[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

The System Cobaltous Chloride–Water–*t*-Butyl Alcohol at 25°

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The system cobaltous chloride–water–*t*-butyl alcohol at 25° shows as equilibrium solids the generally accepted hydrates (hexa-, di- and monohydrate), and in addition a tetrahydrate-dialcoholate. The anhydrous equilibrium solid is probably alcoholated. Concentrations of cobaltous chloride as high as 9 mole % over the monohydrate may be compared with 7 mole % for the saturated aqueous solution. A region of two liquid phases in equilibrium is found.

It has been shown previously that in the systems uranyl nitrate–water–organic solvent,[1] cobaltous nitrate–water–organic solvent,[2] and cobaltous chloride–water–acetone,[3] higher mole fractions of salt were found in some mixed water–organic solutions than in pure water. It was also found that with the strongest base solvents (*t*-butyl alcohol and some ethers for uranyl nitrate, *t*-butyl alcohol for cobaltous nitrate) mixed solvates were found as solid phases. Similar findings were obtained in the system presently reported. Unlike the previously investigated ternary systems with *t*-butyl alcohol, however, a two-liquid phase region exists in the cobaltous chloride–water–*t*-butyl alcohol system.

Experimental

Mixtures of solid and liquid were equilibrated by rotation at 25.00 ± 0.03° for periods of 72. hours or longer. Liquid–liquid distribution mixtures were equilibrated for a few hours only. Aliquots of liquid for analysis were obtained with proper precautions against contamination, and solids were analyzed as wet residues. Some single points on the binodal liquid–liquid distribution curve were obtained by adding alcohol by buret, to the point of phase separation, to a solution of salt in water made up by weight. The amount of alcohol added was determined by weighing the flask again. A series of points of phase separation could be obtained by weighing in more water, and then repeating the alcohol addition.

For starting salt, the commercial, chemically pure hexahydrate was recrystallized from water. The dihydrate[4] was prepared from this by desiccation over concentrated sulfuric acid, under reduced pressure, for one week. Monohydrate was obtained from longer desiccation (*Anal.* Calcd.: Co, 39.86; water, 12.17. Found: Co, 39.89; water, 12.26). Anhydrous cobaltous chloride[4] was prepared by heating the dihydrate in an atmosphere of hydrogen chloride. The *t*-butyl alcohol was pure commercial synthetic material, containing 0.37% water.

Water was determined by titration with Karl Fischer reagent, as in previous studies.[1-3] Cobalt was determined by standard electrolytic deposition procedures. The organic component, which interfered with the electrolysis, was first driven off by heating. Completeness of electrolysis was verified by testing the solutions with ammonium sulfide.

Discussion

The data on the system are summarized in Table I and Fig. 1. The most striking feature of the diagram is the region of two liquid phases found for the two liquid components (water and *t*-butyl alcohol) which normally give a uniform solution at the temperature and relative concentrations involved, since such separation was not observed in the ternary systems of uranyl nitrate and cobaltous nitrate with water and the alcohol, nor in the system cobaltous chloride–water–acetone. The phenomenon of a third (salt) component breaking the miscibility of water and an alcohol is not a new one, and a number of examples appear in the literature.[5,6]

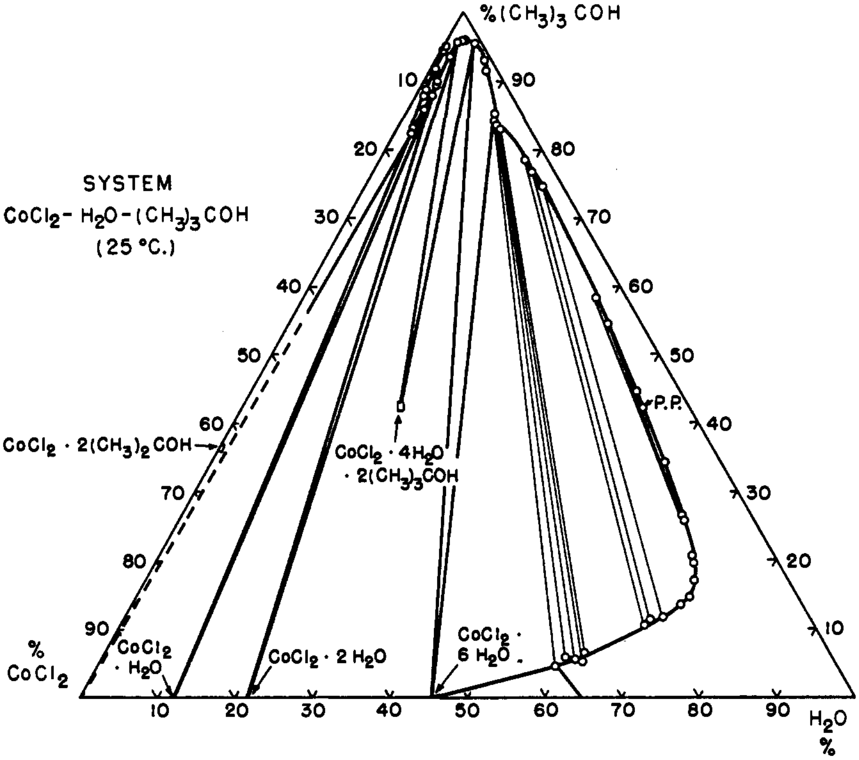

Fig. 1.

The salts effective are generally alkali metal carbonates, hydroxides, sulfates, nitrates and halides. They share the properties of being quite insoluble

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[1] L. I. Katzin and J. C. Sullivan, *J. Phys. Colloid Chem.*, **55**, 346 (1951).

[2] L. I. Katzin and J. R. Ferraro, THIS JOURNAL, **72**, 5451 (1950).

[3] L. I. Katzin and J. R. Ferraro, *ibid.*, **74**, 2752 (1952).

[4] G. L. Clark, A. J. Quick and W. D. Harkins, *ibid.*, **42**, 2483 (1920).

[5] G. B. Frankforter and F. C. Frary, *J. Phys. Chem.*, **17**, 402 (1913).

[6] A. W. Francis, pp. 823 ff. in A. Seidell and W. F. Linke, "Solubilities of Inorganic and Organic Compounds." Supplement to the Third Edition, D. Van Nostrand Co., New York, N. Y., 1952.

TABLE I

COBALTOUS CHLORIDE–WATER–BUTYL ALCOHOL AT 25°

Liquid phase				Solid phase, %		
Organic-rich, %		Water-rich, %				
H_2O	$CoCl_2$	H_2O	$CoCl_2$	H_2O	$CoCl_2$	Equilibrium solid
51.74	42.33	(Plait Point)				
49.94	5.50					
		58.41	7.18			
41.25	4.30	64.53	8.82			
37.77	3.99	65.08	8.61			
		68.86	10.38			
		69.46	10.94			
		70.76	12.00			
		71.19	13.91			
		70.80	15.40			
22.75	2.46	69.41	18.97			
20.68	2.93	67.98	20.63			
18.80	2.73	67.74	21.84			
13.24	3.64	61.95	31.40			
12.57	4.05	59.54	34.41			
12.45	4.01	60.92	33.53			
12.40	3.95	62.06	32.50			
11.99	3.97	59.15	36.51	45.72	54.42	$CoCl_2 \cdot 6H_2O$
11.54	3.32			43.24	52.45	$CoCl_2 \cdot 6H_2O$
7.33	1.31			41.09	49.18	$CoCl_2 \cdot 6H_2O$
6.15	0.97			30.88	35.53	$CoCl_2 \cdot 6H_2O$
3.93	0.86			32.18	45.36	$CoCl_2 \cdot 6H_2O + CoCl_2 \cdot 4H_2O \cdot 2TBA$
3.62	0.87			15.28	24.90	$CoCl_2 \cdot 6H_2O + CoCl_2 \cdot 4H_2O \cdot 2TBA$
3.62	0.74			16.25	28.73	$CoCl_2 \cdot 6H_2O + CoCl_2 \cdot 4H_2O \cdot 2TBA$
2.28	1.80			13.89	23.57	$CoCl_2 \cdot 4H_2O \cdot 2TBA$
1.91	2.38			13.01	24.43	$CoCl_2 \cdot 4H_2O \cdot 2TBA$
1.59	2.70			17.71	56.16	$CoCl_2 \cdot 4H_2O \cdot 2TBA + CoCl_2 \cdot 2H_2O$
1.48	2.89			11.88	21.25	$CoCl_2 \cdot 4H_2O \cdot 2TBA + CoCl_2 \cdot 2H_2O$
1.81	2.81			17.82	63.52	$CoCl_2 \cdot 4H_2O \cdot 2TBA + CoCl_2 \cdot 2H_2O$
1.47	4.71			18.79	66.10	$CoCl_2 \cdot 2H_2O$
1.69	8.57			11.60	38.80	$CoCl_2 \cdot 2H_2O$
1.27	8.66			12.69	49.09	$CoCl_2 \cdot 2H_2O$
1.57	8.92			17.10	60.28	$CoCl_2 \cdot 2H_2O + CoCl_2 \cdot H_2O$
2.19	8.90			18.11	59.35	$CoCl_2 \cdot 2H_2O + CoCl_2 \cdot H_2O$
1.95	8.70			11.19	57.68	$CoCl_2 \cdot 2H_2O + CoCl_2 \cdot H_2O$
2.10	8.70			11.60	67.29	$CoCl_2 \cdot 2H_2O + CoCl_2 \cdot H_2O$
2.24	10.10			10.10	55.37	$CoCl_2 \cdot H_2O$
2.10	12.06			13.71	64.77	$CoCl_2 \cdot H_2O$
1.89	14.98			11.80	60.00	$CoCl_2 \cdot H_2O$
2.24	15.35			4.60	34.95	$CoCl_2 \cdot H_2O + CoCl_2$
2.25	15.18			2.84	54.95	
1.05	11.29			1.38	50.64	$CoCl_2$
0.98	10.49			1.10	44.97	$CoCl_2$
0.77	8.03			1.12	27.32	$CoCl_2$
0.65	7.87			1.14	46.13	$CoCl_2$
0.23	5.38			3.80	66.18	$CoCl_2$
0.37	4.55			1.10	56.22	$CoCl_2$

in the pure organic component, and quite soluble in water. This pair of properties is also shared by $CoCl_2 \cdot 6H_2O$ in this system, since the solubility (in terms of $CoCl_2$) is over 35% by weight in water and 0.8% by weight at the minimum solubility point (over 95% *t*-butyl alcohol). In contrast, the lowest concentration found for $CoCl_2$ in the ternary system with acetone is 3.6%, and for cobaltous nitrate and uranyl nitrate, respectively, in the ternary systems with the alcohol, 15.2 and 15.15%. It may be of some significance, in the case of these last two systems, that the solid in equilibrium with these liquids of minimum salt content is not the hexahydrate but a mixed hexasolvate.

From the point at which the water-rich liquid phase disappears the solubility curve of the hexahydrate salt continues to drop to the minimum at 0.8% $CoCl_2$ and 3.7% water, which is the liquid composition at transition from the hexahydrated solid phase to the tetrahydrate-dialcoholate. The color of the water-rich liquid is always a red, and for the most part so is that of the alcohol-rich liquid. At a composition of the latter containing between 18% water and 13% water a blue coloration becomes noticeable, and at lower water concentrations, the equilibrium liquids are blue. There seems to be good reason, therefore, to correlate the sharp upturn in solubility as the equilibrium solid changes from hexahydrate to mixed hexasolvate to dihydrate with the preponderance of the blue[7] 4-coördinated [$CoCl_2 \cdot 2(H_2O$, alcohol)] in the solution. The maximum solubility of 15.35% for the salt is found at the liquid composition at which the equilibrium solid is changing from the monohydrate to the anhydrous form, and may perhaps be a basis for considering the solute form achieving maximum concentration to be ($CoCl_2 \cdot H_2O \cdot (CH_3)_3OH$). The decrease in solubility as the system becomes anhydrous is found also in the $CoCl_2$–water–acetone system, and the cobaltous nitrate–water–solvent systems.

The equilibration data alone give no clear answer to the question of whether the anhydrous solid is alcoholated. The physical nature of the solid makes it difficult mechanically to separate the liquid phase sufficiently to be sure whether or not the solid might contain solvation alcohol. Two samples of anhydrous $CoCl_2$ were therefore refluxed with *t*-butyl alcohol for periods of several hours, and allowed to cool. In one sample the supernatant was poured off, the residual solid press-dried between sheets of filter paper, and analyzed. In the second sample, the light-blue solid formed a recrystallization ring above the top of the liquid, which could be cleanly separated to leave a fairly dry brittle solid which was allowed to drain further. The analysis of the first solid was 13.26% cobalt, 0.65% water; of the second solid, 14.06% cobalt, 1.93% water. For $CoCl_2$, Co = 45.4%. The alcohol is equivalent to about 4 molecules per cobalt, which for the second sample is certainly beyond the amount for which mere physical wetting might readily account. Alcoholation of the anhydrous solid therefore seems probable. Stable alcoholates of $CoCl_2$ are known for other alcohols.[8-12]

The pair of equilibrium liquids obtained closest to the plait point (Table I) analyzed 41.25% water–4.30% $CoCl_2$ and 64.53% water–8.82% $CoCl_2$, respectively. Points in between these compositions were covered with particular care by the method of phase separation described above. At a composition 51.74% water–5.93% $CoCl_2$–42.33% alcohol the separation of phases could be distinguished only with difficulty on approaching from the high-water side. The next point, at 49.34% water–5.50% $CoCl_2$–45.16% alcohol, showed a reversal in relative densities of the more abundant and less abundant phases. The plait point is therefore near the composition 51.74% water–5.93% cobaltous chloride–42.33% *t*-butyl alcohol, which is reasonable from the symmetry of the solubility curve and the tie-lines.

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[7] L. I. Katzin and E. Gebert, THIS JOURNAL, **72**, 5464 (1950).

[8] F. Bourion, *Compt. rend.*, **134**, 556 (1902).

[9] A. Benrath, *Z. anorg. Chem.*, **54**, 328 (1907).

[10] A. Hantzsch and F. Schlegel, *ibid.*, **159**, 273 (1927).

[11] E. Lloyd, C. B. Brown, D. G. R. Bonnell and W. J. Jones, *J. Chem. Soc.*, 658 (1928).

[12] O. E. Zvyagintsev and S. N. Matatashvili, *Bull. Acad. Sci. Georgian S.S.S.R.*, **3**, 1035 (1942); cited in *C. A.*, **41**, 2956 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, AND RADIATION LABORATORY
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The Heat and Free Energy of Formation of Bromate Ion

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In an effort to clear up an inconsistency in the thermodynamic data for BrO_3^- ion, the heat of solution of $KBrO_3$ and the heats of reduction of $KBrO_3$ with I^- and Br^- have been measured calorimetrically at 25°. For $KBrO_3(c) = K^+ + BrO_3^-$, $\Delta H^0 = 9.76 \pm 0.05$ kcal./mole; for $KBrO_3(c) + 9I^- + 6H^+ = 3I_3^- + K^+ + Br^- + 3H_2O$, $\Delta H^0 = -122.26 \pm 0.8$ kcal./mole; and for $KBrO_3(c) + 8Br^- + 6H^+ = 3Br_3^- + K^+ + 3H_2O$, $\Delta H^0 = -42.17 \pm 0.3$ kcal./mole. Combining these heats with other heat and entropy data, we have calculated for BrO_3^- ion: $\Delta H_f^0 = -18.3$ kcal./mole and $\Delta F_f^0 = 2.1$ kcal./mole. These values have been discussed with respect to other experimental data.

I. Introduction

Lewis and Randall[1] calculate from the measurements of Sammet[2] on the bromine–bromate electrode that the free energy of formation of BrO_3^- is 2.3 kcal./mole. The National Bureau of Standards[3] gives 10.9 kcal./mole for the free energy of formation. This latter quantity was calculated from Thomsen's[4] heat for the reduction of BrO_3^- by Sn^{++} and Ahlberg and Latimer's[5] entropy data for BrO_3^-. The large discrepancy was thought to be primarily due to an inaccurate value for the heat of formation of BrO_3^-. Hence, the present investigation was undertaken to establish a more accurate value for this quantity. Two main reactions were studied, (1) the heat of reduction of $KBrO_3$ by iodide, and (2) the heat of reduction by bromide. The heat of solution of $KBrO_3$ in water was also measured.

Unless specifically stated, all heat calculations were made using heats of formation tabulated by the Bureau of Standards.[3]

II. Experimental

Calorimeter.—The calorimeter has been described previously.[6,7] The possibility of variation in the calorimeter stirring rate has been reduced by the use of a synchronous motor with chain and sprocket drive. The standard re-

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[1] G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 521.

[2] V. Sammet, *Z. physik. Chem.*, **53**, 678 (1905).

[3] National Bureau of Standards Circular 500, "Selected Values of Chemical Thermodynamic Properties," Washington, D. C., 1952.

[4] J. Thomsen, "Thermochemische Untersuchungen," Leipzig, J. A. Barth, 1882.

[5] J. E. Ahlberg and W. M. Latimer, THIS JOURNAL, **56**, 856 (1934).

[6] B. J. Fontana, "National Nuclear Energy Series IV-19B," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 321.

[7] H. W. Zimmerman and W. M. Latimer, THIS JOURNAL, **61**, 1550 (1939).