Ternary Systems

Water–2-Chloroethanol–Salt and Water–Tetrahydrofurfuryl Alcohol–Salt

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IN THE COURSE of work on the azeotropic dehydration of some alcohols, it became necessary to study the salting out of 2-chloroethanol and of tetrahydrofurfuryl alcohol from aqueous solutions by the addition of inorganic salts. A literature survey showed that similar work has been done on methanol (*1, 6, 23*), ethyl alcohol (*6, 18, 20*), isopropyl alcohol (*6, 7*), *n*-propyl alcohol (*7, 9, 18, 19*), allyl alcohol (*7, 10*), isobutyl alcohol (*8*), *tert*-butyl alcohol (*11, 12*), acetone (*3, 5*), methyl ethyl ketone (2-butanone) (*16*), and dioxane (*13, 14, 21, 22*). Studies have been made on the surface salting out of surface active substances by electrolytes and the stability of their foam (*4*) and of the salting out effects of complex cobalt salts (*15*). Relationships have been proposed between salting out power and vapor pressure of the saturated salt solution (*6, 17*). Mathematical relationships for the binodal curves have been developed (*10, 11*).

EXPERIMENTAL

A series of qualitative tests showed that some salts are effective while others are ineffective in salting out or are themselves precipitated from the aqueous solution by the addition of one of these alcohols. Table I summarizes the effectiveness of the salt survey.

The ternary diagrams for water-2-chloroethanol-$MgSO_4$, water-2-chloroethanol-$(NH_4)_2SO_4$, water-tetrahydrofurfuryl alcohol-K_2CO_3, and water-tetrahydrofurfuryl alcohol-$(NH_4)_2SO_4$ were constructed at 25° C.; the well known cloud point method was used and the system of graphical representation of the binodal and conjugation curves, interpolation to the plait point, was that of Coolidge (*2*). Data for the systems at 25° C. are given in Tables II and III and on triangular coordinates in Figure 1 to 4.

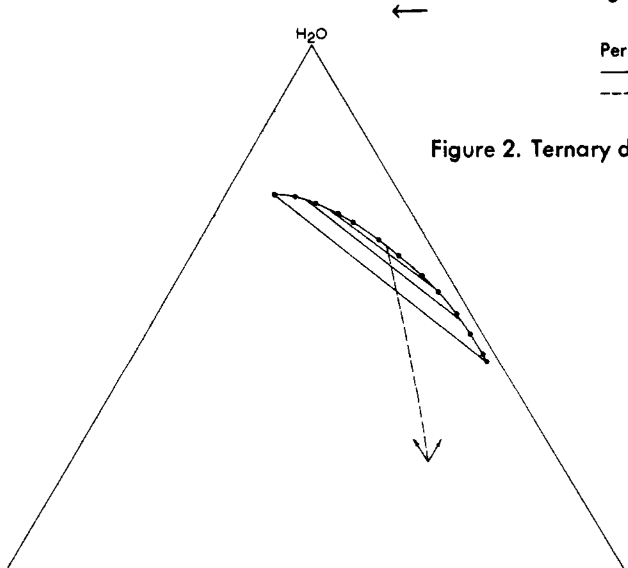
Table I. Effectiveness of Salts

Alcohol	Effective	Ineffective	Precipitated
2-Chloroethanol	$MgSO_4$	KI	Na_2SO_4
	$(NH_4)_2SO_4$	KBr	K_2SO_4
	$CdSO_4$	LiCl	$CuSO_4$
	Li_2SO_4	$NaC_2H_3O_2$	KCl
	$NaHSO_4$	$AlCl_3$	K_2CO_3
	$Na_2S_2O_3$	$Mg(C_2H_3O_2)_2$	Na_2CO_3
	Na citrate	$Pb(C_2H_3O_2)_2$	$NaNO_3$
	KF	NH_4NO_3	$Na_4P_2O_7$
		$Al(NO_3)_3$	$(NH_4)_2HPO_4$
		$(NH_4)_2C_2O_4$	$LiC_2H_3O_2$
Tetrahydrofurfuryl alcohol	$(NH_4)_2SO_4$	KI	$MgSO_4$
	$CdSO_4$	$AlCl_3$	$CuSO_4$
	K_2CO_3	LiCl	Li_2SO_4
	$Na_2S_2O_3$	$NaC_2H_3O_2$	Na_2SO_4
	KF	$Mg(C_2H_3O_2)_2$	$NaHSO_4$
		$Pb(C_2H_3O_2)_2$	KCl
		NaCl	NaCl
		NH_4Cl	NH_4Cl
		KBr	KBr
			Na_2CO_3
			$Na_3C_6H_5O_4$
			$(NH_4)_2C_2O_4$
			$(NH_4)_2HPO_4$
			$Na_4P_2O_7$

MATERIALS

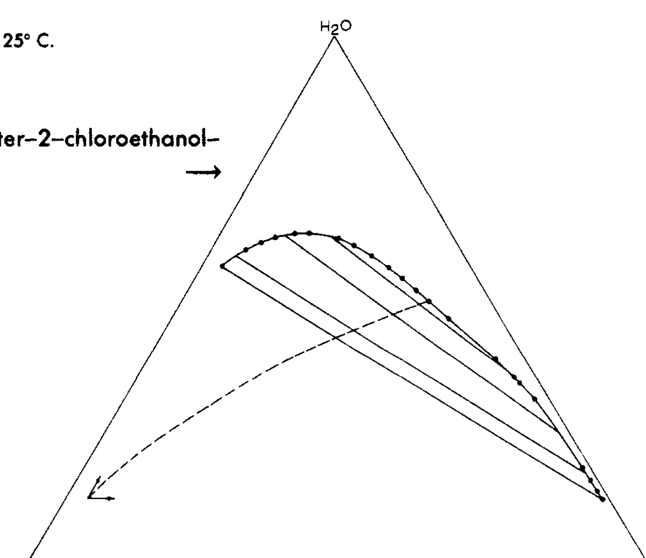
The salts used were Baker analyzed reagents: $(NH_4)_2SO_4$ granular No. 0792, $MgSO_4 \cdot 7H_2O$ No. 2500, and K_2CO_3 anhydrous granular No. 3012. For each the percentage of moisture was checked before each test. The 2-chloroethanol

Figure 1. Ternary diagram of water-2-chloroethanol-magnesium sulfate



Per cent by weight at 25° C.
——— Tie lines
- - - Conjugation line

Figure 2. Ternary diagram of water-2-chloroethanol-



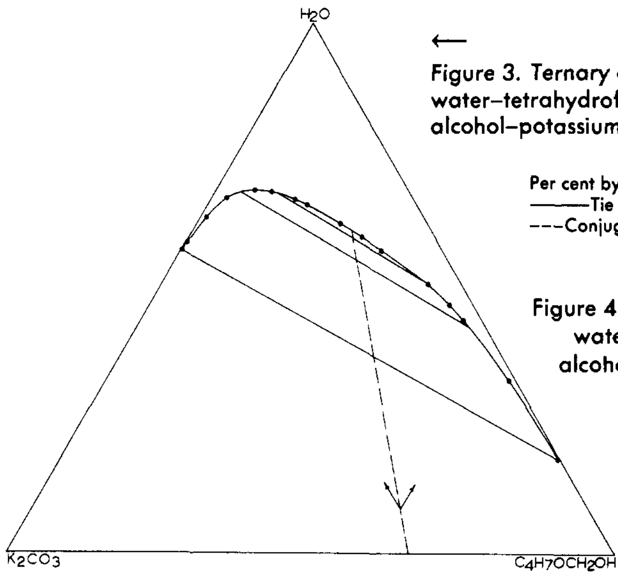


Figure 3. Ternary diagram of water–tetrahydrofurfuryl alcohol–potassium carbonate

Per cent by weight 25° C.
——Tie lines
---Conjugation line

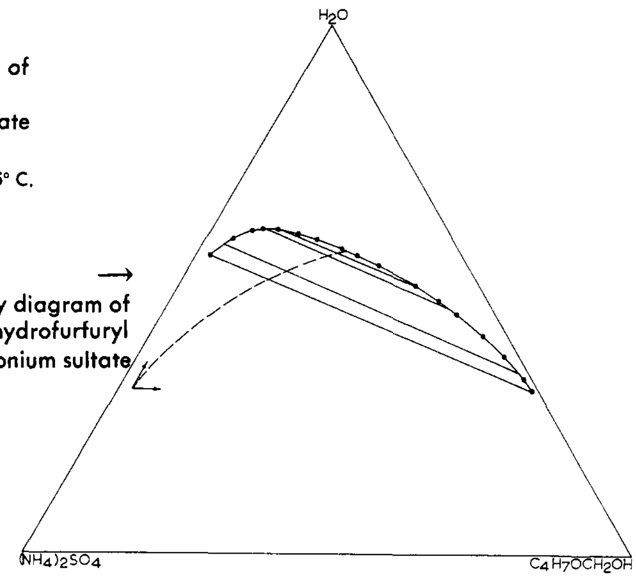


Figure 4. Ternary diagram of water–tetrahydrofurfuryl alcohol–ammonium sulfate

Table II. Binodal Data at 25° C.

(Weight per cent)

The System 2-ChloroEtOH-$MgSO_4$-H_2O

2-Chloro EtOH	$MgSO_4$	H_2O
7.2	21	71.8
7.6	20.5	71.9
11.2	17.3	71.5
17.0	13.3	69.7
23.4	10.1	66.5
28.9	7.7	63.4
33.9	6.0	60.1
39.6	3.9	56.5
43.7	2.8	53.5
48.4	2.1	49.5
52.7	2.0	45.3
56.5	1.9	41.6
58.2	1.9	39.9

The System 2-ChloroEtOH-$(NH_4)_2SO_4$-H_2O

2-Chloro EtOH	$(NH_4)_2SO_4$	H_2O
3.4	46.0	54.0
5.8	34.9	59.3
7.4	30.8	61.8
9.3	28.6	62.1
12.3	25.2	62.5
14.6	22.5	62.9
19.6	18.9	61.5
23.0	16.8	60.2
26.9	15.0	58.1
30.9	13.4	55.7
33.8	12.2	54.0
37.5	10.9	51.6
40.6	9.8	49.6
45.2	8.2	46.6
56.3	4.8	38.9
61.2	3.2	35.6
62.9	2.9	34.2
66.8	2.2	31.0
81.3	0.8	17.9
82.2	0.7	17.1
83.7	0.5	15.8
84.7	0.4	14.8
86.0	0.3	13.7
87.5	0.3	12.2

The System THFA-K_2CO_3-H_2O

THFA	K_2CO_3	H_2O
0.1	43.0	56.9
0.4	41.3	58.3
1.0	36.0	63.0
2.5	30.5	67.0
6.4	25.6	68.0
9.4	22.8	67.8
13.6	20.2	66.2
16.4	18.4	65.2
23.6	14.8	61.6
28.4	12.4	59.2
33.2	10.2	56.6
43.6	5.9	50.5
49.3	4.3	46.4
52.5	3.5	44.0
65.9	1.5	32.6
81.8	0.5	17.7

The System THFA-$(NH_4)_2SO_4$-H_2O

THFA	$(NH_4)_2SO_4$	H_2O
2.1	41.4	56.5
6.8	32.4	60.8
9.4	29.5	61.1
14.8	25.1	60.1
18.3	22.6	59.1
22.6	19.6	57.8
26.5	17.2	56.3
31.0	14.3	54.7
39.1	10.9	50.0
44.0	8.3	47.7
48.3	6.3	45.4
54.9	3.9	41.2
60.3	2.3	37.4
65.5	1.5	33.0
68.0	1.0	31.0

was the highest grade Eastman organic chemical, No. 131, b. p. 127–29° C., refractive index 1.4420. The tetrahydrofurfuryl alcohol, Eastman practical grade No. P.2422, was fractionated to obtain a cut boiling at 172–73° C. at 684.7 mm., refractive index 1.4500 at 25.4° C. Distilled water was used in all the experimental work.

DISCUSSION

In the ternary systems with 2-chloroethanol, ammonium sulfate is a better salting out agent than magnesium sulfate.

Potassium carbonate takes the advantage over ammonium sulfate in the systems with tetrahydrofurfuryl alcohol.

Of the 28 salts investigated with 2-chloroethanol and of the 25 checked with tetrahydrofurfuryl alcohol, only eight

Table III. Conjugation Data

(Weight per cent)

Salt-Rich Phase			Alcohol-Rich Phase		
$MgSO_4$	H_2O	2-Chloro EtOH	2-Chloro EtOH	H_2O	$MgSO_4$
13.1	69.9	17.0	44.9	52.3	2.8
16.0	71.2	13.8	50.2	47.6	2.2
21.0	71.8	7.2	58.2	39.9	1.9
7.1		P.P.	30.2		
$(NH_4)_2SO_4$	H_2O	2-Chloro EtOH	2-Chloro EtOH	H_2O	$(NH_4)_2SO_4$
40.6	56.0	3.4	87.5	12.2	0.3
36.1	58.9	5.0	82.0	17.3	0.5
27.2	62.4	10.4	73.5	25.0	1.5
19.3	61.8	18.9	60.0	36.0	4.0
10.0		P.P.	40.1		
K_2CO_3	H_2O	THFA	THFA	H_2O	K_2CO_3
21.3	67.0	11.7	41.3	52.0	6.7
27.6	67.8	4.6	54.0	42.7	3.3
43.0	56.9	0.1	81.8	17.7	0.5
13.4		P.P.	25.8		
$(NH_4)_2SO_4$	H_2O	THFA	THFA	H_2O	$(NH_4)_2SO_4$
26.4	60.9	12.7	38.2	50.9	10.9
29.7	61.1	9.2	46.0	46.8	7.2
38.1	58.3	3.6	62.4	35.8	1.8
41.4	56.5	2.1	68.0	31.0	1.0
18.3		P.P.	24.6		

have a salting out power in the first case and five in the second.

Dehydration by salting out, when applicable, is generally the most economical process, particularly when the organic compound forms, during distillation, a binary azeotrope with water with a percentage of water higher than the percentage of water in the organic liquid-rich layer obtained in the salting out process.

An elegant example of application of absorption of water by a concentrated salt solution would be in an esterification operation where the water of esterification would be removed continuously by distillation in the form of a binary or ternary azeotrope and the water would be absorbed in a concentrated solution of an appropriate salt; meanwhile the alcohol and eventual entraining agent would be recycled in the esterification apparatus.

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Vapor-Liquid Equilibrium Data for the Binary Mixtures Carbon Tetrachloride–1,1,2-Trichloroethane and 1,2-Dichloroethane–1,1,2-Trichloroethane

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INDUSTRIAL CHLORINATION of hydrocarbons produces a mixture of many products which are often separated by fractionation. Design of these distillation columns is severely limited by lack of experimental data; accordingly vapor-liquid equilibrium data for two such binary systems, carbon tetrachloride–1,1,2-trichloroethane and 1,2-dichloroethane–1,1,2-trichloroethane have been obtained by using an Othmer still. The system 1,2-dichloro–1,1,2-trichloroethane obeys Raoult's law, in contrast to the previous data of Portnov and Seferovich (3). However, the activity coefficient from the latter data do not satisfy the Gibbs-Duhem equation. Activity coefficients for the carbon tetrachloride–1,1,2-trichloroethane system can be represented by $\log \gamma = A(1 - x)^2$, where A is calculated by the method of least squares to be 0.153 ± 0.015 with 95% confidence limits. This tolerance corresponds to a standard deviation of 0.0073 and a correlation coefficient of 0.958.

EXPERIMENTAL COMPOUNDS

Carbon tetrachloride (Fischer Scientific, reagent grade) and 1,2-dichloroethane (Fischer Scientific, reagent grade) were used. The 1,1,2-trichloroethane was obtained by distilling the technical grade (Fischer Scientific Laboratory Chemical) in a Podbielniak column (10 feet long, 1 inch in diameter, glass spiral packing having an equivalent of 500 theoretical plates at a reflux ratio of 40 to 1), and collecting the fraction boiling between 113.7° and 114.1° C.

PROCEDURE

A conventional Othmer still was used, and constant pressure of 740 mm. of Hg was maintained by a Cartesian

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