Oxidation of Trimethyl-*p*-lithiophenylsilane.—A solution of trimethyl-*p*-lithiophenylsilane was prepared from 1 g. (0.14 g. atom) of lithium in 20 cc. of ether and 16 g. (0.07 mole) of trimethyl-*p*-bromophenylsilane in 100 cc. of ether according to the method of Clark.[12] To this solution was added 0.07 mole of *n*-butylmagnesium bromide. The mixture was cooled to −10° and dry air passed through the solution for three hours. Color Test I[6] was negative at the end of this time so the reaction mixture was treated with water and dilute hydrochloric acid. There was obtained 3 g. of material distilling at 80–82° (15 mm.), subsequently identified as phenol (phenoxyacetic acid—mixed melting point).

A study of the results of this reaction and of the two preceding reactions would indicate that *o*-hydroxyphenyl- and *p*-hydroxyphenyltrimethylsilane may be readily hydrolyzable compounds under these experimental conditions. Since Color Test I showed the absence of any organometallic compounds previous to hydrolysis, it is possible that these hydroxyphenyltrimethylsilanes were formed in solution but cleaved to give phenol and trimethylsilanol on hydrolysis.

Triphenyl-α-chloroethylsilane.—To 17.5 g. (0.088 mole) of α-chloroethyltrichlorosilane[19] in 50 cc. of ether was added 0.257 mole of phenyllithium in 216 cc. of ether. The rate of addition was approximately 4 cc. per minute. Color Test I[6] was negative thirty minutes after the addition was complete. The reaction mixture was worked up in the usual manner to give 6 g. (21%) of product melting at 90–110°). Recrystallization from petroleum ether (b. p., 65–78°), ethanol, and petroleum ether, in the order given, raised the melting point to 129–130° but reduced the yield to 14% (4 g.).

Anal. Calcd. for $C_{20}H_{19}ClSi$: Si, 8.67; Cl, 10.90. Found: Si, 8.69; Cl, 11.01.

This compound was also prepared by treating triphenylethylsilane with sulfuryl chloride in the presence of benzoyl peroxide.[20] The yield was 11%.

It was found that triphenyl-α-chloroethylsilane does not react with 10% sodium hydroxide at 100° (one hour), nor did it form a Grignard reagent (one attempt).

Triphenyl-β-chloroethylsilane.—To 13.35 g. (0.068 mole) of β-chloroethyltrichlorosilane[19] was added 0.203 mole of phenyllithium in 155 cc. of ether. The reaction flask was cooled in ice during the addition and Color Test I[6] was negative when the addition was complete. There was obtained 1 g. (5.2%) of product melting at 124–125° after recrystallization from petroleum ether (b. p., 65–78°). A mixed melting point with triphenyl-α-chloroethylsilane melted between 90 and 100°.

Anal. Calcd. for $C_{20}H_{19}ClSi$: Si, 8.67. Found: Si, 8.60. The cleavage of these chloroethylsilanes was not examined because of secondary reactions observed, incidental to a related study.[2b]

Summary

Hydrogen chloride cleavage studies have been made on a number of new organosilicon compounds. The stabilizing effect of a sulfone group in 4-trimethylsilyldibenzothiophene-5-dioxide was particularly noted. Evidence for the instability of *o*-hydroxyphenyl- and *p*-hydroxyphenyltrimethylsilane has been presented.

AMES, IOWA RECEIVED JUNE 24, 1949

---

[19] Sommer and Whitmore, THIS JOURNAL, **68**, 485 (1946).

[20] For a discussion of the general use of sulfuryl chloride, see Kharasch and Brown, *ibid.*, **62**, 926 (1940).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF DELAWARE]

The Ternary Systems Magnesium Chloride–Dioxane–Water, Cadmium Chloride–Dioxane–Water and Cupric Chloride–Dioxane–Water

BY J. ARNDT WEICKSEL AND CECIL C. LYNCH

In the further study of ternary systems of metal chlorides–dioxane–water[1,2] the systems magnesium chloride–dioxane–water, cadmium chloride–dioxane–water and cupric chloride–dioxane–water have been examined. In these systems we should expect some compound formation with dioxane, since a didioxanate of magnesium chloride,[3] a monodioxanate, and hemidioxanate of cadmium chloride,[3,4] and a mono and didioxanate of cupric chloride[3,5] have been reported in the literature. A preliminary examination of the cupric chloride–dioxane–water system showed several color changes in the solid phase over a wide range of dioxane concentration, indicating the probability of an interesting phase system.

Preparation of Materials

Dioxane.—Technical 1,4-dioxane from the Eastman Kodak Company was purified by the method described by Eigenberger.[6] The product was kept over metallic sodium, from which it was distilled when needed.

Saturated Solutions.—These were made from reagent chemicals and analyzed for chloride. The calculated solubilities agreed well with the literature values, as follows

	Solubility, per cent. anhydrous salt by weight Found	Literature value
$MgCl_2$	35.41	35.36[7]
$CdCl_2$	54.67	54.64[8]
$CuCl_2$	42.85	43.6[9]

Anhydrous Chlorides.—Magnesium chloride was made from the hydrated dioxanate by heating in a rapid stream of anhydrous hydrogen chloride for two hours. *Anal.* 99.5% $MgCl_2$. Cupric chloride was made by heating the dihydrate for 24 hours at 110°. *Anal.* 99.8% $CuCl_2$.

Apparatus

All solutions were prepared in two hundred and

---

[1] Lynch, *J. Phys. Chem.*, **46**, 366 (1942).

[2] Bogardus and Lynch, *ibid.*, **47**, 650 (1943).

[3] Rheinboldt, Luyken and Schmittman, *J. prakt. Chem.*, **149**, 30 (1937).

[4] Jahasz and Yntema, THIS JOURNAL, **62**, 3522 (1940).

[5] Heines and Yntema, *Trans. Kentucky Acad. Sci.*, **7**, 85 (1938); *Chem. Abs.*, **35**, 1717 (1941).

[6] Eigenberger, *J. prakt. Chem.*, **130**, 75 (1931).

[7] Kupper, *Caliche*, **8**, 467 (1927); *C. A.*, **21**, 3713 (1927).

[8] Hering, *Ann. chim.*, [11] **5**, 483 (1936).

[9] Chretien and Weil, *Bull. soc. chim.*, [5] **2**, 1577 (1935); *C. A.*, **30**, 2475 (1936).

fifty milliliter ground-glass stoppered Erlenmeyer flasks. The solutions were heated to approximately 30° and placed in the water-bath for at least forty-eight hours to allow equilibrium to be established.

The cell (Fig. 1) used in separating the liquid for analysis consisted of two major portions which could be joined and immersed in the water-bath so that a temperature equilibrium could be retained during the separation. The upper half consisted of a sinter filter with a reservoir and a ground-glass stopper. A slurry of the equilibrium mixture was pipetted from the Erlenmeyer flask and placed in the upper portion of the cell through the side arm. After the slurry had been in the cell for at least six hours, suction was put on the long side arm of the bottom portion of the cell, the stopcock was opened, and the ground-glass stopper was opened by lifting the plunger. The vacuum pulled the liquid through the sinter filter. The entire cell could then be raised in the water-bath so that the level of the bath water was below the joint connecting the halves of the cell. The joint could then be broken, and samples for analysis could be pipetted from the lower half of the cell.

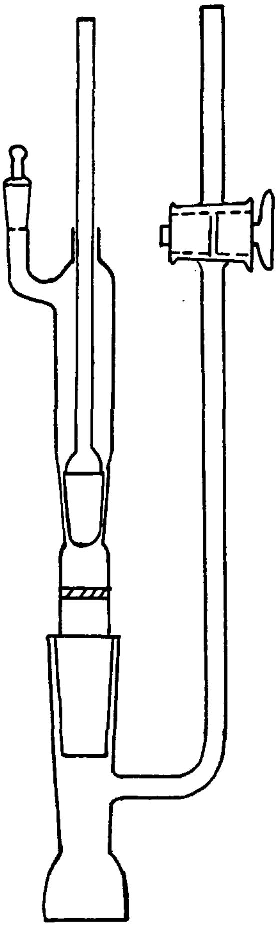

Fig. 1.—Filter cell.

Constant temperature was obtained with a water thermostat (25 ± 0.05°).

The water content of all solutions and solids was determined by the Karl Fischer Reagent method, using a modification of the method described by Almy, Griffin and Wilcox.[10] The titrating vessel was a four-necked five hundred milliliter round-bottomed flask. One neck contained a mercury seal stirrer for agitation of the titrating mixture. Two one and one-half liter automatic burets served as reservoirs for the two titrating solutions which were introduced into the titrating vessel through separate necks. The fourth neck of the titrating vessel served as an entrance for a platinum and a tungsten electrode which were connected to a Beckman *p*H meter, used as a millivoltmeter. Cork stoppers were used throughout, and were changed frequently, since they tended to absorb liquid slowly, and become moist. Bakelite was found unsatisfactory for the purpose because of its lack of flexibility. Titrating solutions were made up as outlined in the article mentioned and the procedure there described was followed throughout. All liquids for analysis were delivered from weighing pipets, and solids were delivered from weighing bottles. The precision of the method is estimated to be within ±0.3%.

25° Isotherm for the Magnesium Chloride–Dioxane–Water System.—Mixtures of solid phase and mother liquor were prepared by use of the saturated aqueous solution of magnesium chloride referred to above. The solution in equilibrium with the corresponding solid phase was separated by use of the filter cell already described and analyzed for magnesium chloride by titration with silver nitrate by the Mohr method, and for water by the Karl Fischer reagent method previously described.

In the immiscible region mixtures of approximate composition were prepared and each layer was analyzed for magnesium chloride and water as before. The plait point of the binodal curve was estimated by the graphical construction method[11] to be 1.0% magnesium chloride, 73.5% dioxane and 25.5% water (P on Fig. 2).

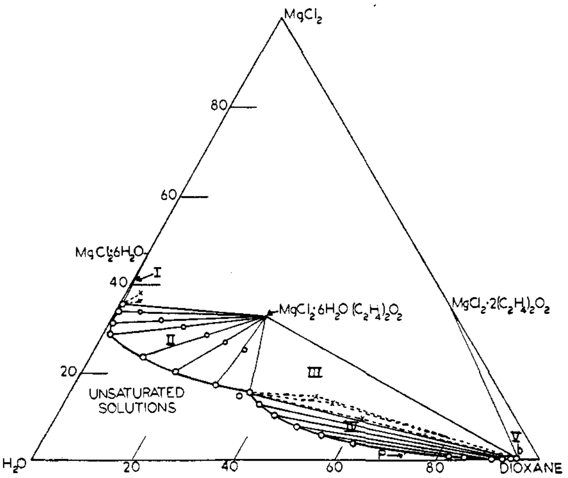

Fig. 2.—25° isotherm of the system $MgCl_2$–dioxane–water.

In the high dioxane concentration solutions, anhydrous magnesium chloride was refluxed with pure dioxane. The solid phase resulting was analyzed for water and magnesium chloride. Such analyses indicated the solid phase to be $MgCl_2 \cdot 2(C_2H_4)_2O_2$ within experimental error. The solid phase appeared to be the stable phase

---

[10] Almy, Griffin and Eilcox, *Ind. Eng. Chem.*, *Anal. Ed.*, **12**, 392 (1940).

[11] "International Critical Tables," Vol. 3, p. 398.

in contact with solutions of greater than 95% dioxane.

Synthetic mixtures of magnesium chloride hexahydrate, water and dioxane were used to check the 0.33 per cent. dioxane triple point.

The isothermally invariant points were determined in triplicate and the average value is included in Table I.

TABLE I

DATA FOR THE 25° ISOTHERM OF THE SYSTEM MAGNESIUM CHLORIDE–DIOXANE–WATER

Composition of the solid phase–mother liquor mixture, %			Composition of solution in equilibrium with solid phase, %		
$MgCl_2$	Dioxane	H_2O	$MgCl_2$	Dioxane	H_2O
Miscible Region (one liquid phase)					
37.97	2.81	59.21	35.33	0.33	64.34[a]
34.67	2.05	63.28	34.98	0.42	64.60
33.65	5.01	61.34	34.03	0.07	65.90
31.96	9.71	58.33	31.79	0.26	68.05
30.02	15.19	54.79	28.65	1.55	69.80
28.17	20.42	51.41	23.25	10.55	66.20
26.46	25.26	48.28	19.91	18.76	61.33
24.79	29.98	45.23	16.91	27.74	55.35
Immiscible Region (two liquid phases)					
Composition of lighter layer, %			Composition of heavier layer, %		
0.00	95.96	4.04	15.09	35.52	49.39[b]
.01	94.45	5.54	12.69	38.70	48.61
.04	92.92	7.04	10.00	42.80	47.20
.12	90.34	9.54	7.50	48.72	43.78
.28	86.32	13.40	5.18	54.58	40.24
.66	82.19	17.15	3.64	61.53	34.83

[a] Equilibrium with two solid phases, $MgCl_2 \cdot 6H_2O$ and $MgCl_2 \cdot 6H_2O(C_2H_4)_2O_2$ and saturated solution. [b] Equilibrium between solid phase, $MgCl_2 \cdot 6H_2O \cdot (C_2H_4)_2O_2$ and two liquid phases.

The solvate $MgCl_2 \cdot 6H_2O \cdot (C_2H_4)_2O_2$ was separated from solution and dried over a mixture of an excess of the solvate and some partially desolvated material in a desiccator over a period of four months, until no further change in mass resulted. No decomposition of the crystals was indicated during the process. Analysis of the crystals for water and magnesium chloride gave the results:

	Experimental %	Theoretical for $CdCl_2 \cdot (C_2H_4)_2O_2$, %
Magnesium chloride	32.7	32.68
Water	37.4	37.09

The data for this isotherm are given in Table I and in Fig. 2. Region I is an area in which $MgCl_2 \cdot 6H_2O$ is the equilibrium solid phase; region II is one where the solvate $MgCl_2 \cdot 6H_2O \cdot (C_2H_4)_2O_2$ is the solid phase in equilibrium with the saturated solution; region III is one where solution a, solution b and $MgCl_2 \cdot 6H_2O \cdot (C_2H_4)_2O_2$ are in equilibrium; region IV is the immiscible portion of the system and region V is one where the solvate $MgCl_2 \cdot 2(C_2H_4)_2O_2$ is the solid phase in equilibrium with the saturated solution.

25° Isotherm for the Cadmium Chloride–Dioxane–Water System.—Mixtures of solid phase and mother liquor were prepared by use of the saturated aqueous solution of cadmium chloride referred to above. Water was added to the mixture if only a small liquid phase was produced by this method. The solution in equilibrium with the corresponding solid phase was separated by use of the filter cell already described and analyzed for cadmium chloride by titration with silver nitrate by Mohr's method, and for water by the Karl Fischer method previously described.

The triple point was checked by use of synthetic mixtures of cadmium chloride five halves water, dioxane and water. It was determined in triplicate and the average value is included in Table II.

TABLE II

DATA FOR THE 25° ISOTHERM OF THE SYSTEM CADMIUM CHLORIDE–DIOXANE–WATER

Composition of the solid phase mother liquor mixture, %			Composition of solution in equilibrium with solid phase, %		
$CdCl_2$	Dioxane	H_2O	$CdCl_2$	Dioxane	H_2O
58.74	4.97	36.29	54.21	0.43	45.36[a]
53.24	2.13	44.63	52.07	0.50	47.49
51.61	5.12	43.27	48.01	0.60	51.39
40.31	10.39	49.30	28.08	1.00	70.90
34.71	14.76	50.52	13.29	3.82	82.89
31.98	20.02	48.00	5.42	10.55	84.03
27.97	25.04	46.98	2.88	20.70	76.42
24.88	30.73	44.39	1.74	29.80	68.46
22.56	36.43	41.01	1.01	39.00	59.99
21.16	40.28	38.56	0.82	44.55	54.63
30.00	44.85	25.15	.48	54.61	45.03
24.10	48.30	27.60	.36	57.00	42.64
24.73	54.53	20.73	.19	67.27	32.54
20.20	62.86	16.93	.11	75.62	24.27
16.86	68.98	14.15	.06	80.95	18.99
13.12	75.86	11.01	.03	86.24	13.73
9.74	82.10	8.16	.00	90.32	9.68
5.60	89.71	4.69	.00	94.87	5.13
2.85	94.76	2.39	.00	97.48	2.52

[a] Equilibrium with two solid phases, $CdCl \cdot 2.5H_2O$ and $CdCl_2 \cdot (C_2H_4)_2O_2$ and saturated solution.

The solvate $CdCl_2 \cdot (C_2H_4)_2O_2$ was separated from solution and dried over a mixture of an excess of the solvate and some partially desolvated material in a desiccator over a period of six months, until no further change in mass resulted. No decomposition of the crystals was indicated during the process. Analysis of the crystals for cadmium chloride gave the results.

	Experimental, %	Theoretical for $CdCl_2 \cdot (C_2H_4)_2O_2$, %
Cadmium chloride	67.76	67.54
Dioxane	32.24	32.46

Several samples were analyzed for water and showed no water content within the limits of experimental error.

The data for this isotherm are given in Table II and are shown graphically in Fig. 3. The region around the low dioxane content invariant

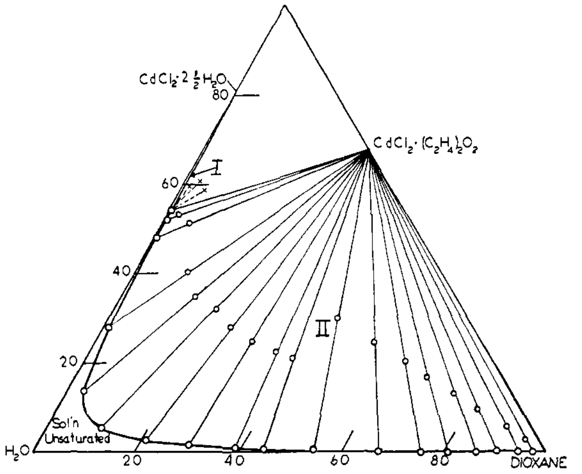

Fig. 3.—25° isotherm of the system $CdCl_2$–dioxane–water.

point has been enlarged in Fig. 4. Region I is an area in which $CdCl_2{\cdot}2.5H_2O$ is the equilibrium solid phase and region II is one in which the dioxanate $CdCl_2{\cdot}(C_2H_4)_2O_2$ is the solid phase in equilibrium with the saturated solution.

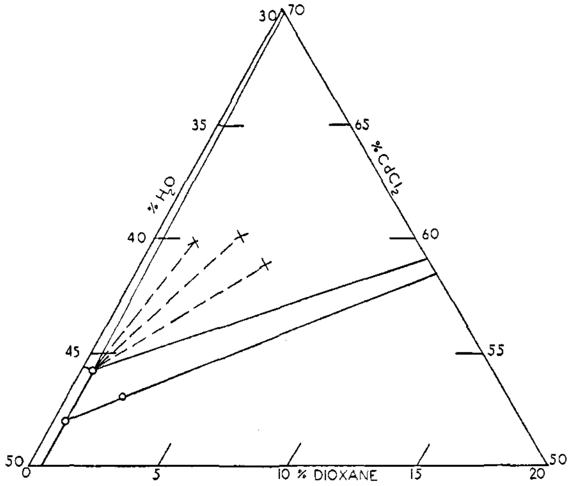

Fig. 4.—Enlargement of region about low dioxane content invariant point of system $CdCl_2$–dioxane–water.

It was determined that by careful heating of $CdCl_2{\cdot}(C_2H_4)_2O_2$, a relatively pure form of anhydrous cadmium chloride could be obtained.

25° Isotherm for the Cupric Chloride–Dioxane–Water System.—Mixtures of solid phase and mother liquor were prepared by use of the saturated aqueous solution of cupric chloride mentioned above. Water was added to the mixture if only a small phase was produced by this method. The solution in equilibrium with the corresponding solid phase was separated by use of the separation cell already described and analyzed for water by the Karl Fischer reagent method, and for cupric chloride by titration with silver nitrate by Volhard's method, using the modification suggested by Caldwell and Moyer.[12]

The low dioxane content triple point was checked by use of synthetic mixtures of cupric chloride dihydrate, dioxane and water. The intermediate triple point was determined by use of synthetic mixtures of saturated cupric chloride solution and dioxane. The high dioxane triple point was checked by use of synthetic mixtures of anhydrous cupric chloride, dioxane and water.

TABLE III

DATA FOR THE 25° ISOTHERM FOR THE SYSTEM CUPRIC CHLORIDE–DIOXANE–WATER

Composition of the solid phase mother liquor mixture, %			Composition of solution in equilibrium with solid phase, %		
$CuCl_2$	Dioxane	H_2O	$CuCl_2$	Dioxane	H_2O
48.28	1.26	50.46	43.10	0.75	56.15
41.22	3.99	54.79	39.77	3.62	56.61[a]
39.02	9.05	51.93	34.70	4.36	60.94
30.08	10.21	59.71	25.48	7.13	67.39
29.34	14.57	56.09	22.30	9.38	68.32
23.92	17.83	58.25	18.80	15.49	65.71
24.19	26.56	49.25	15.38	24.44	60.18
20.77	34.87	44.36	12.48	35.08	52.44
19.84	40.88	39.28	11.55	40.15	48.30[b]
16.85	48.15	34.99	9.44	47.82	42.74
19.11	55.39	25.50	6.93	38.66	34.41
15.12	64.70	20.18	4.51	71.01	24.48
12.03	71.91	16.06	3.01	79.27	17.72
8.69	79.71	11.60	1.86	86.53	11.61
5.00	88.33	6.67	0.86	92.90	6.24
2.16	94.96	2.88	0.27	97.14	2.59
13.65	83.14	3.21	0.00	99.34	0.66[c]

[a] Equilibrium with two solid phases, $CuCl_2{\cdot}2H_2O$ and $CuCl_2{\cdot}2H_2O{\cdot}(C_2H_4)_2O_2$ and saturated solution. [b] Equilibrium with two solid phases, $CuCl_2{\cdot}2H_2O(C_2H_4)_2O_2$ and $CuCl_2{\cdot}2H_2O{\cdot}2(C_2H_4)_2O_2$ and saturated solution. [c] Equilibrium with two solid phases, $CuCl_2{\cdot}2H_2O{\cdot}2(C_2H_4)_2O_2$ and $CuCl_2{\cdot}(C_2H_4)_2O_2$ and saturated solution.

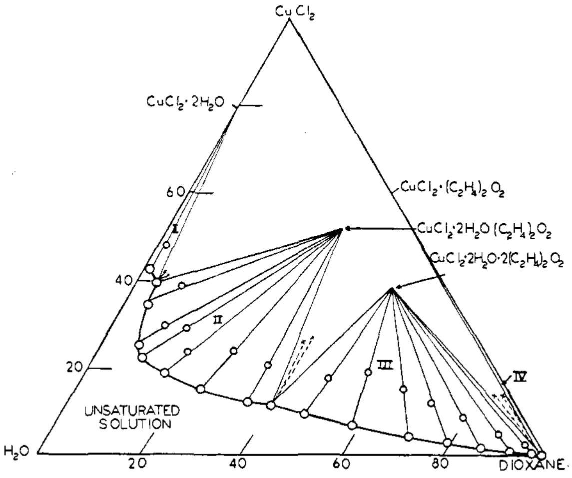

Fig. 5.—25° isotherm of the system $CuCl_2$–dioxane–water.

---

[12] Caldwell and Moyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).

All triple points were determined in triplicate and the average value is included in Table III.

A green solvate $CuCl_2 \cdot 2H_2O \cdot (C_2H_4)_2O_2$ was separated from solution and attempts were made to dry it over a mixture of an excess of the solvate and some partially desolvated material in a desiccator, but all attempts failed. It was dried repeatedly between filter papers until a constant analysis was obtained. Analysis of the crystals for water and cupric chloride gave the results

	Experimental, %	Theoretical for $CuCl_2 \cdot 2H_2O \cdot (C_2H_4)_2O_2$, %
Cupric chloride	51.9 ± 0.2	52.00
Water	13.8 ± 0.3	13.93

This solvate was relatively unstable in air, tending to lose dioxane.

A light blue solvate $CuCl_2 \cdot 2H_2O \cdot 2(C_2H_4)_2O_2$ was separated from solution and dried over a mixture of an excess of the solvate and some partially desolvated material in a desiccator. This was continued over a period of several months, until no further change in mass resulted. No decomposition of the crystals was indicated during the process. Analysis of the crystals for water and cupric chloride gave the results:

	Experimental, %	Theoretical for $CuCl_2 \cdot 2H_2O \cdot 2(C_2H_4)_2O_2$, %
Cupric chloride	38.3 ± 0.2	38.79
Water	10.7 ± 0.3	10.39

This solvate was relatively unstable in air, showing a pronounced tendency to lose water.

In the extremely high dioxane concentration solutions, the stable solid phase, brown-orange in color, was dried between filter papers and analyzed for cupric chloride and water. Such analyses indicated the orange colored solid phase to be $CuCl_2 \cdot (C_2H_4)_2O_2$ within experimental limits. The liquid above this solid was colorless and analyses for cupric chloride showed that the solid was practically insoluble in dioxane. The data for this isotherm are given in Table III and are shown graphically in Fig. 5.

Summary

1. The 25° isotherms for the systems magnesium chloride–dioxane–water cadmium chloride–dioxane–water and cupric chloride–dioxane–water have been presented.

2. The new solvates $MgCl_2 \cdot 6H_2O \cdot (C_2H_4)_2O_2$, $CuCl_2 \cdot 2H_2O \cdot (C_2H_4)_2O_2$ and $CuCl_2 \cdot 2H_2O \cdot 2(C_2H_4)_2O_2$ have been separated and identified.

NEWARK, DELAWARE RECEIVED OCTOBER 31, 1949

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Electrolytic Properties of Aqueous Solutions of Polyacrylic Acid and Sodium Hydroxide. I. Transference Experiments Using Radioactive Sodium[1]

BY JOHN R. HUIZENGA,[2] PHILIP F. GRIEGER AND FREDERICK T. WALL

Introduction

A considerable amount of evidence available at the present time indicates that in aqueous solutions of polyacrylic acid and sodium hydroxide, the sodium ions are associated with polyacrylate ions to an important extent. The results of Kern[3] as well as those of previous workers in this laboratory are in qualitative agreement on this point. However, they are in quantitative disagreement, so additional experimental information appears necessary to clarify the situation. This paper reports such additional information obtained by transference experiments involving the use of radioactive sodium tracer.

II. Experimental

Basis of the Experiments.—The experiments here reported involved the method employed by Brady and Salley[4] for the determination of the transference number of sodium ion in sodium long-chain electrolyte solutions using radioactive sodium tracer. Their solutions contained sodium ions, long-chain anions, and large complex ions (micelles) composed of the two simple ions. In their experiments tracer concentration was initially discontinuous (at a sintered glass frit) in an otherwise uniform solution. They took the flow of radioactive sodium across this boundary to be proportional to the total flow of sodium. Thus they implicitly assumed that the rate of exchange of sodium ions between micelles and free sodium ions is effectively infinite.

In solutions containing polyacrylic acid and sodium hydroxide, it turns out that the rate of exchange of sodium ions between polyacrylate ion and sodium ion is finite. This circumstance makes the interpretation of the experiments rather difficult unless the radioactive tracer concentration is initially uniform throughout the transference cell rather than discontinuous at an initial boundary as in Brady and Salley's experiments. Accordingly, it seems appropriate to discuss briefly the use of radioactive tracers in transference experiments from a somewhat more general point of view than that adopted by Brady and Salley.

---

(1) This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

(2) Present address: Argonne National Laboratories, Chicago, Ill.

(3) Kern, *Z. physik. Chem.*, **A181**, 249 (1937–1938); **A181**, 283 (1937–1938); **A184**, 197 (1939); **A184**, 302 (1939).

(4) Brady and Salley, THIS JOURNAL, **70**, 914 (1948).