Effect of Alkaline-Earth Chlorides on Vapor-Liquid Equilibrium of Acetic-Water System

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Experimental data concerning the isobaric vapor-liquid equilibrium of the system acetic acid-water saturated with the chlorides of calcium, strontium, and barium at one atmosphere are presented. The results show a considerable effect due to salt addition. Reversal of relative volatilities was observed in all cases. Composition and boiling points of the azeotropes thus formed are reported.

IN FRACTIONAL DISTILLATION of binary systems the ease with which the components may be separated is most clearly indicated by the relative volatility—the greater its value, the greater the ease of separation.

If a system contains compounds whose boiling points are spread over a relatively small temperature range, they cannot be readily separated by distillation. The addition of a substance that reduces the vapor pressure of one of the components, while having little or no effect on the others may result in an easier separation and consequently may decrease the initial size and cost of equipment.

There have been several publications (*1, 3, 6, 7, 8, 9*) containing data for ternary systems of two liquid components and an inorganic salt whose solubility is considerably greater in one component than the other. The results of these studies have brought out interesting effects of salt addition such as increased relative volatilities (*6, 8, 9*), shifting of azeotropes (*1*), and in some instances, complete inversion of the binary systems (*3*).

This investigation was aimed at determining the effect of alkaline earth chlorides on the acetic acid-water system.

EXPERIMENTAL EQUIPMENT AND MEASUREMENTS

The equilibrium still was an improved Othmer still, Catalog No. G7373E, manufactured by the Emil Greiner Co. The upper part of the still was wrapped with an Electrothermal heating tape to prevent refluxing. The still was fitted with a ground glass standard taper thermometer graduated in one degree increments which could be read within ±0.5° C. The volumes of the distillate container and the still proper were approximately 35 ml. and 200 ml., respectively. The pressure was maintained at 760 ± 1 mm. Hg by a Cartesian Manostat, Model G15070, manufactured by the Emil Greiner Co. All chemicals were of analytical reagent grade.

Performance tests such as ability to reproduce data for well known binary systems, approach to steady state, and distillate entrainment tests were conducted and indicated satisfactory operation of the equipment.

At the beginning of the experiments with any given salt, the still was charged with approximately 90 wt. % glacial acetic acid and 10 wt. % of water, salt free basis, from a solution saturated at room temperature with the salt. Additional salt was added, as needed during the experimental runs, to provide precipitated salt at the bottom of the still at all times. All solutions were saturated as it was thought that the greatest effect would be observed in this case. Care was taken not to obstruct the circulatory system of the still with salt. Salt in the circulatory system would greatly increase the bumping hazard. After the liquid in the still reached its boiling temperature and the pressure was carefully adjusted, three hours were allowed for the system to come to equilibrium. Several preliminary runs indicated this period was more than adequate.

At the end of a run the still was shut off and allowed to cool slightly before the samples were withdrawn. The samples had to be taken before the salt started to crystallize. All analyses were made in duplicate and average values are reported. After obtaining samples, the still was heated again without altering the concentration except by the amount withdrawn for samples and a small amount required to purge the withdrawal spigots. At the beginning of the subsequent run, water was added to make the charge approximately 80% acid on a salt free basis. Additional salt was added as required. This procedure was continued until the entire range of vapor-liquid equilibrium data for the given system was encompassed.

The samples were weighed and the acid present was determined by titrating with 0.10 normal sodium hydroxide, using phenolphtalein as the indicator. The chloride ion present in the sample of the residue from the still was determined by the Mohr method for calcium, strontium, and magnesium. Barium was determined by the Volhard method because it precipitates as a chromate. Prior to the chloride analysis the pink phenolphthalein end point from the acid titration was discharged with a drop or two of dilute nitric acid. The water present was found by difference.

It was impossible to obtain good boiling point data from the readings of the Othmer still thermometer, since it was necessary to superheat the upper portion of the still to prevent refluxing. The boiling point curves were determined separately using a conventional Beckmann boiling point apparatus, provided with a reflux condenser. The pressure was maintained constant at 760 ± 1 mm. Hg by the Cartesian manostat. Boiling point data thus obtained are presented in Figure 1. The boiling temperatures reported in Tables I–VI were obtained by interpolation from the smoothed boiling point curves.

DATA AND RESULTS

The data for the acetic-acid-water system as well as those for the system saturated with the chlorides of barium, strontium, calcium, and magnesium are shown in Figures 2 and 3 and presented in Tables I–V.

Table I. Experimental and Smoothed Data for Acetic Acid-Water System

Weight Fraction			Mole Fraction						
Experimental			Experimental		Smoothed Data		Literature (*1*)		
Temp., ° C.	*x*	*y*	*x*	*y*	*x*	*y*	*x*	*y*	Temp., ° C.
					0.050	0.082	0.050	0.092	115.4
					0.100	0.159	0.100	0.167	113.8
					0.200	0.297	0.200	0.302	110.1
					0.300	0.418	0.300	0.425	107.5
					0.400	0.528	0.400	0.530	105.8
116.6	0.025	0.043	0.079	0.131	0.500	0.625	0.500	0.626	104.4
114.0	0.080	0.128	0.224	0.329	0.600	0.716	0.600	0.716	103.2
109.3	0.203	0.299	0.460	0.587	0.700	0.798	0.700	0.795	102.1
107.5	0.278	0.403	0.562	0.692	0.800	0.872	0.800	0.864	101.3
105.7	0.390	0.530	0.681	0.790	0.900	0.939	0.900	0.930	100.6
100.3	0.951	0.965	0.985	0.989	0.950	0.970	0.950	0.963	100.3

Table II. Results of Acetic Acid-Water Solution Saturated with Anhydrous Calcium Chloride

	Weight Per Cent of Water		
Salt[a]	*x* (Salt-Free basis)	*y*	*t*, ° C.
32.9	9.6	11.0	122.2
35.0	9.9	10.5	122.1
50.3	19.2	14.1	122.4
52.6	20.1	13.6	122.5
62.5	41.5	19.9	125.8
63.9	44.3	20.6	126.2
73.2	63.6	29.8	. . .
75.6	64.7	26.6	. . .
82.4	86.8	47.3	. . .
84.3	94.8	76.1	. . .

[a] Reported as $CaCl_2 \cdot 2H_2O$ (*5*).

Table III. Results for Acetic Acid-Water Solution Saturated with Barium Chloride Dehydrate

	Weight Per Cent of Water		
Salt[a]	*x*	*y*	*t*, ° C.
0.5	13.3	22.4	. . .
0.4	14.6	23.3	. . .
4.4	28.1	38.8	107.2
6.1	36.3	49.6	105.5
9.6	45.3	54.1	104.0
13.1	46.4	56.2	103.8
16.9	59.8	62.2	102.5
20.5	59.8	61.9	102.5
24.9	73.6	71.5	102.4
34.9	88.4	83.7	103.4
37.0	88.5	83.1	103.4

[a] Reported as $BaCl_2 \cdot 2H_2O$ (*5*)

Table IV. Results for Acetic Acid-Water Solution Saturated with Strontium Chloride Hexahydrate

	Weight Per Cent of Water		
Salt[a]	*x*	*y*	*t*, ° C.
9.0	11.1	16.2	110.0
9.2	11.6	14.8	109.9
15.0	21.1	24.3	109.0
14.7	21.2	22.9	109.0
17.9	26.9	27.0	108.9
18.2	27.2	26.9	108.9
25.1	39.0	32.3	109.3
31.5	51.1	35.8	110.2
34.8	61.0	41.8	111.1
36.4	62.9	41.6	111.3
45.3	82.7	51.5	. . .
47.6	84.9	52.9	. . .
48.2	90.2	64.2	. . .
50.4	92.0	67.2	. . .

[a] Reported as $SrCl_2 \cdot 2H_2O$ (*5*)

Table V. Results for Acetic Acid-Water Solution Saturated with Magnesium Chloride Hexahydrate

	Weight Per Cent of Water	
Salt	*x*	*y*
27.6	7.3	9.7
29.4	6.5	9.2
49.6	14.3	12.0
52.8	14.6	12.2

Table VI. Azeotropic Data for the System Acetic Acid-Water Saturated with Alkaline Earth Chlorides

Salt	*x* Weight Fraction of Water (Salt Free basis)	*x* Mol Fraction of Water (Salt Free basis)	*t*, Boiling Point, ° C.
Calcium chloride	0.115	0.301	122.2
Barium chloride	0.660	0.866	102.3
Strontium chloride	0.266	0.548	108.9

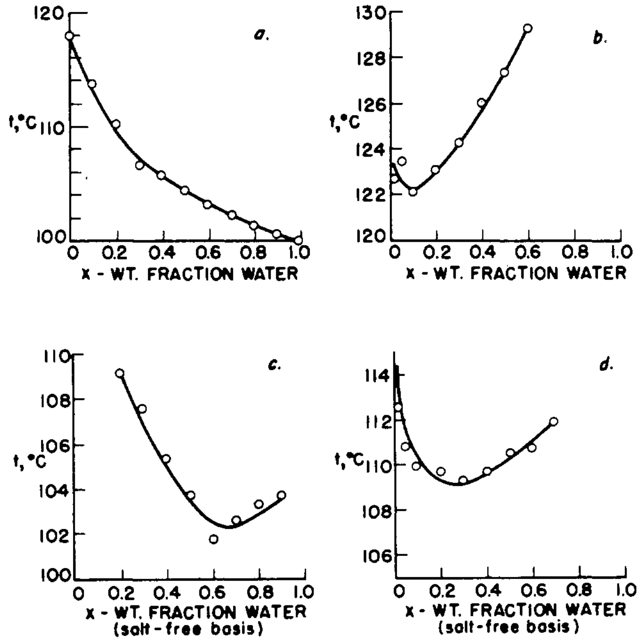

Figure 1. Boiling point data

1a. acetic acid-water system; 1b. acetic acid-water system saturated with calcium chloride; 1c. acetic acid-water system saturated with barium chloride; 1d. acetic acid-water system with strontium chloride

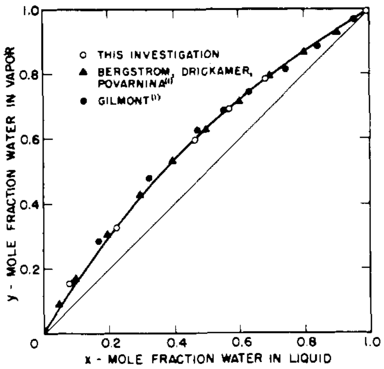

Figure 2. Vapor-liquid equilibrium data for the acetic acid-water system

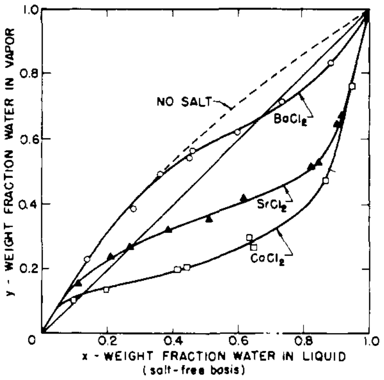

Figure 3. Vapor-liquid equilibrium data for the acetic acid-water system saturated with various inorganic salts at one atmosphere pressure

Figure 3 shows that the presence of the salt affects markedly the vapor-liquid data.

It was impossible to obtain a complete range of data for a saturated magnesium chloride solution as magnesium hexahydrate melts and decomposes at 113° C. This temperature was exceeded at about 15 wt. % water. Anhydrous magnesium chloride was not available. The number of moles of water of hydration for the different salt solutions, at their boiling temperatures was taken into account in the calculations (*5*). Interestingly, each of the salts produced an azeotrope. The composition and boiling points of these azeotropes is presented in Table VI.

Hala (*4*) points out that application of the ordinary tests for thermodynamic consistency is not feasible for the system acetic acid-water due to the nonideal behavior of the vapor phase caused by association of the acetic acid. Therefore, no consistency checks are presented for the data obtained in this investigation.

It was attempted to obtain a correlation between the change in relative volatility and the solubility of the salts in the solution. For the system ethanol-water saturated with several salts Tursi and Thompson (*9*) were successful in finding a simple linear expression relating change in relative volatility to solubility of the salts in water. All of the salts used by these investigators were relatively insoluble in ethanol. Also, because of the small temperature range involved (4 ° C.), they were able to consider the temperature as a constant parameter in their correlation.

The attempt to find a simple relationship between the change in relative volatility and the salt solubilities failed in the present study. The reason for this is the fact that the change in relative volatility is a function of the solubility and the temperature.

NOMENCLATURE

t = boiling temperatures, ° C.
x = water concentration in the liquid phase, mol fraction or weight fraction as indicated (salt-free bases)
y = water concentration in the vapor phase, mol fraction or weight fraction as indicated

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