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Separation of Acetic Acid and Water by Distillation

EFFECT OF CALCIUM CHLORIDE ADDITION

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Experimental data are presented on the vapor-liquid equilibrium of the system acetic acid–water–calcium chloride at 1 atmosphere. These data were obtained with a view to ascertaining the possibility of separating acetic acid and water under conditions of reversed relative volatility by extractive distillation with calcium chloride. The results show a considerable effect of calcium chloride addition, with a reversal taking place at approximately 8 weight % calcium chloride in the liquid phase.

BECAUSE acetic acid and water are not too readily separated by ordinary distillation, methods involving auxiliary techniques have been used for some time. These methods include (*10*) azeotropic distillation with a water-immiscible organic compound such as butyl acetate (Othmer process), liquid-liquid extraction with ethyl ether or ethyl acetate, followed by the removal of the solvent from the extract by fractional distillation, and simple extractive distillation (without reflux) using a wood oil (Suida process). In the last-named method, the water is removed overhead and the acetic acid–wood oil bottoms mixture is separated by a second distillation under vacuum.

The aqueous acetic acid solution to be separated is very frequently a dilute one, and it was thought worth while to investigate further the separation of the components of such a mixture by an extractive distillation process in which the acetic acid would be taken overhead and the bulk of the mixture (water) would be removed as bottoms. In order to do this—i.e., reverse the normal relative volatility of acetic acid and water—it would be necessary to use, as the extractive distillation agent, a substance which would tend to form a loose combination with the water. Inorganic salts seemed to offer good prospects for this purpose.

McBain and Kam (*5*) reported some work on the distillation of dilute solutions of acetic acid in water in the presence of lithium chloride, sodium chloride, potassium chloride, potassium thiocyanate, sodium sulfate, potassium nitrate, and sodium acetate. Quartaroli (*9*) did a somewhat similar study with sodium chloride, lithium chloride, calcium chloride, and sodium bromide. Calculations based on the data of these investigators showed that, of the salts possessing commercial possibilities, lithium chloride, calcium chloride, and sodium chloride were the most effective, with expected relative volatility reversals taking place in dilute

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acetic acid solution at about 6.5 weight % lithium chloride, 10 weight % calcium chloride, and 12 weight % sodium chloride.

In order for this relative volatility reversal to take place throughout the distillation column, it is necessary that the extractive distillation agent be present in the liquid in the proper concentration on all of the trays of the column. That is to say, it must be soluble in glacial acetic acid as well as in water. Semiquantitative solubility studies by Davidson (*1*) show sodium chloride and potassium chloride to be rather insoluble in glacial acetic acid. On this basis, it might be expected that lithium chloride, an alkali chloride, would also be insoluble. Calcium chloride, however, is quite soluble in acetic acid and data for its solubility as a function of temperature (*6*) are given in Figure 1. It was selected, therefore, as the salt for further investigation.

EXPERIMENTAL

All chemicals used in this work were analytical reagent grade.

The glass, electrically-heated equilibrium still employed was essentially the one described by Jones, Schoenborn, and Colburn (*4*), but modified in the following respects:

The condensate chamber was filled with glass beads to reduce its volume relative to that of the residue chamber to the greatest possible extent. During operation the condensate-residue volume ratio was about 1 to 4.

A wick of glass wool was substituted for the wire helix in the flash boiler. This permitted better distribution of the distillate over the boiler heating surface, avoiding local overheating, and minimizing the danger of the glass cracking.

The pressure on the still was maintained at 760 ± 0.5 mm. by means of a Model No. 5 industrial cartesian manostat (The Emil Greiner Company), actuated by compressed nitrogen gas from a cylinder.
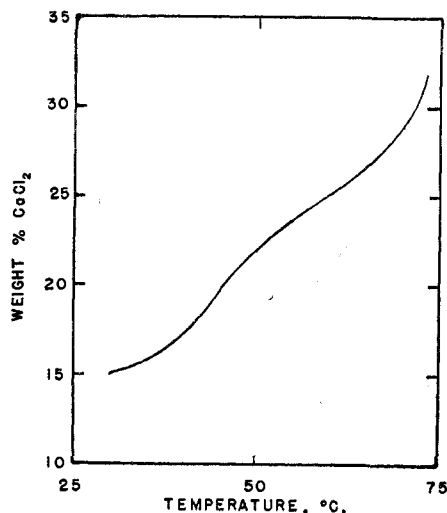
Figure 1.   Solubility of Calcium Chloride in Glacial Acetic Acid

Menschutkin (6)

The temperature of the boiling liquid in the residue chamber was measured to 0.1° C. with a mercury thermometer inserted in a thermometer well. Glycerine was used as the contact fluid. The thermometer was checked and found to be accurate at the 100° C. point by making a trial run with distilled water.

The experimental runs were designed to cover the complete range of water–acetic acid ratios with calcium chloride concentrations varying from zero to the maximum possible value, this limit being determined by the solubility of the salt in the liquid. Be-

TABLE I.   VAPOR-LIQUID EQUILIBRIUM AND BOILING POINT DATA FOR ACETIC ACID–WATER–CALCIUM CHLORIDE SYSTEM

(Pressure, 760 mm. Hg)

Run No.	Wt. % S	X	Y	T, ° C.
1A	0.0	91.9	93.9	100.2
2A	0.0	74.5	81.5	100.9
3E	0.0	61.9	71.9	101.3
4A	0.0	44.2	56.5	101.9
5A	0.0	23.6	34.6	104.4
6A	0.0	10.6	17.4	108.0
7	9.3	85.3	83.7	102.0
8	10.1	76.5	73.5	102.4
9	9.7	62.5	59.7	103.2
10	9.4	41.3	39.6	105.0
11	9.6	26.5	25.4	107.6
12	9.5	11.8	11.5	111.6
13	19.7	88.8	79.9	104.2
14	19.3	79.2	65.7	104.8
15	20.0	66.8	49.4	106.2
16	19.8	45.1	30.2	109.0
17	19.0	28.1	18.8	112.0
18A	18.4	15.3	11.0	115.0
19	29.8	93.5	81.5	110.0
20	29.2	83.6	59.7	110.2
21	31.0	79.8	51.3	111.1
22	30.4	48.7	25.0	115.0
23	31.6	32.1	16.0	120.3
25A	37.6	91.0	67.8	115.3
26	40.1	85.0	50.8	116.8
27	35.6	71.7	39.2	114.0
28	39.1	55.1	25.4	118.9
29A	36.8	36.5	16.4	121.6
30	36.2	18.4	7.2	127.2
31	44.7	84.8	47.8	121.2
32	45.1	85.5	48.6	120.9
33	45.8	73.4	33.0	121.9
34	49.5	57.1	20.0	128.0
36	53.4	90.4	51.8	127.9
37	53.2	88.6	47.5	127.5
38	60.3	97.0	65.0	132.3
39	60.5	98.5	80.7	138.9
40	61.0	91.2	50.8	136.0

cause calcium chloride is more soluble in water than in acetic acid, it was possible to go to as high as 60 weight % salt in the water-rich region but only to about 30 weight % in the acid-rich range.

For any particular run, the acetic acid–water mixture of the approximate proper concentration was introduced into the condensate chamber. Another portion, to which the necessary amount of anhydrous calcium chloride had been added, was introduced into the residue chamber.   The still was allowed to operate for 3 hours before the taking of samples.   Preliminary tests showed that 3 hours were ample, even without the glass beads in the condensate chamber.

ANALYTICAL METHODS.   The condensate, which was considered to consist of acetic acid and water, was analyzed for the acid by titration with standard sodium hydroxide, using phenolphthalein as the indicator.

The residue, when it contained calcium chloride, was first titrated for acetic acid content as described above.   It was found that the presence of calcium chloride had no effect on this titration.   The sample thus titrated was titrated further for chloride content with silver nitrate, using sodium chromate as the indicator (Mohr's method) (2).   It was only necessary, prior to this second titration, to discharge the caustic-phenolphthalein end point color with a fraction of a drop of acetic acid. This method of determining chloride in the presence of sodium acetate and phenolphthalein indicator was found quite satisfactory by a series of test analyses on known mixtures.

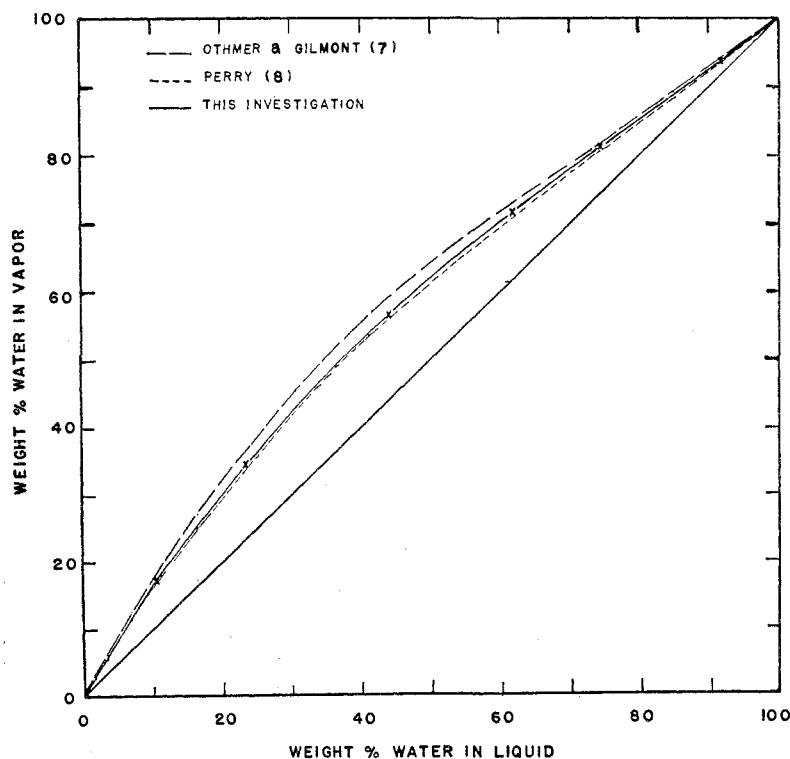All analytical determinations were made in duplicate; average values are reported.

Figure 2.   Vapor-Liquid Equilibrium Behavior of Acetic Acid–Water System
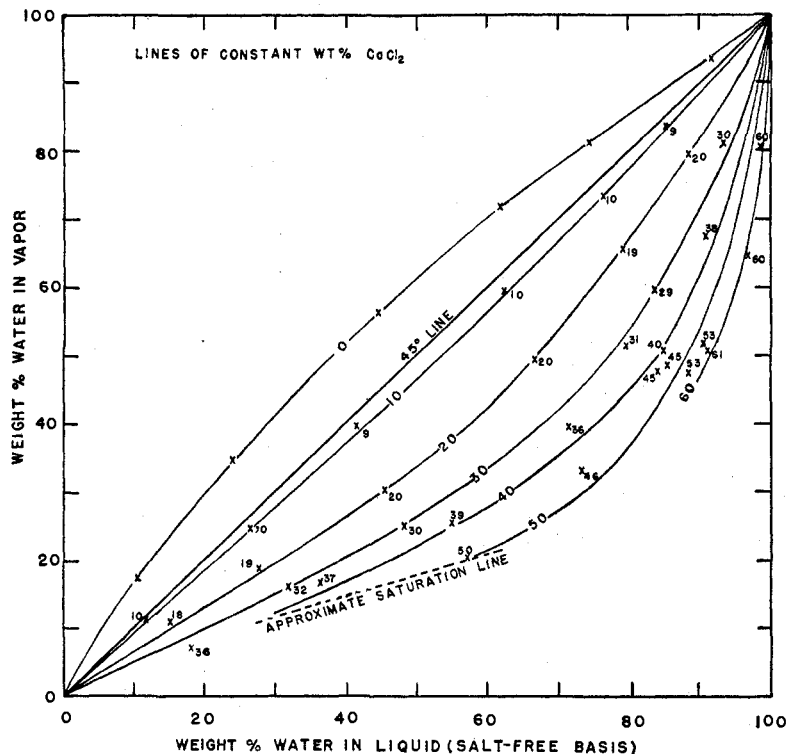
Pressure, 760 mm. Hg

Figure 3. Vapor-Liquid Equilibrium Behavior of Acetic Acid-Water-Calcium Chloride System

Pressure, 760 mm. Hg

20% calcium chloride was relocated to exactly 20% by the same graphical method, using now as the reference curve, the 10% curve just drawn. The process was continued until the family of curves was complete.

In two of the experimental runs (No. 30 and No. 34), the liquid phase was very nearly saturated with salt. The results of these runs were used to locate the approximate saturation line shown in Figure 3.

A plot of the boiling points of acetic acid-water-calcium chloride mixtures is presented in Figure 4. The boiling point is shown as a function of the salt-free composition of the liquid, with the calcium chloride concentration as the parameter. The number adjacent to each experimental point represents, as previously, the calcium chloride concentration in the liquid to the nearest weight per cent. The smoothing operation was the graphical one described above, with the experimental points being moved vertically in this case.

The dotted portions of the curves lying outside the range of investigation were located by extrapolation to the known boiling points of calcium chloride-water solutions (3). A similar extrapolation in the other direction was not possible

RESULTS

The experimental data are summarized in Table I. All concentrations are expressed in weight per cent. The results for the two-component system acetic acid-water are plotted in Figure 2, in which they are compared with the findings of Othmer and Gilmont (7) and with the set of data in Perry's "Chemical Engineers' Handbook" (8). The curve obtained in this investigation lies between the other two curves and rather close to that drawn from the data in Perry.

Boiling points are also compared with those provided by these sources. Smoothed values at even 10 weight % increments are presented for comparison in Table II. It can be seen that the agreement is quite good.

Complete smoothed vapor-liquid equilibrium data are given in Table III and are plotted in Figure 3. The number adjacent to each experimental point in the figure represents the calcium chloride content of the liquid to the nearest weight per cent. The curves were plotted in the following manner: The best 0% calcium chloride curve was first plotted. Each of the experimental points for approximately 10 weight % calcium chloride in the liquid was relocated to exactly 10% calcium chloride by linear interpolation or extrapolation, relative to the 0% calcium chloride curve and moving along a line perpendicular to the 45° line—i.e., in the general direction of change in the position of the curve with increasing calcium chloride content. After the 10% points had thus been relocated, the best 10% curve was drawn through them. Each of the experimental points for approximately

TABLE II. BOILING POINT VERSUS CONCENTRATION FOR ACETIC ACID-WATER SYSTEM

(Pressure, 760 mm. Hg)

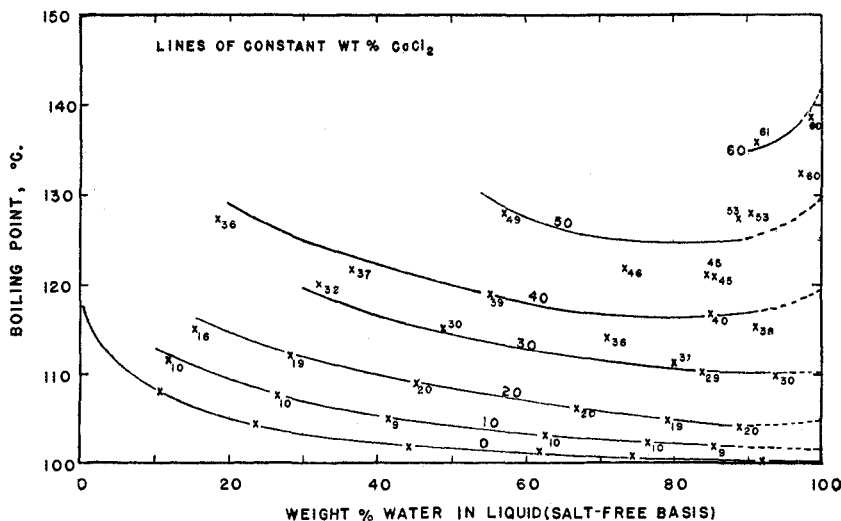|	T, ° C.		
X, Wt. %	Othmer and Gilmont (7)	Perry (8)	This investigation
0	118.0	118.1	...
10	108.6	108.2	108.2
20	105.1	105.1	105.1
30	103.4	103.4	103.4
40	102.3	102.3	102.3
50	101.6	101.6	101.7
60	101.1	101.1	101.2
70	100.7	100.7	100.8
80	100.4	100.4	100.5
90	100.2	100.2	100.2
100	100.0	100.0	100.0

Figure 4. Boiling Points of Acetic Acid-Water-Calcium Chloride Mixtures

Pressure, 760 mm. Hg

TABLE III. SMOOTHED VAPOR-LIQUID EQUILIBRIUM AND BOIL-
ING POINT DATA FOR ACETIC ACID–WATER–CALCIUM CHLORIDE
SYSTEM

(Pressure, 760 mm. Hg)

Wt. %				Wt. %			
S	X	Y	T, ° C.	S	X	Y	T, ° C.
0.0	5.0	8.5	111.0	30.0	5.0	2.4	...
0.0	10.0	16.5	108.2	30.0	10.0	4.9	...
0.0	20.0	30.3	105.1	30.0	20.0	10.0	...
0.0	30.0	41.8	103.4	30.0	30.0	15.1	119.6
0.0	40.0	52.5	102.3	30.0	40.0	20.6	116.8
0.0	50.0	62.2	101.7	30.0	50.0	26.5	114.5
0.0	60.0	70.7	101.2	30.0	60.0	33.8	112.8
0.0	70.0	78.2	100.8	30.0	70.0	42.6	111.5
0.0	80.0	85.5	100.5	30.0	80.0	53.6	110.6
0.0	90.0	92.8	100.2	30.0	90.0	71.5	110.2
0.0	95.0	96.3	100.0	30.0	95.0	84.5	110.3
10.0	5.0	4.5	...	40.0	30.0	12.0	125.0
10.0	10.0	9.0	112.8	40.0	40.0	16.5	122.1
10.0	20.0	18.2	109.3	40.0	50.0	21.7	120.0
10.0	30.0	27.6	107.0	40.0	60.0	27.7	118.3
10.0	40.0	37.2	105.4	40.0	70.0	35.0	116.9
10.0	50.0	46.8	104.2	40.0	80.0	44.6	116.3
10.0	60.0	56.8	103.5	40.0	90.0	61.5	117.0
10.0	70.0	67.0	102.8	40.0	95.0	76.5	117.8
10.0	80.0	77.5	102.3	50.0	60.0	21.0	127.5
10.0	90.0	88.2	102.0	50.0	70.0	26.9	125.5
10.0	95.0	93.8	101.8	50.0	80.0	36.5	124.8
20.0	5.0	3.3	...	50.0	90.0	53.2	125.1
20.0	10.0	6.5	...	50.0	95.0	69.0	126.2
20.0	20.0	13.0	114.6	60.0	90.0	46.5	134.7
20.0	30.0	19.6	112.1	60.0	92.5	52.0	135.0
20.0	40.0	26.2	110.1	60.0	95.0	59.2	136.5
20.0	50.0	33.7	108.4	60.0	97.0	67.0	138.0
20.0	60.0	42.3	107.0	60.0	99.0	81.0	140.0
20.0	70.0	53.2	105.9				
20.0	80.0	67.0	104.9				
20.0	90.0	81.6	104.4				
20.0	95.0	90.0	104.5				

because of the lack of available data on the boiling points of solutions of calcium chloride in glacial acetic acid.

CONCLUSIONS

The results confirm the observation of Quartaroli (9) that the addition of calcium chloride tends to reverse the relative volatility of acetic acid and water. The reversal takes place at about 8 weight % calcium chloride in the liquid phase and it is possible, by the addition of moderate quantities of calcium chloride, to obtain a reversed relative volatility which is greater in magnitude than that for the ordinary distillation.

In order to explore fully the potentialities of such a separation process, further work on the continuous extractive distillation aspect will be required.

NOMENCLATURE

S = weight per cent calcium chloride in liquid
T = temperature, ° C.
X = weight per cent water in liquid (salt-free basis)
Y = weight per cent water in vapor

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Salt Effect in Cellulose Acetate

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Salt effect is a measure of the increase in viscosity of cellulose acetate caused by the presence of certain salts. A procedure for the measurement of the salt effect has been developed. The influence of salts on viscosity depends on: the nature of the salt; amount of salt; pH of the solution from which the salt is applied; solvent for the cellulose acetate in solution; degree of hydrolysis of cellulose acetate; and the amounts of carboxyl and combined sulfate in the cellulose acetate.

THE term "salt effect" is used in this paper to designate the ratio of the viscosity of one portion of a cellulose acetate washed with water containing a certain salt to the viscosity of a second portion of the same acetate washed with salt-free water or with water containing a salt known to have no effect on the viscosity. In general, salts of monovalent cations—e.g., sodium chloride—are without effect on the viscosity, whereas salts of polyvalent cations—e.g., calcium chloride—increase the viscosity.

This behavior was observed in cellulose acetate by Rogovin (8) who found a salt effect in acetone but not in formic acid. Lohmann (2) has studied the salt effect in a variety of solvents and found that it was manifested especially in concentrated solutions in solvents such as ketones and esters which do not contain hydroxyl groups. The salt effect in acetone was reduced by the addition of water or methanol. High viscosity, due either to high solids content or to high molecular weight of the cellulose acetate, increased the effect. He observed the salt effect mainly with calcium chloride and found that it increased with the amount of salt added. An especially significant observation was that the increased viscosity of cellulose acetate due to certain salts did not add to the tensile strength of fibers spun from these solutions.

Other findings in this field have been that the salt effect was more pronounced with products made from wood pulp than from cotton linters (4). Also, it increased with the degree of hydrolysis of the cellulose ester (3) and with the pH of the wash solution from which the salts are applied (7).

Lohmann's finding that the increased viscosity due to salts failed to give a corresponding increase in the yarn strength makes this increase in viscosity undesirable. With this background an investigation was undertaken to develop a procedure for measuring salt effect and to establish factors responsible for the effect.

First, several of the above observations were verified using production batches of yarn-type cellulose acetate containing approximately 39% acetyl. Table I gives the effect of various salts on the viscosity of this type of cellulose acetates. The acetates of the alkaline earth elements all gave about the same