(37) MASSON, D. O.: Phil. Mag. [7] **8**, 218 (1929).
(38) NERNST, W.: Z. physik. Chem. **38**, 487 (1901).
(39) PASSYNSKI, A.: Acta Physicochim. U.R.S.S. **8**, 385 (1938).
(40) PRANG, W.: Ann. Physik [5] **31**, 681 (1938).
(41) REDLICH, O.: Naturwissenschaften **19**, 251 (1931).
(42) REDLICH, O., AND KLINGER, H.: Sitzber. Akad. Wiss. Wien IIb, **143**, 489 (1934) or Monatsh. **65**, 137 (1934). Data from PLATO, F., DOMKE, J., AND HASTINGS, H.: Wiss. Abhandl. Normaleichungskommission (J. Springer, Berlin (1900)).
(43) REDLICH, O., AND ROSENFELD, P.: Z. physik. Chem. **A155**, 65 (1931).
(44) REDLICH, O., AND ROSENFELD, P.: Z. Elektrochem. **37**, 705 (1931).
(45) ROOT, W. C.: J. Am. Chem. Soc. **55**, 850 (1933).
(46) SCATCHARD, G.: Chem. Rev. **8**, 321 (1931). Trans. Faraday Soc. **33**, 161 (1937).
(47) SCATCHARD, G., AND PRENTISS, S. S.: J. Am. Chem. Soc. **54**, 2696 (1932).
(48) STARK, J. B., AND GILBERT, E. C.: J. Am. Chem. Soc. **59**, 1818 (1937).
(49) STEWART, G. S.: Trans. Faraday Soc. **33**, 238 (1937).
(50) STEWART, G. S.: J. Chem. Phys. **7**, 381 (1939).
(51) VOSBURGH, W. C., CONNELL, L. C., AND BUTLER, J. A. V.: J. Chem. Soc. **1933**, 933.
(52) WIRTH, H. E.: J. Am. Chem. Soc. **59**, 2549 (1937).

THE TERNARY SYSTEMS ETHYLENE GLYCOL–POTASSIUM CARBONATE–WATER AND DIOXANE–POTASSIUM CARBONATE–WATER

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The study of ternary systems of water-miscible organic liquids, salts, and water was initiated by Frankforter and Frary (2), who studied methanol, ethanol, and 1-propanol and various salts and reported that potassium carbonate was the only salt that would salt out methanol, while many salts salt out ethanol. Frankforter and Cohen (1) studied acetone and several salts, and Frankforter and Temple (3) studied some of the higher alcohols. Further work has been done since 1930 by Ginnings and Chen (4), who used 2-propanol and various salts at 25°C.; by Ginnings and Robbins (7), who used tertiary butyl alcohol (2-methyl-2-propanol); by Ginnings, Herring, and Webb (6), who used 1-butanol; and by Ginnings and Dies (5), who used allyl alcohol. Ginnings and coworkers developed mathematical relationships for the equilibrium curve.

This work was started to study the salting-out effect on the dihydric

alcohol ethylene glycol and its dehydration product dioxane. Both compounds are miscible with water in all proportions.

<div align="center">EXPERIMENTAL</div>

Ethylene glycol could not be salted out from its aqueous solution by potassium carbonate. Eleven solutions were made up, varying in known weight composition from pure water to pure glycol; each was then shaken with a small excess of solid anhydrous potassium carbonate until saturated. The potassium carbonate in a weighed sample was titrated, and the composition of the liquid phase was determined by a materials balance.
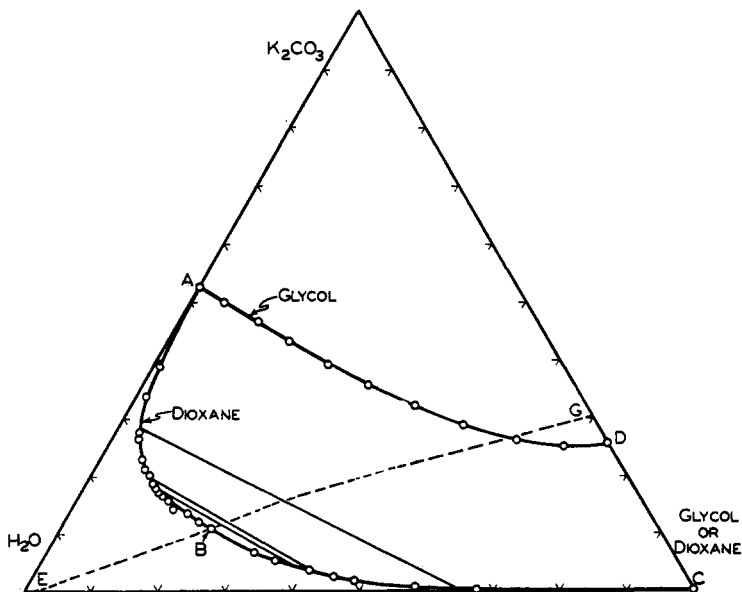

Fig. 1. The systems ethylene glycol–potassium carbonate–water and dioxane–potassium carbonate–water.

The dioxane was found to be salted out of water solution by potassium carbonate. The synthetic method was used to determine the phase relationships. A few milliliters of concentrated potassium carbonate solution of known density and composition was placed in an oil sample bottle, and dioxane was delivered from a buret until two layers formed. Water was delivered to the mixture from a buret until the mixture just became homogeneous. The weight composition of this solution was calculated from the known volumes and densities and represented a single point on the equilibrium curve. Additional dioxane was added to

this homogeneous solution, and the procedure was repeated to give additional points. Phenolphthalein was used to assist in determining the

TABLE 1

The system ethylene glycol–potassium carbonate–water

COMPOSITION AT 25°C.			COMPOSITION AT 40°C.		
Glycol	Potassium carbonate	Water	Glycol	Potassium carbonate	Water
weight per cent	weight per cent	weight per cent	weight per cent	weight per cent	weight per cent
0	52.8	47.2	0	53.9	46.1
5.5	50.0	44.5	5.4	50.9	43.7
11.8	46.2	42.0			
18.4	43.0	38.6	17.8	44.7	37.5
26.1	38.7	35.2			
33.9	35.7	30.4	33.6	36.3	30.1
42.5	32.1	25.4	41.7	33.5	24.8
51.5	28.8	19.7	51.5	28.8	19.7
60.4	26.2	13.4			
68.2	24.8	7.0	67.7	25.4	6.9
74.4	25.6	0	73.5	26.5	0

TABLE 2

The system dioxane–potassium carbonate–water

Representative points selected from a large number of experimental values

COMPOSITION AT 0°C.			COMPOSITION AT 25°C.			COMPOSITION AT 40°C.		
Dioxane	Potassium carbonate	Water	Dioxane	Potassium carbonate	Water	Dioxane	Potassium carbonate	Water
weight per cent	weight per cent	weight per cent	weight per cent	weight per cent	weight per cent	weight per cent	weight per cent	weight per cent
0	51.7	48.3	0	52.8	47.2	0	53.9	46.1
0.56	40.64	58.8	0.9	39.0	60.1	1.0	39.7	59.3
1.06	37.6	61.34	1.7	33.7	64.6	2.5	30.0	67.5
2.1	32.0	65.9	3.7	27.5	68.8	4.1	25.3	70.6
5.0	25.7	69.3	6.2	22.9	70.9	5.7	22.6	71.7
8.8	21.0	70.2	10.9	17.6	71.5	9.1	19.0	71.9
11.0	18.9	70.1	13.9	15.5	70.6	14.2	15.1	70.7
16.5	14.5	69.0	22.5	10.8	66.7	22.6	10.6	66.8
20.2	12.3	67.5	31.0	6.8	62.2	26.4	8.7	64.9
23.3	10.6	66.1	41.12	3.22	55.66	32.67	5.96	61.37
25.0	9.8	65.2	48.38	1.66	49.96	44.12	2.54	53.34
27.9	8.3	63.8	58.44	0.31	41.25	58.44	0.31	41.25
35.8	4.8	59.4	67.59	0.21	32.2	67.59	0.21	32.2
100	0	0	100	0	0	100	0	0

presence of two phases, as it is soluble in the dioxane-rich phase. Several tie lines were determined by analyzing solutions containing two liquid

layers. From these the conjugate line was determined and the plait point found as the intersections of the equilibrium curve and the conjugate line.

RESULTS

The data at 25°C. are shown in figure 1. The equilibrium curve for glycol is shown by line AD; that for dioxane by ABC, for which the conjugate line is EBG showing the plait point at B. The data for glycol at 25° and 40°C. are given in table 1; for dioxane at 0°, 25°, and 40°C. in table 2.

The equation for the equilibrium curve for dioxane–potassium carbonate–water was determined:

Water-rich layer, AB: $\quad y = -0.35 + 60.2(10)^{-0.042x}$

Dioxane-rich layer, BC: $\quad y = 100 - 45.7x^{0.22}$

y = weight per cent of dioxane; x = weight per cent of potassium carbonate.

The effect of temperature is very slight, as the various isotherms practically coincide. The only change with temperature is the increased solubility of the potassium carbonate in water with a corresponding shift upward of the water-rich layer.

SALTING-OUT EFFECTS

The theory of salting out is not well understood, and no theory has been advanced which will account for all the phenomena involved. Thirty-one salts were qualitatively tested to determine whether or not they would salt out glycol and dioxane. A saturated aqueous solution of the salt was made, the non-electrolyte was added dropwise, and the formation of two immiscible layers was noted. None of the salts salted out ethylene glycol from its aqueous solution. Dioxane was salted out by the following: sodium hydroxide, sodium chloride, sodium carbonate, sodium sulfate, sodium acetate, ammonium chloride, ammonium sulfate, potassium carbonate, potassium fluoride, potassium formate, potassium acetate, lithium bromide, lithium acetate, calcium chloride, strontium chloride, and strontium chlorate.

SUMMARY

1. Solubilities in the system ethylene glycol–potassium carbonate–water at 25° and 40°C. have been determined. The liquid phase remains homogeneous for all compositions.

2. Solubilities in the system dioxane–potassium carbonate–water at 0°, 25°, and 40°C. have been determined. Two liquid phases are formed in this system.

3. Of thirty-one electrolytes tried, none would salt out ethylene glycol but sixteen salted out dioxane.

REFERENCES

(1) FRANKFORTER AND COHEN: J. Am. Chem. Soc. **36**, 1103-34 (1914).
(2) FRANKFORTER AND FRARY: J. Phys. Chem. **17**, 402-73 (1913).
(3) FRANKFORTER AND TEMPLE: J. Am. Chem. Soc. **37**, 2697-716 (1915).
(4) GINNINGS AND CHEN: J. Am. Chem. Soc. **52**, 2282-6 (1930).
(5) GINNINGS AND DIES: J. Am. Chem. Soc. **57**, 1038-40 (1935).
(6) GINNINGS, HERRING, AND WEBB: J. Am. Chem. Soc. **55**, 875-8 (1933).
(7) GINNINGS AND ROBBINS: J. Am. Chem. Soc. **53**, 3765-9 (1931).

SOLID POLYIODIDES OF RUBIDIUM[1]

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Rubidium triiodide was first prepared by Wells and Wheeler (9). Solubility results in water solutions at 25°C. by Foote and Chalker (5) and freezing point measurements by Briggs and Patterson (2) on rubidium iodide–iodine mixtures show that this is the only binary polyiodide of rubidium at temperatures of 25°C. or above. However, the work of Abegg and Hamburger (1) by the solubility method with benzene as solvent indicated the existence of three compounds which they believed to be RbI_3, RbI_7, and RbI_9. In the light of the results obtained in this laboratory on the polyiodides of potassium (3) and cesium (4), it seemed likely that the two higher polyiodides of rubidium reported by Abegg and Hamburger were actually ternary compounds containing benzene of crystallization. We have therefore studied the systems rubidium iodide–iodine–benzene and rubidium iodide–iodine–toluene at 6° and 25°C.

The experimental procedure and the purification of materials have been described (3). Rubidium iodide was prepared from a pure sample of the nitrate by fusion in platinum with oxalic acid and subsequent evaporation with excess hydriodic acid. The material was twice recrystallized as the triiodide, and was converted to the iodide by gentle heating.

The system rubidium iodide–iodine–toluene proved to be very simple (see table 1). No solvated compounds exist, as shown by closed-tube tests on residues, and both the iodide and triiodide are insoluble in the solvent, so that the composition of all residues could be calculated from the known original charges and the analytically determined iodine con-

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[1] This article is based on a thesis presented by Michael Fleischer to the Faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1933.