[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The System Silver Nitrate–Dioxane–Water at 25°

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In connection with studies on the solubility of silver salts in dioxane–water mixtures, the occurrence at 25° of a solid phase other than pure silver nitrate was noted. The present investigation of the equilibrium relations of the system silver nitrate–dioxane–water was carried out in an attempt to identify this phase, suspected of being a solid dioxanate of silver.

Materials Used.—The silver nitrate was a C. P. product used without further purification, after pulverizing and drying at 150°. The dioxane was fractionally distilled after standing over sodium wire for over a week, and had the same properties and degree of purity as the material used in corresponding investigations.[1]

Procedure.—Known amounts of dioxane, water and silver nitrate were mixed in glass-stoppered Pyrex solubility tubes (230 cc. capacity), and rotated in a thermostat at 25 ± 0.02°, for periods of about one week, to ensure the attainment of equilibrium; tests by repeated analysis showed that one day's stirring was sufficient. Most of the high-dioxane mixtures were enclosed in an atmosphere of nitrogen, to avoid any effect of ordinary air on the stability of the dioxane during shaking of the samples.

As long as the saturating solid phase remains unsolvated silver nitrate, the composition of the saturated liquid phase can be calculated by the mere determination of its silver nitrate content, by evaporation, inasmuch as the ratio of water to dioxane in the solvent itself has remained unchanged. Hence one determination was always that of the solid residue left by evaporation of a weighed amount of filtered solution, dried to constant weight at 110°. Since it was evident, however, that some new solid phase was being formed over most of the solubility curve, it became necessary to determine a second component, both in the liquid and in the solid phase. It should be possible, of course, to determine the ratio of water to dioxane in the solvent after distillation from silver nitrate, by making use of some physical property of the mixture such as boiling point, freezing point, density, refractive index, etc. Most of these properties show too small a variation to be sensitive enough for the purpose of this investigation, which, it was felt, required a rather precise determination of the composition to distinguish between the two solubility curves involved. It is possible that the determination of the dielectric constant of the distillate might be a sensitive enough analysis, but because of the difficulties foreseen in the complete recovery of the distillate without decomposition of the residue of silver nitrate and subsequent inclusion of oxides of nitrogen in the product, such methods were not used. Various methods for the chemical determination of water were tried, and the procedure finally adopted consisted in the evaporation of the solvent and absorption of the water in barium oxide for weighing.

The method was used both for liquid solution and for solid wet residues. The sample was weighed into a 10-ml. distilling flask connected in an air-tight train with a source of dry nitrogen and weighed U-tubes containing barium oxide. The nitrogen was purified by passage through pyrogallol solution to remove oxygen and through concentrated sulfuric acid for drying. The sample being analyzed was evaporated by the stream of nitrogen blowing upon its surface at room temperature for twelve to eighteen hours. The vapors were passed directly into two weighed barium oxide tubes in series, the second acting as a safety-tube to check on the complete absorption of water, and finally through a tube containing ascarite to prevent absorption of carbon dioxide and water from the air. When liquid was no longer visible, the distilling flask was heated for an hour in boiling water to expel any water entrapped in the residue; it was then heated further with a free flame until the silver nitrate melted, the residue being kept in the molten state for a few minutes. The gas was then allowed to flow through the train for an hour more to sweep out any dioxane condensed in the U-tubes containing the barium oxide. Drierite, first tried as the absorbing agent, was found to retain dioxane to some extent under these conditions. For samples containing about 0.5 g. of water, barium oxide proved a suitable absorbing agent; the second barium oxide tube generally caught only negligible amounts of water, namely, 1 or 2 mg. The method was tested on known weights of water, with and without dioxane and silver nitrate. On twelve test runs, using from 0.15 to 1.5 g. of water, the average error was 3.7 mg., with a maximum discrepancy of 10 mg. in a 1-g. sample. With samples containing about 0.5 g. of water, therefore, the method, though slow and tedious, can be accurate to within 1% (relative), which is probably much better than could be attained with the measurement of some physical property of the distilled solvent, under the circumstances.

Finally, some of the solid phases (wet and centrifuged) were also analyzed for their silver content by volumetric titration with standard thiocyanate, using Volhard's method.

Because of the unfavorable angle for the extrapolation of tie-lines for most of the complexes on the equilibrium diagram, the graphical or the algebraic methods for the determination of solid phases by extrapolation from the liquid composition through original complex or wet residue could not be relied upon; a few direct analyses of centrifuged residues were therefore also made, by determination of their silver nitrate content by titration or evaporation. Extrapolation is further rendered doubtful in the present case because of the small amount of solid remaining in the various tubes; it was thought necessary to use only small excesses of solid in order to ensure the attainment of equilibrium for any possible phase transformation.

Results.—Table I summarizes the results, showing the composition of the original com-

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[1] Davis and Ricci with Sauter, THIS JOURNAL, 61, 3274 (1939).

TABLE I

SYSTEM $AgNO_3$–DIOXANE–WATER AT 25°

Original complex		Satd. soln.		Wet residue		Centrifuged solid, % dioxane by analysis	% Dioxane in solid, by extrapolation[c]	Solid phase[d]
$AgNO_3$	H_2O	$AgNO_3$	H_2O	$AgNO_3$	H_2O			
..	..	71.8	28.2[a]					A
72.1	25.3	69.4	27.8[b]					A
70.2	24.8	66.8	27.6[b]					A
67.3	23.7	63.0	26.9[b]					A
64.0	24.1	60.4	26.4[b]					A
73.5	16.2	58.0	25.7[b]					A
60.1	23.4	56.8	25.4				1.3	A
60.0	22.5	55.8	25.1			3.4	3.6	A
62.8	20.2	54.8	24.5			0.0	−0.4	A
61.3	19.7	52.9	24.0			.0	.2	A
61.3	19.0	52.1	23.5[b]					A
60.2	18.3	50.3	22.9			.0	.4	A
56.0	18.8	48.5	22.1			.0	1.3	A
50.3	20.6	47.9	21.7			.0	4.8	A
49.1	20.0	46.6	21.0				0.9	A
After seeding		44.6	22.1			4.8	8.0	D
58.1	22.9	55.1	25.0			7.3	9.2	D
55.0	21.7	50.8	24.1			7.1	7.0	D
53.8	21.3	49.4	23.8			6.5	8.7	D
57.7	17.8	47.2	23.0	78.2	8.3		(2.8)	D
55.8	18.2	46.4	22.9			0.0	7.8	D
58.0	16.5	45.3	22.2	72.2	10.2		(5.1)	D
55.1	17.1	43.8	21.8	79.9	6.6		(4.1)	D
57.5	15.7	43.3	21.6				4.7	D
47.7	18.6	41.8	21.0			4.8	6.6	D
54.5	14.2	38.6	19.6	78.8	7.0		(1.3)	D
37.6	16.0	32.9	17.4			6.4	8.7	D
50.1	11.3	29.8	16.3				4.0	D
39.3	13.2	28.3	15.8	83.6	2.9		(4.4)	D
36.5	13.1	26.7	15.3	73.2	5.0		(4.7)	D
43.7	9.8	22.6	13.8	76.5	3.7		(4.2)	D
25.0	11.3	18.2	12.5			7.6	11.0	D
33.6	8.6	14.8	11.2				3.2	D
25.2	8.8	12.8	10.5	72.5	3.1		(7.3)	D
41.2	5.1	7.3	8.5				7.9	D
17.9	3.8	1.3	4.6				3.2	
	0.0	0.003	0.0					

[a] By difference. [b] Calculated from ratio of water to dioxane in original complex assuming solid phase to be silver nitrate. [c] Through satd. soln. and original complex; those in parentheses averaged with extrapolation through wet residue also. [d] A, silver nitrate; D, dioxanate of silver nitrate.

plexes in each case (prepared by weighing the three components), the composition of the saturated solution, and some analyses of corresponding wet and centrifuged residues. All compositions are in weight per cent. With the exception of five cases, the results listed are the average of duplicate analyses on each sample. These duplicates agreed very closely (within $^1/_{1000}$) for the silver nitrate determination; for the water determination the average disagreement between duplicates was relatively $^5/_{1000}$.

The plot of the results on triangular coördinates shows two branches to the solubility curve, that for saturation with unsolvated silver nitrate extending, in metastable equilibrium, considerably beyond the intersection of the two curves, which occurs at approximately 55.5% $AgNO_3$ and 25.0% H_2O. To avoid confusion, the compositions of complexes and wet residues have not been shown on the diagram. The difference between the curves, however, is quite evident, and the nature of the saturating solid can be inferred from the extrapolation of tie-lines and analysis of centrifuged residues. By extrapolation the first solid phase is found to contain 1.6% of dioxane as the average of the eight extrapolations listed in

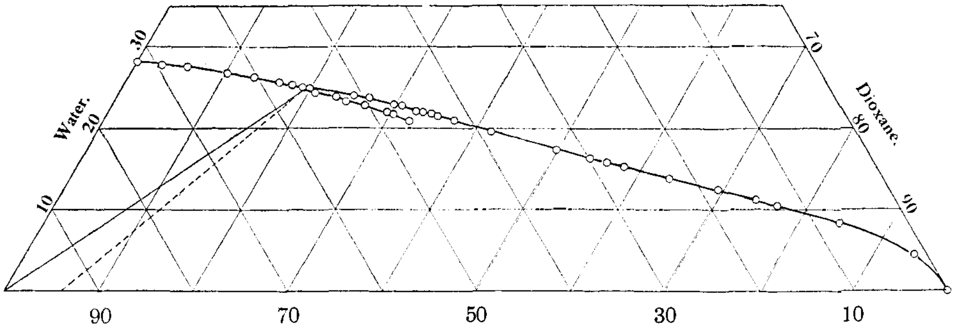

Fig. 1.—System silver nitrate–dioxane–water at 25°.

the table; this may well be attributed to experimental error. The centrifuged residues for this curve were found to be 100% $AgNO_3$ (± about 0.1%), so that the phase is plainly pure silver nitrate. The tie-lines for the longer curve extrapolate to values ranging from 1.3 to 11.0%, with an average value of 5.7% dioxane on the base of the diagram, and the analysis of centrifuged residues, for silver content, gives a dioxane percentage of 6.0, on the assumption that the phase consists of silver nitrate and dioxane. The relation between the two curves was also brought out by seeding a solution on the metastable part of the silver nitrate curve with the "dioxanate" solid, thus obtaining a marked change in composition of the solution, giving a point on the stable "dioxanate" curve; this experiment is reported in the table with the others.

It is difficult to assign a reasonable formula to this dioxanate of silver nitrate. The average composition of the centrifuged solids is 94% $AgNO_3$, but with rather low precision. This may be compared with the theoretical 93.91% for the ratio $8AgNO_3:1C_4H_8O_2$ (the ratios 6:1, 7:1, 9:1, 10:1, contain the percentages 92.06, 93.11, 94.55, 95.07, respectively). The extrapolations, although even less reliable, agree roughly with the same composition, giving an average of 94.3% $AgNO_3$. The experiments leave no doubt that there is such a solvated phase, but although the formula $(AgNO_3)_8 \cdot C_4H_8O_2$ may be suggested for it, we do so only with considerable reserve. The solid has a less crystalline, more voluminous appearance than silver nitrate itself.

On the Solubility of Silver Nitrate in Water at 25°.—Special attention was given to this simple determination in view of the rather wide variation of the literature values for the aqueous solubility of silver nitrate, despite the fundamental and direct nature of the analytical method involved. The cause of the discrepancy may perhaps lie in the marked viscosity and high density of the saturated solution with consequent difficulty in sampling and filtration. The results here given are corrected for buoyancy in weighing

By evaporation	71.85 ± 0.01%;
By titration (Volhard)	71.82 ± .02%;
Average	71.83 ± .02%;
Density of solution	2.307

This value may be compared with the more recent literature references:

Kazantzew[2] (1925)	71.88%
Sirokin[3] (1927)	72.0
Bailey[4] (1930)	71.0

The average given by Seidell[3] is 71.8%; that in the "International Critical Tables,"[5] based on work reaching only to 1911, is 70.4 ± 2%.

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Summary

The ternary system silver nitrate–water–dioxane has been studied at 25°. Evidence is given for a solid dioxanate of silver nitrate, containing about 94.0% $AgNO_3$, and to which the tentative formula $(AgNO_3)_8 \cdot C_4H_8O_2$ is assigned.

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(2) Kazantzew, *C. A.* **19**, 1218 (1925).

(3) Seidell, "Solubilities, etc.," 1940, Vol. 1, p. 62.

(4) Bailey, *J. Chem. Soc.*, 1534 (1930).

(5) "International Critical Tables," Vol. IV, p. 223, 1936.