] Hence it seemed desirable to make a detailed study of the three salts to see if they can be readily distinguished by their optical properties.

The crystalline compounds used in this work were prepared as follows: One volume of a solution of cp alkali chloride was mixed with 10 volumes of the zinc uranyl acetate reagent [4] and stirred frequently during 30 minutes. The precipitate was filtered and washed free from the excess reagent with 95 percent alcohol and finally with ether.

The precipitate was dissolved in a minimum amount of distilled water and recrystallized by slowly concentrating the solution in a dessicator over sulphuric acid. In the case of the potassium salt a few drops of acetic acid were added to prevent hydrolysis.

Microscopic examination of the sodium and lithium salts showed them to be perfectly homogeneous and without visible impurity. Analyses of these two salts were made as follows: The uranium was converted to sulphate by fuming with sulphuric acid, reduced in a Jones reductor, oxidized to quadrivalent uranium with air and

[1] Jour. Am. Chem. Soc., vol. 50, pp. 1625-1631, 1928.
[2] F. W. Glaze, Jour Am. Cer. Soc., vol. 14, no. 6, pp. 450-453, 1931.
[3] B.S. Technical News Bulletin No. 94, p. 68, June 1933.
[4] Barber and Kolthoff, op. cit., p. 1626.

titrated with permanganate. The zinc was precipitated from a 0.008 *N* sulphuric acid solution by hydrogen sulphide. The precipitate was dissolved and reprecipitated until white in color, filtered, and ignited to the oxide. The alkali was determined as sulphate on a separate sample after removing the uranium and zinc as sulphides from an ammoniacal solution. On the lithium salt water was determined at 100 C and 3 mm pressure and the acetic acid was determined by distilling from a phosphoric acid solution and titrating with standard sodium hydroxide. The results of the analyses are given in table 1 together with the compositions calculated from the formulas (see footnote 4).

TABLE 1.—*Results of analyses*

Components	$NaZn(UO_2)_3(CH_3COO)_9.6H_2O$		$LiZn(UO_2)_3(CH_3COO)_9.6H_2O$	
	Found	Calculated	Found	Calculated
	Percent	*Percent*	*Percent*	*Percent*
UO_2	52.90	52.69	53.29	53.25
Zn	4.35	4.25	4.36	4.30
Na	1.47	1.495		
Li			.46	.456
$CH_3.COO$	(a)	34.54	34.77	34.90
H_2O	(b)	7.03	7.12	7.10

[a] Not determined.
[b] Not determined. See Barber and Kolthoff, op. cit., p. 1628.

The potassium salt contained a very small amount (estimated at less than 1 percent) of an unidentified crystalline impurity.

The indices of refraction of the crystals were determined by the usual microscopic immersion method using sodium light and a series of mixtures of petroleum oil and alpha monobromnaphthalene, the members of which differed in index by approximately 0.005. Immediately thereafter the indices of the liquids were measured with an Abbe refractometer. The temperatures at both the microscope and the refractometer were known within one degree centigrade. The optic axial angle of the sodium salt was measured with a condenser apertometer plate.

Diffraction patterns of the powdered crystals for purposes of comparison were made with a Coolidge X-ray tube with molybdenum target and zirconium oxide filter.

The sodium zinc uranyl acetate occurs as monoclinic crystals of tabular habit with the crystallographic *b* axis as the long dimension. Of the crystals studied the largest were about 0.08 mm long and 0.33 mm wide. Indices of refraction are:

$$\alpha_{Na} = 1.475 \pm .002$$

$$\gamma_{Na} = 1.480 \pm .002$$

The optical character is negative, the optic axial angle ($2V$) being about 25°.[5] The obtuse bisectrix γ is parallel to the crystallographic *b* axis. The form of the crystal and the optical orientation are shown

[5] The optical character and size of optic angle reported in the Technical News Bulletin, Bureau of Standards, November 1933, were incorrect.

in figure 1. The angular relations between faces and between optical and crystallographical directions as shown in the figure are those obtained by microscopic measurement and consequently are only approximate. Accurate determinations of the β index of refraction and of the optic axial angle could not be made, because of the difficulty of maintaining the crystals in the proper orientation for these measurements. Beautiful pseudo-rhombohedral forms produced by cyclic twinning are very abundant. The γ vibration direction makes an angle of about 31° with the trace of the twinning plane.

Individual crystals of lithium zinc uranyl acetate made by the method used were exceedingly rare. The few present evidently belonged to the monoclinic system and had faces similar to those of the sodium salt. All the other crystals observed were cyclic pseudo-rhombohedral twins with the same form and about the same optical orientation as the sodium salt. Indices of refraction are:

$$\alpha_{Na} = 1.495 \pm .002$$

$$\gamma_{Na} = 1.503 \pm .002$$

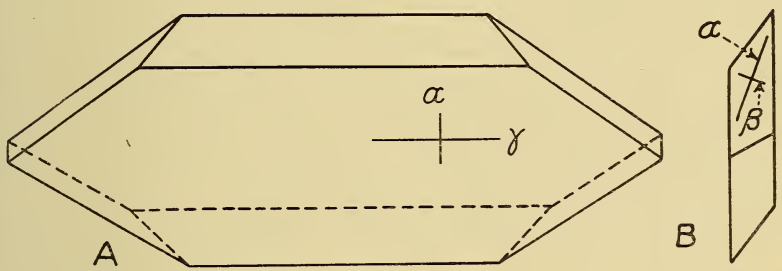

FIGURE 1.—*Diagrammatic representation of crystal of sodium zinc uranyl acetate, (A) with the tabular faces parallel to the plane of the paper and (B) with the crystallographic b axis normal to the plane of the paper. The approximate optical orientation is indicated.*

Satisfactory values for the β index of refraction and the optic axial angle were not obtainable.

The potassium zinc uranyl acetate consisted of well formed prismatic holohedral tetragonal crystals with simple combinations of prism (110) faces and first and second order pyramids. There is a perfect cleavage parallel to (110). Indices of refraction are:

$$\epsilon_{Na} = 1.487 \pm .002$$

$$\omega_{Na} = 1.477 \pm .002$$

The marked similarity in optical properties and in crystal form of the sodium and lithium salts suggests that they are isomorphous and may show complete solid miscibility. X-ray powder diffraction patterns of these two compounds confirm this supposition, the patterns showing complete similarity in arrangement and intensity of the lines, the interplanar spacings only being slightly different.

An X-ray photograph of the crystals made by adding the precipitating reagent to a solution containing equimolecular amounts of sodium and lithium chlorides gave a pattern in which the lines were intermediate in position between those of the pure sodium and the pure

lithium salts. Microscopically the crystals of the mixed salt appeared completely homogeneous and had indices of refraction between those of the pure end members. Evidently there is complete solid miscibility between the sodium and lithium salts.

The powder diffraction pattern of the potassium zinc uranyl acetate shows, as would be expected from the crystallographic data, little similarity in position, arrangement, or intensity of lines to those of the sodium and lithium salts.

Evidence obtained indicates that there is little prospect that separations of sodium and lithium by precipitation with zinc uranyl acetate can be made.

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