The principal reaction products are ethylene oxide and formaldehyde; other products whose formation depends on the conditions of experiment are dioxymethyl peroxide, acetaldehyde, formic acid, the oxides of carbon and water. At temperatures above 450° the polymerization of ethylene to higher mono-olefins becomes an important reaction. Propylene and small amounts of butylene are the primary polymerization products of ethylene.

The primary process in the reaction between oxygen and ethylene is the activation of ethylene, probably by the formation of an addition complex or peroxide. The reaction takes place in a stepwise sequence of consecutive reactions, ethylene oxide and formaldehyde are formed in the early stages of the oxidation preceding the appearance of acetaldehyde, dioxymethyl peroxide, formic acid, carbon oxides and water.

Hydrogen peroxide is formed in the reaction; dioxymethyl peroxide is probably formed from hydrogen peroxide and formaldehyde.

A scheme of the mechanism of the oxidation of ethylene has been outlined. Experiments on the oxidation of propylene have indicated that this mechanism of the oxidation applies to the slow combustion of the other members of the mono-olefin hydrocarbon series.

WILMINGTON, DELAWARE

TERNARY SYSTEMS: WATER, ISOPROPANOL AND SALTS AT 25°

BY P. M. GINNINGS AND ZOK TSUNG CHEN

A search of the literature recently in connection with another investigation[1] revealed only one paper on the above systems.[2] Only two salts, potassium carbonate and potassium fluoride, were investigated in the systems with isopropanol. Some difficulties such as the precipitation of the salt by the addition of the alcohol and also the slow rate of separation of the two liquid phases seem to have deterred further work with other salts. It appeared desirable to extend the knowledge of the above systems in order to obtain some comparative data with other aliphatic alcohols and also on account of the increased commercial interest in recent years. This has been done by the authors qualitatively with about seventy-five common inorganic salts and quantitatively with ten of these salts. Qualitatively, it was found that out of these seventy-five inorganic salts chosen more or less at random two liquid phases were formed by more salts with isopropanol than with ethanol or methanol but with fewer salts if normal propanol and tertiary butanol were used for comparison. These five

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[1] P. M. Ginnings and Dorothy Robbins, THIS JOURNAL, **52**, 2282 (1930).

[2] G. B. Frankforter and S. Temple, *ibid.*, **37**, 2697 (1915).

include all of the water miscible, saturated, monatomic aliphatic alcohols. Qualitatively, then, it can be stated that isopropanol is easier to salt out than ethanol or methanol but more difficult than normal propanol or tertiary butanol. From the chemical nature of these alcohols, this was of course to be expected.

Ten of the salts were selected for the quantitative work and considerable attention was paid to the binodal curves in an effort to obtain data which would reveal any mathematical relationships between the components of the systems. At first, the conventional triangular diagram was used to express graphically the binodal curves but, while it is undoubtedly the best for visualizing this type of system, it does not lend itself readily to the derivation of mathematical relationships and laws. However, if the weight per cent. of the isopropanol in the system is plotted as a function of the weight per cent. of the salt in the system (these weight percentages from various binodal points), the resulting curve is similar to a decreasing exponential function curve. So as a test for this type of function, the logarithmic values of the weight percentages of isopropanol were plotted as a function of the weight percentage of salt. The resulting curves on close inspection seemed to be made up of two sections, each section either a straight line or a curve with slight curvature and the two sections intersecting in the plait point. Evidently each liquid phase follows a separate mathematical law. When a section was a straight line, an empirical mathematical equation was easily derived to approximate closely the experimental data. When the section had some curvature, as several did, it was necessary to introduce another constant in the empirical equation in order to approximate the experimental data more closely. The curvature of these sections near the axes may be due partially to experimental error, as the *relative* error increases quite rapidly near the axes, although the actual weight per cent. error does not change appreciably. If y is taken as the weight per cent. of isopropanol and x as the weight per cent. of salt of any binodal point, and a, b, c are numerical constants, the empirical equation of the type

$$y = a + b(10)^{-cx}$$

can be used to express the mathematical relationships usually with close approximation. From the above equation can be derived the differential equation $-d(y-a)/dx = cy$; or, the rate of decrease of weight per cent. of isoproponal with respect to the weight per cent. of salt is a direct function of the weight per cent. of isopropanol. Often constant a approaches zero, with the resulting simplification of the empirical equation and its differential equation.

If the per cent. of isopropanol in the salt rich phase at its saturation point with salt is taken as a measure of the salting out efficiency, potassium carbonate and potassium fluoride seem to excel the rest in this respect.

The results obtained by Frankforter and Temple for these two salts are similar to those obtained in this work if the temperature differential is taken into consideration. 25° was chosen here on account of the greater ease in its maintenance as a room temperature instead of 20° as used by Frankforter and Temple.

Experimental

The experimental method used in this investigation was almost identical with that used previously[1] with the incorporation of some improvements and refinements tending toward greater precision in the values of the points on the binodal curves. One major source of error encountered was in the evaporation of the volatile components (especially the alcohol) upon opening and closing the centrifuge tube. This also gives a cumulative error if more than one binodal point is taken from the same contents of a tube. To reduce this error as far as possible in this work, tentative values for the binodal points were first determined by two similar runs. Then the precision points were run with quantities of fresh materials based upon data from the tentative points. This enabled the final values to be determined with relatively few mechanical operations and consequently little loss of the volatile components. In the precision determinations, the total weight of the three components usually amounted to 40–60 g., which also increased the precision of the measurements. The

TABLE I

EXPERIMENTAL RESULTS

Weight percentages of components

i-PrOH	(NH₄)₂HPO₄	i-PrOH	Na₂CO₃	i-PrOH	MgSO₄	i-PrOH	NaNO₃	i-PrOH	K₂CO₃
39.20	3.48	63.50	0.10	39.30	1.43	49.50	10.90	69.60	0.10
32.84	5.55	47.60	.91	32.80	2.77	39.50	14.75	42.20	2.80
24.80	9.53	35.80	2.34	28.40	4.20	33.80	17.17	28.40	6.04
20.10	12.74	19.34	6.54	23.70	5.90	31.50	18.20	17.25	9.65
14.90	16.48	12.80	9.35	12.10	11.80	19.25	24.40	10.10	13.86
14.11	17.19	8.96	11.70	9.40	14.00	11.54	29.25	4.42	19.83
13.19	18.10	5.61	14.50	7.10	16.40	8.20	32.65	1.93	25.50
8.79	23.20	3.24	17.33	5.00	19.40	4.90	37.70	0.65	33.20
6.18	27.14	2.15	19.18	3.00	22.50	4.04	40.56	0.23	52.67
3.62	32.84	1.60	19.60			3.00	43.80		

Weight percentages of components

i-PrOH	(NH₄)₂SO₄	i-PrOH	KCl	i-PrOH	KF	i-PrOH	NaCl	i-PrOH	NaBr
45.58	3.12	53.95	5.12	65.80	1.00	75.20	1.70	62.10	11.30
31.45	6.85	42.56	7.65	39.20	4.00	64.35	2.95	53.10	13.70
22.20	9.95	37.50	8.93	23.40	6.50	49.50	5.20	41.50	18.00
14.20	14.10	36.14	9.17	15.10	9.30	25.45	10.17	29.50	23.60
8.98	18.96	29.34	11.04	7.70	14.30	23.90	10.62	20.40	27.20
5.35	24.20	22.87	12.95	4.45	18.68	15.70	13.70	8.70	35.00
3.93	27.54	17.64	15.17	2.20	25.00	5.90	21.10	4.10	42.60
0.97	41.50	13.72	17.48	0.16	46.75				

TABLE II

$$y = a + b(10)^{-cx}$$

y = wt. % of isopropanol; x = wt. % of salt; a, b, c are numerical constants

Salt	Alcohol-rich phase			Salt-rich phase		
	a	b	c	a	b	c
$(NH_4)_2HPO_4$	13.4	42.0	0.0604	−1.37	53.3	0.0313
$(NH_4)_2SO_4$	0	64.5	.0459	0	58.1	.0429
NaBr	0	123.0	.0261	0	367	.0460
$NaNO_3$	0	97.6	.0267	0	239	.0449
NaCl	0	92.2	.0513	0	100	.0583
$MgSO_4$	16.4	33.1	.1120	−24.0	49.0	.0115
KF	0	78.0	.0757	1.21	72.4	.0750
K_2CO_3	19.9	50.7	.1288	−0.15	65.3	.0579
KCl	0	87.7	.0411	7.08	151.2	.0775
Na_2CO_3	15.73	51.0	.1725	−2.55	49.4	.0538

TABLE III

CONJUGATION DATA

Salt	i-PrOH in alc.-rich phase	Salt in salt-rich phase	Salt	i-PrOH in alc.-rich phase	Salt in salt-rich phase
$(NH_4)_2HPO_4$	39.2	32.8	$(NH_4)_2SO_4$	45.6	41.5
$(NH_4)_2HPO_4$	21.6	11.8 P.P.	$(NH_4)_2SO_4$	18.6	11.6 P.P.
$(NH_4)_2HPO_4$	3.6	3.5	$(NH_4)_2SO_4$	0.97	3.1
NaBr	62.1	42.6	$NaNO_3$	49.5	43.8
NaBr	29.5	23.6 P.P.	$NaNO_3$	26.0	21.5 P.P.
NaBr	4.1	11.3	$NaNO_3$	3.0	10.9
NaCl	75.2	21.1	$MgSO_4$	39.3	22.5
NaCl	49.5	5.2 P.P.	$MgSO_4$	21.4	7.3 P.P.
NaCl	5.9	1.7	$MgSO_4$	3.0	1.4
KF	65.8	46.7	K_2CO_3	69.6	52.7
KF	36.8	4.3 P.P.	K_2CO_3	27.8	6.2 P.P.
KF	0.16	1.0	K_2CO_3	0.23	0.10
KCl	53.9	17.5	Na_2CO_3	63.5	19.6
KCl	37.5	8.9 P.P.	Na_2CO_3	19.9	6.3 P.P.
KCl	13.8	5.1	Na_2CO_3	1.6	0.10

room temperature and the water-bath were kept to 25 ± 0.2°. The centrifuge was quite a convenience for the estimation and detection of the liquid phases, especially at the extremes of the binodal curves. A Babcock milk tube was quite useful for those systems where small amounts of the top layer (alcohol rich phase) were to be detected. A special centrifuge tube, capacity about 70 ml., and tapered at the bottom, was useful for detecting small amounts of the lower layer (salt rich phase). The plait point was taken as that point where equal volumes of the two liquid phases existed but with the further condition that the addition of a very small quantity of water would cause the contents to become homogeneous. The line of demarcation between the two liquid phases near the plait point is easily overlooked because the refractive indices of the two layers approach the same value. The extremes of the conjugation data were

taken from the extremes of the binodal data, which seemed to be more accurate than the data obtained by the analytical method as used previously.

Eastman's best grade of isopropanol was used after it was refluxed and distilled with anhydrous calcium oxide and anhydrous potassium fluoride. It then had d_{20}^{20} 0.7894. However, the small amount of water originally present did not seem to have an important influence on the experimental results, judging from the results obtained by using the isopropanol both before and after dehydration. The authors feel that the error in binodal data does not exceed 1.0% in any case and is usually less than 0.5%.

Summary

Tabular data are given for the ternary systems of water and isopropanol with ten inorganic salts at 25°. Isopropanol is compared with the other water-miscible, saturated aliphatic alcohols. Potassium carbonate and potassium fluoride are the most effective of the ten salts investigated. The rate of decrease of the weight per cent. of isopropanol with respect to the weight per cent. of salt in a liquid phase seems to be a direct function of the weight per cent. of the isopropanol. Values for the numerical constants in the empirical equation are given for ten different systems.

GREENSBORO, NORTH CAROLINA

EQUILIBRIUM IN BINARY SYSTEMS UNDER PRESSURE. I. AN EXPERIMENTAL AND THERMODYNAMIC INVESTIGATION OF THE SYSTEM, NaCl-H₂O, AT 25°

BY L. H. ADAMS

Introduction

Nature of the Problem.—Very little is known concerning the effect of high pressure on systems containing more than a single component. Despite the scant attention this subject has received, it does not lack interest or importance, for, in a complete investigation of the stability of the various phases in a system, pressure is a factor coördinate with temperature, and its consideration over an extended range is equally desirable. Doubtless the scarcity of data in this field is due to the relative slowness in the development of the necessary technique. Materials under pressure, being difficult to observe directly, require special devices for the study of their behavior; moreover, there are certain complications connected with the production and measurement of very high pressures.

It has now been found possible to study a binary system under high pres-