ratio, *p*H 8.0) were used as catholytes and equimolar potassium nitrate solutions as anolytes. After electrolysis for five hours, the anolyte and catholyte gave, respectively, positive and negative tests for neodymium with ammonium acetate and aluminon.[18] Since in the absence of the current, no physical diffusion could be detected after the same period of time, the presence of anionic neodymium was shown. Absence of a positive test for neodymium on the catholyte is not to be taken as indicating complete transfer to the anode compartment. As electrolysis is continued, the catholyte becomes more alkaline, rendering the complex too stable to permit detection of neodymium by the aluminon reagent.

Continued electrolysis caused precipitation of hydrous neodymium hydroxide on the cathode side of the sintered glass disc and gave an anolyte containing no detectable neodymium. Under these conditions, the major portion of the complexing agent was transferred to the anode compartment where, because of increased acidity, dissociation of the complex occurred. Released neodymium ions then migrated to the alkaline cathode solution where they are precipitated.

Acknowledgment.—The authors express their sincere appreciation to the Office of Naval Research for the support which rendered this investigation possible.

Summary

1. The absorption spectra of neodymium chloride solutions containing varying quantities of added ethylenediaminetetraacetate have been measured over the wave length range 2500–10,000 Å.

2. In the range 5100–10,000 Å. every neodymium absorption band is split into two or more bands. The most pronounced effects occur in the range 5100–6000 Å. where the 5218 Å. band is split into four definite bands with two additional inflections and the 5750 Å. band is split into five definite bands with two additional inflections. These effects are interpreted as indicating interactions between neodymium and ethylenediaminetetraacetate ions in solution.

3. Spectrophotometric measurements at 2500–2600 Å. suggest the presence of at least a 1:1 complex, but cannot be regarded as conclusive.

4. Electrometric titration studies indicate clearly the presence of a 1:1 complex. No evidence for any other species has been obtained.

5. Electrophoretic migration studies show the neodymium complex to be anionic in character. The complex is stable in alkaline solutions.

URBANA, ILLINOIS RECEIVED MAY 24, 1950

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[18] Welcher, "Organic Analytical Reagents," Vol. II. D. Van Nostrand Co., Inc., New York, N. Y., 1947, p. 101.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

The Systems Cobaltous Nitrate–Water–Acetone and Cobaltous Nitrate–Water–*t*-Butyl Alcohol at 25°

BY LEONARD I. KATZIN AND JOHN R. FERRARO

High solubilities of inorganic salts in organic liquids are still generally viewed with surprise. Accumulating evidence shows that many types of salts are soluble in oxygenated organic liquids—alcohols, ketones, ethers and esters. The system uranyl nitrate–water–organic solvent was investigated for a number of organic liquids by Katzin and Sullivan.[1] They found the solubilities of uranyl nitrate on a mole % basis to be markedly greater in mixed aqueous organic systems than in pure water. Thus, although uranyl nitrate at 25° attains a concentration of 54.5% in water solution, amounting to about 5.5 mole %, it has even greater solubility in a number of water–solvent mixtures, as shown by the ternary phase studies. In some cases the concentration of uranyl nitrate may approximate 15 mole %. One or more mixed water–organic solvates could be isolated from most of these systems as stable equilibrium solid phases. As might be expected, there was a marked correlation between the tendency toward mixed solvate formation and the electron donor strength of the solvent.

To see to what extent the behavior is a function of the particular salt used and to what extent it is general, the ternary systems with water and acetone, and water and *t*-butyl alcohol, have been investigated for the salt cobaltous nitrate. The solvents chosen were those giving the least solvation (acetone) and the most solvation (*t*-butyl alcohol) in the uranyl nitrate system. Preliminary experiments had indicated that cobaltous nitrate was soluble to some extent in organic solvents.

The results to be given in detail in this paper indicate that the behavior found for the uranyl nitrate system is not limited to that salt, and is in large part a characteristic function of the solvents used. The same mixed solvates with total solvation of six were found for cobalt nitrate in the *t*-butyl alcohol system, the water component corresponding to the hydrates found in the acetone system. In the latter, the simple hydrates were formed in preference to mixed sol-

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[1] Katzin and Sullivan, *J. Phys. Colloid Chem.*, February, 1951; Atomic Energy Commission Declassified Document No. 2537.

vates, as in the uranyl nitrate case. In further analogy to the uranyl nitrate situation, a tetrahydrate was found for cobalt nitrate in the acetone system which had not been recognized in the binary system cobalt nitrate–water. This tetrahydrate, however, is stable over a considerable range of liquid compositions in the acetone system, and can be prepared pure by various means. Tests made indicate that it should appear in the binary nitrate–water system, between the melting point of the hexahydrate and its own melting point. A final analogy to the uranyl nitrate system is found for cobalt nitrate in the low-water region of the salt–water–acetone system in which liquid compositions are found with very high mole fractions of salt, amounting to almost 25 mole % of cobalt nitrate, as compared with the 9.2 mole % for the saturated aqueous solution.

Procedure

Mixtures of solid and liquid were equilibrated by rotation at 25 ± 0.03° for a period of at least 72 hours. Glass-stoppered test-tubes (2.5 cm. × 12.5 cm.) served as the equilibration vessels. These were placed horizontally in a rotator and completely immersed in the water-bath. During the period of equilibration the test-tubes were protected from strong light. Glass beads were placed in the tubes to give a better dispersion of solid in the liquid.

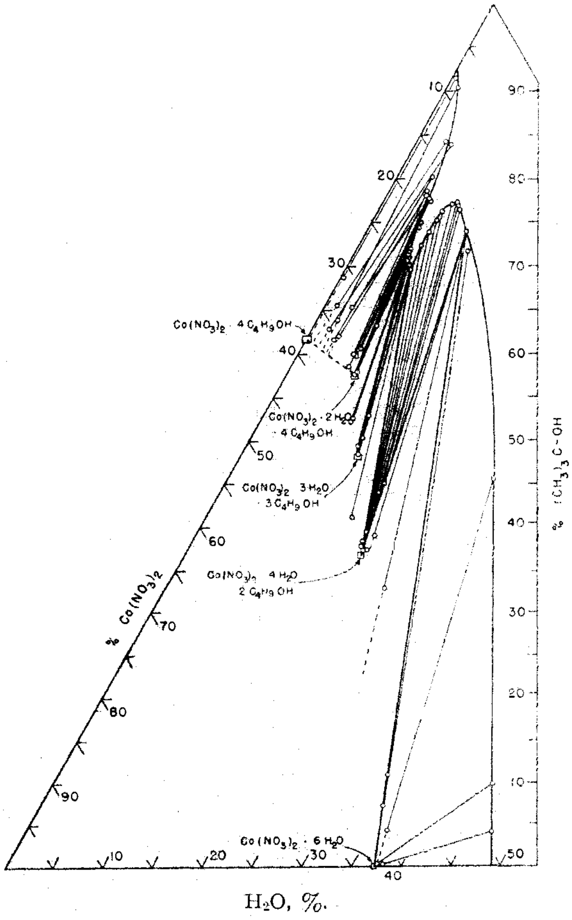

Fig. 1.—System $Co(NO_3)_2$–H_2O–$(CH_3)_3COH$ at (25°).

Analyses were carried out by the method of "wet residues."[2] Sampling was done in a dry box. The liquid phases were sampled by pipetting from the vessel to a weighing bottle. Solid phases were dried by pressure between sheets of filter paper, the solids being left somewhat damp. Two samples of each phase were weighed for cobalt analysis and three samples were weighed for water analysis. Organic components were estimated by difference.

The analysis for cobalt was done by means of electrolysis. The organic component was driven off by heating prior to electrolysis, since it interfered. All electrolyzed solutions were tested with ammonium sulfide to confirm quantitative deposition. Water was determined by the Karl Fischer method[3] using the apparatus of Zerban and Sattler,[4] as in the uranyl nitrate study.[1]

Cobalt Nitrate.—This was the commercially pure hexahydrate (Merck and Baker). The trihydrate was made by heating molten hexahydrate under reduced pressure at a temperature of 90–100° (oil-bath temperature). The dihydrate was made by heating molten trihydrate under reduced pressure at a temperature of 100–110° (oil-bath temperature), and also by long desiccation over concentrated sulfuric acid under reduced pressure. Purity was checked by combined water and cobalt analysis.

Solvents.—It was necessary to dry the commercial acetone and *t*-butyl alcohol. The acetone was dried by allowing it to stand over potassium carbonate for at least 48 hours and then distilling. The distilled acetone was then refluxed for a short time with calcium hydride and again distilled. The *t*-butyl alcohol was dried with sodium and distilled. All distillations were carried out with precautions to exclude moisture.

Experimental

In the low water region of the diagrams some difficulty was found in obtaining pure solids. In the *t*-butyl alcohol system hygroscopicity made it difficult to obtain perfectly anhydrous solids, and the water content varied from a few tenths of 1 to 3% or more for solids which by the phase diagram should be anhydrous. In the acetone system similar difficulties were encountered. Here additional troubles were met because of the lower solvating power of the acetone. Thus, in order to reach portions of the diagram with an average of less than two waters per cobalt (the ratio in the lowest hydrate we could prepare), it was necessary to evaporate solutions under reduced pressure. When this was done there were found occasionally definite signs of chemical decomposition, perhaps initiated by reaction between the nitrate and organic material, but possibly due to simple decomposition of unsolvated cobalt nitrate. In general, anhydrous cobaltous nitrate solids which are obtained have organic electron donor molecules coördinated to them. Attempts to desolvate these substances,[5,6] as in the case of the dihydrate, lead to decomposition of the solid. Preparation of anhydrous cobaltous nitrate has been reported by Guntz and Martin[7] through the action of nitric anhydride on the hydrated salt, as well as by the action of finely divided cobalt on a solution of silver nitrate in liquid ammonia. It would be necessary to establish in this case that nitrogen-containing materials were not in fact coördinated to the salt, stabilizing it. Verified preparations of pure simple nitrates of transition elements are extremely few in number.

System Cobaltous Nitrate–Water–Acetone (Fig. 1, Table I).—The solubility curve of cobalt nitrate hexahydrate runs almost linearly from the water saturation value of 50.7% to the intersection with the tetrahydrate curve at 43.0% cobalt nitrate, 31.2% acetone, 25.8% water. The water to cobalt mole ratio at this point is 6.1:1. The

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(2) Schreinemakers, *Z. physik. Chem.*, **11**, 81 (1893).

(3) Smith, Bryant and Mitchell, Jr., THIS JOURNAL, **61**, 2407 (1939).

(4) Zerban and Sattler, *Ind. Eng. Chem.*, *Anal. Ed.*, **18**, 138 (1946).

(5) Funk, *Z. anorg. Chem.*, **20**, 407 (1899).

(6) Lescoeur, *Ann. chim. phys.*, [7] **7**, 416 (1896).

(7) Guntz and Martin, *Bull. soc. chim. France*, [4] **5**, 1009 (1909); [4] **7**, 322 (1910).

solubility curve of the tetrahydrate shows a rather more marked curvature, with a minimum cobalt nitrate content of 39.4%, and intersects the solubility curve of the trihydrate at the composition 49.2% cobalt nitrate, 8.6% water, 42.2% acetone. The water to cobalt ratio at this point is less than 2. The solubility curve of the trihydrate is short, the dihydrate commencing to appear as a solid phase when the liquid composition is 52.9% cobalt nitrate, 8.1% water and 39.0% acetone. The solubility curve of the dihydrate shows a maximum at the composition 57.3% cobalt nitrate, 6.7% water and 36.0% acetone, and terminates at the composition 55.1% cobalt, 5.3% water and 39.6% acetone.

TABLE I

COBALTOUS NITRATE–WATER–ACETONE AT 25°

Liquid phase		Solid phase		
H_2O, %	$Co(NO_3)_2$, %	H_2O, %	$Co(NO_3)_2$, %	
48.68	50.36			
44.45	48.98			$Co(NO_3)_2 \cdot 6H_2O$
36.83	46.39	37.15	62.08	
27.04	43.54	36.84	62.75	
25.83	43.01	34.91	57.92	$Co(NO_3)_2 \cdot 6H_2O$ +
25.83	42.99	28.82	63.15	$Co(NO_3)_2 \cdot 4H_2O$
23.86	42.94	27.94	63.28	
20.41	41.00	27.40	65.08	
20.28	41.34	26.98	67.88	
16.41	40.38	23.87	61.03	
13.93	39.83	25.20	64.82	$Co(NO_3)_2 \cdot 4H_2O$
13.06	39.38	25.55	64.75	
11.55	42.44	24.02	64.15	
9.17	47.14	25.32	68.05	
8.90	46.88	23.97	65.54	
8.73	47.00	24.48	66.52	
8.66	49.37	22.03	64.86	
8.58	49.05	19.83	65.54	$Co(NO_3)_2 \cdot 4H_2O$ +
8.68	49.12	21.06	65.18	$Co(NO_3)_2 \cdot 3H_2O$
8.54	49.26	21.48	68.47	
8.95	49.94	22.22	66.80	
8.92	50.00	20.82	66.52	
8.45	50.05	20.80	67.75	
8.79	51.44	16.07	65.80	$Co(NO_3)_2 \cdot 3H_2O$
7.89	52.83	19.10	71.17	
7.98	52.35	19.67	72.00	$Co(NO_3)_2 \cdot 3H_2O$ +
7.67	52.37	16.09	74.43	$Co(NO_3)_2 \cdot 2H_2O$
8.15	52.51	15.93	76.62	
8.27	52.93	15.07	70.13	
8.00	53.10	15.48	71.41	
8.43	53.84	13.43	72.50	
7.92	56.01	14.18	73.67	$Co(NO_3)_2 \cdot 2H_2O$
6.65	57.32	12.84	74.99	
6.39	57.00	12.88	75.80	
6.38	56.54	9.62	67.04	
5.94	56.11	10.36	69.09	
5.34	55.04	10.89	74.05	$Co(NO_3)_2 \cdot 2H_2O$ +
5.29	55.14	8.37	65.02	$Co(NO_3)_2 \cdot 2$-
3.57	50.39	7.29	67.43	(CH_3COCH_3)(?)

The long solubility curve of the tetrahydrate indicates it to be a stable solid. It has also been found as the first product of desiccation of the hexahydrate *in vacuo* over sulfuric acid, by ourselves and by Funk.[5] We also have prepared this hydrate by subjecting the melted hexahydrate to suction at temperatures below the melting point of tetrahydrate. It was not possible to establish whether fusion of the tetrahydrate was complete before decomposition to give solid trihydrate, but the apparent melting point of 84° was sharp and reproducible. It is therefore clear that the work of Funk on the binary cobalt nitrate–water system is in error, in that he did not recognize the presence of this solid. To check the point, hexahydrate was melted, and tetrahydrate prepared by desiccation was mixed with it. The material was held for 20 minutes at a temperature below the melting point of the tetrahydrate, and the hot liquid phase then sucked off on a sintered surface. The residual solid still analyzed as tetrahydrate. Because difficulty was experienced in reaching the lowest water part of the diagram, it cannot be said definitely whether the anhydrous solid is $Co(NO_3)_2$ or $Co(NO_3)_2 \cdot 2$ acetone.

System Cobaltous Nitrate-Water-*t*-Butyl Alcohol (Fig. 2, Table II).—The solubility curve of the hexahydrated solid runs from the water saturation value of 50.7% to the composition 15.7% cobalt nitrate, 10.1% water, 74.2% alcohol. At this point a solid of the composition cobalt nitrate tetrahydrate dialcoholate appears. Its solubility curve shows a sharp curvature, with a minimum cobalt concentration of 15.2% at 7.9% water, and a maximum at the composition 23.8% cobalt nitrate, 6.7% water and 69.5% *t*-butyl alcohol. At this point transition takes place to the trihydrated-trialcoholated solid. A short solubility curve intersects the curve for the dihydrate-tetraalcoholate at the composition 22.9% cobalt nitrate, 5.7% water and 71.4% *t*-butyl alcohol. The solubility of the anhydrous tetraalcoholate follows a curve from 8.0% cobalt nitrate and 92.0% alcohol to its intersection with the curve for the dihydrate-tetraalcoholate at 17.7% cobalt nitrate, 4.7% water and 77.6% *t*-butyl alcohol.

TABLE II

COBALTOUS NITRATE–WATER–*t*-BUTYL ALCOHOL AT 25°

Liquid phase		Solid phase		
H_2O, %	$Co(NO_3)_2$, %	H_2O, %	$Co(NO_3)_2$, %	
47.11	48.93	38.08	61.84	
44.51	45.67	37.35	62.43	$Co(NO_3)_2 \cdot 6H_2O$
26.97	27.54	36.59	59.28	
11.44	16.88	34.64	58.35	
10.16	15.61	33.43	55.67	
10.22	15.71	22.15	44.95	$Co(NO_3)_2 \cdot 6H_2O$ + $Co(NO_3)_2 \cdot 4 \cdot$
10.06	15.65	18.20	42.94	$H_2O \cdot 2(CH_3)_3COH$
8.17	15.38	16.01	38.94	
7.85	15.22	16.24	39.03	
7.65	15.23	18.21	44.47	
7.15	15.71	16.37	39.81	$Co(NO_3)_2 \cdot 4H_2O \cdot 2(CH_3)_3COH$
6.64	17.19	17.90	44.87	
6.66	18.47	17.10	43.57	
6.41	19.59	17.25	44.90	
6.22	21.42	17.21	44.43	
6.61	23.74	14.73	44.08	$Co(NO_3)_2 \cdot 4H_2O \cdot 2(CH_3)_3COH$
6.83	23.81	11.79	39.70	$Co(NO_3)_2 \cdot 3H_2O \cdot 3(3H_3)_3COI.$
6.21	23.58	11.23	39.32	$Co(NO_3)_2 \cdot 3H_2O \cdot 3(CH_3)_3COH$
5.86	23.50	11.49	38.45	
5.88	23.06	9.31	38.24	$Co(NO_3)_2 \cdot 3H_2O \cdot 3(CH_3)_3COH$
5.87	22.92	10.81	36.85	$Co(NO_3)_2 \cdot 2H_2O \cdot 4(CH_3)_3CO$
5.59	22.91	9.38	38.60	
5.49	22.71	5.85	35.63	
5.46	22.60	7.07	35.04	$Co(NO_3)_2 \cdot 2H_2O \cdot 4(CH_2)_3COH$
5.45	23.13	6.67	30.58	
4.98	20.66	5.64	33.36	
4.87	20.01	5.63	34.49	
4.77	17.83	6.99	35.46	$Co(NO_3)_2 \cdot 2H_2O \cdot 4(CH_2)_3COH$ +
4.57	17.58	2.85	31.72	$Co(NO_3)_2 \cdot 4(CH_3)_3COH$ (?)
4.00	17.80	3.19	34.79	
3.89	17.53	5.14	34.85	
3.65	16.27	2.91	35.69	$Co(NO_3)_2 \cdot 4(CH_2)_3COH$ (?)
3.85	12.35	1.76	35.40	
3.07	12.73	1.24	33.24	
1.19	8.49	2.14	34.04	
0.40	8.09	0.31	30.90	

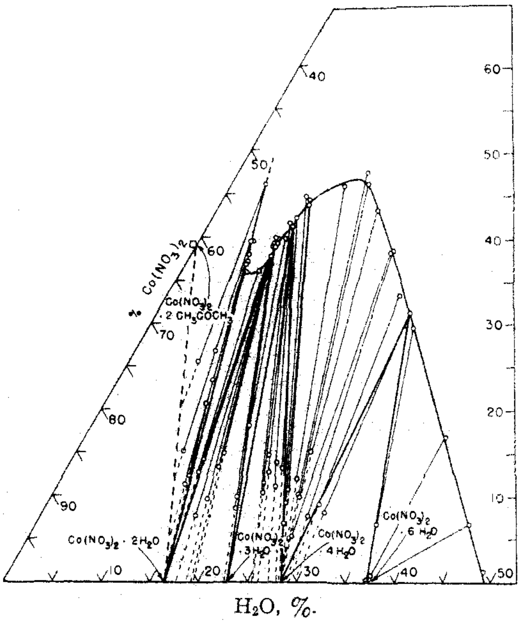

Fig. 2.—System $Co(NO_3)_2$–H_2O–CH_3COCH_3 at 25°.

Discussion

The pictures of the ternary systems cobaltous nitrate–water–acetone and cobaltous nitrate–water–*t*-butyl alcohol are very similar to those found for uranyl nitrate. The equilibrium solid hexahydrate, in the *t*-butyl alcohol system, first loses two molecules of water, then the third and fourth singly, in favor of the competing alcohol. Finally the last two molecules of water are lost as a unit, without being replaced by alcohol molecules. The reason for the tetrasolvation of the anhydrous solid, in contrast to the hexasolvation of the partially hydrated solids, would seem to lie in geometric (lattice energy difference) considerations, since with four waters the cobalt holds two alcohol molecules in addition. Differences from the uranyl nitrate system are the presence of a tetrahydrated hexasolvate (presumably because of the markedly greater stability of the tetrahydrated cobalt nitrate), and the apparent tetrasolvation rather than trisolvation of the anhydrous cobalt alcoholated salt. The two differences may both be expressions of greater solvation energy in the case of the cobalt salt. In the liquid phase picture, the outstanding difference seems to be the fact that the cobalt nitrate trihydrate-trialcoholate shows a high solubility relative to the anhydrous salt, while with uranyl nitrate the condition seems reversed. In both cases the first additions of *t*-butyl alcohol to the system depress the solubility of the salt.

In the *t*-butyl alcohol system, the ratio of total solvent to cobalt, on a mole basis, is always high, so that all through the diagram one is able to picture the cobalt in solution as largely hexasolvated. The solids in the acetone system are all simple hydrates, and one can attribute this difference from the alcohol system to the effects of lesser binding energy, such that the lattice energy differences between simple hydrates and the solvated solids are greater than the energy with which the organic component is held. On considering the liquid situation, however, one is faced with the fact that although the solvent–salt ratio in the liquid in equilibrium with the hexahydrate–tetrahydrate pair of solids is greater than eight (Table III), in the region of the tetrahydrate–trihydrate pair the ratio is about 4.3, and one cannot longer think solely in terms of hexasolvation.

TABLE III

MOLE RATIOS, SOLVENT–SALT, AT POINTS OF FIXED WATER ACTIVITY, IN SYSTEM COBALT NITRATE–WATER–ORGANIC SOLVENT

Hydrate pair	Org. solvent	Ratio H_2O/salt	 Org./salt	 Total
6–4	*t*-BuOH	6.6	11.7	18.3
	Acetone	6.1	2.2	8.3
4–3	*t*-BuOH	2.9	7.2	10.1
	Acetone	1.8	2.5	4.3
3–2	*t*-BuOH	2.5	7.7	10.2
	Acetone	1.5	2.2	3.7
2–0	*t*-BuOH	2.4	10.9	13.3
	Acetone	1.0	2.1	3.1

From spectrophotometric studies of the behavior of dilute cobalt nitrate in acetone and *t*-butyl alcohol solutions,[8] in the essentially anhydrous condition, it has been found that formation of undissociated salt occurs practically completely in both solvents. Data have been presented in support of the hypothesis that this is not simple electrostatic attraction in a medium of low dielectric constant, but is the result of displacement of coördinated water or organic solvent. According to the point of view elaborated in detail by Bernal and Fowler[9] and now rather generally accepted, the total coördination number of cobalt is six. When two of the coördination positions are filled by anions, only four are left for solvent groups. There seems to be good evidence, therefore, for the hypothesis that somewhere in the range from pure aqueous solution to solutions rich in organic component, transition occurs from the hexasolvated salt to the compound $Co(NO_2)_2 \cdot 4X$ (where X = a molecule of water or organic compound). Data both for this salt and for cobalt chloride[10] show that the coördination of the alcohol is much stronger than that of acetone. The liquid phase picture for the *t*-butyl alcohol system leaves one with at least the possibility that here the extent of solvation of the solute does not fall below that indicated by the formula $Co(NO_3)_2 \cdot 4X$; for the minimal solvent–salt ratio in the liquid phase is 10, and solid of this formula appears as the equilibrium solid in the anhydrous region of the phase diagram. The

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(8) Katzin and Gebert, THIS JOURNAL, **72**, 5455 (1950).

(9) Bernal and Fowler, *J. Chem. Phys.*, 1, 515 (1933).

(10) Katzin and Gebert, THIS JOURNAL, **72**, 5464 (1950).

acetone situation is apparently much more complicated. Even at the point of equilibrium of tetrahydrated and trihydrated solids, the solvent–salt ratio is only 4.3, and in the region of the dihydrate solid phase it drops to about 3. One must either invoke a decrease in coördination number, or, preferably, consider the possibility that coördination number 6 is maintained by coördination between molecules (*e. g.*, through the nitrate groups) to give polymers of some sort in solution. In agreement with this possibility, the liquid phases are found to be extremely viscous in this region of the phase diagram. X-Ray investigation of these liquids may be expected to give evidence for "super-arrangement" found even in aqueous uranyl nitrate and thorium nitrate systems[11] which are much more dilute (*ca.* 15–20 to one, solvent to salt).

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[11] Prins, *J. Chem. Phys.*, **3**, 72 (1935).

Summary

1. The system cobalt nitrate–water–acetone at 25° shows as equilibrium solids the hexahydrate, tetrahydrate, trihydrate, dihydrate and (probably) the diacetonate.

2. Several methods of preparation of the tetrahydrate are given, its apparent melting point is determined to be 84°, and its place in the cobalt nitrate–water binary system is indicated.

3. The system cobalt nitrate–water–*t*-butyl alcohol at 25° shows as equilibrium solids the hexahydrate, the tetrahydrate-dialcoholate, the trihydrate-trialcoholate, dihydrate-tetraalcoholate and the anhydrous tetraalcoholate.

4. Solvation of the cobalt nitrate in the alcohol solution and polymerization in the acetone solution are suggested as explanations of the liquid phase behavior.

CHICAGO, ILL. RECEIVED MARCH 15, 1950

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Spectrophotometric Investigation of Cobaltous Nitrate in Organic Solvents[1]

BY LEONARD I. KATZIN AND ELIZABETH GEBERT

The spectacular color changes of some cobalt salts (*e. g.*, the chloride) between a salmon-red color and a pure blue, have been known and have attracted interest for many years. Some years ago two extremes of interpretation became differentiated. The one holds that the principal basis for the color change is a change in the hydration of the cobalt, the lower hydrate corresponding to the blue form. The second school holds that the effect is due to formation of a chemical complex, such as $CoCl_4^{--}$. Various hybridizations of these extreme views have of course been proposed.

The data on the halide behavior have been extrapolated to the color changes of other cobalt salts so that the tendency has been to interpret all colors as gradations between the red and blue forms, and hence often as semi-quantitative measures of the degree of admixture of the two forms. An assumption implicit in this procedure is that all tendencies toward visual bluishness represent the same structural alterations and presumably the same spectral changes. This implies further that a given intermediate color should be represented as a mixture of two spectra, that characteristic of the pure red form and that characteristic of the pure blue form.

It will be the endeavor of this paper to demonstrate that not only is all visual bluishness not due to mixture of a blue spectrum (typified by the chloride blue) with the water red spectrum, but that the halide blue spectrum is not typical of all cobaltous complexes, and at least one of them has a spectrum little different from the water red spectrum. Further, as might be anticipated, it will be shown that the complexing–hydration views of these changes are not independent.

Procedure

Spectrophotometric measurements were made with the Beckman model DU quartz spectrophotometer. The density scale of the instrument was calibrated with standards obtained from the National Bureau of Standards. Density settings were found reproducible to 0.002 density unit.

The cobalt nitrate was the chemically pure hexahydrate, usually desiccated to various degrees over sulfuric acid. Cobalt perchlorate was prepared from the carbonate and perchloric acid, and recrystallized twice. Chemically pure lithium nitrate was dried in the oven, at about 95°. Tetrabutylammonium nitrate was kindly prepared for us by Dr. Louis Kaplan, from silver nitrate and tetrabutylammonium iodide.

Dioxane was prepared in dry form by distillation over sodium. Periodic tests were made for peroxide content with potassium iodide. Anhydrous methanol was prepared from commercial anhydrous methanol by treatment with magnesium metal turnings, and distillation. *t*-Butyl alcohol was prepared by distilling the commercial anhydrous solvent over sodium, and sometimes by fractional freezing. The other solvents were commercial products. All were analyzed for water content by titration with Karl Fischer reagent, using an electrical end-point determination.[1a] The standard used for the reagent was sodium acetate trihydrate.

Stock solutions were made of the salts in the desired solvents, and aliquot dilutions were made for spectrophotometric study. The concentrations of the cobalt salts were determined by analysis for cobalt by standard electrodeposition procedures. A few were performed by

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[1] Presented in part at meeting of the American Chemical Society, San Francisco, Calif., March 28–April 1, 1949.

[1a] Katzin and Sullivan, *J. Phys. & Colloid Chem.*, in press; Atomic Energy Commission Declassified Document No. 2537.