

# Measuring the Changes Due To Addition of Calcium Chloride in Acetic Acid Water Mixture and Generate the VLE Data with the Help of Extractive Distillation

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## ABSTRACT

*The study of influence of salt on vapour liquid equilibrium of solvent mixture is of interest, because addition of salt to a mixed solvent will enhance the relative volatility and break azeotrope of the mixture. Salt-Effect distillation is a method of Extractive distillation in which salt is dissolved in the mixture of liquids to be distilled. The salt acts as a separating agent by raising the relative volatility of the mixture and by breaking any azeotropes that may otherwise form. Vapour-liquid equilibrium (VLE), is a condition where a liquid and its vapour (gas phase) are in equilibrium with each other or more precisely a state where the rate of evaporation equals the rate of condensation on a molecular level such that there is no overall vapor-liquid inter-conversion. The addition of calcium chloride to this solvent mixture increases the water concentration in vapour phase at equilibrium. This indicates a preferential association of salt with less volatile component, acetic acid in the acetic acid-water mixture, water is more volatile component in acetic acid-water mixture. Most of the Salt effect studies were carried out at saturated level of salt. The objective is to study the effect of addition of  $\text{CaCl}_2$  on separation of Acetic acid – water mixture and to find out the possibility of the use of concentrated solution of  $\text{CaCl}_2$  as a solvent for separating dilute solution of acetic acid in water by extractive distillation process.*

**KEY WORDS:-** VLE, Extractive distillation,  $\text{CaCl}_2$ , Acetic acid + water + calcium chloride system.

## ❖ INTRODUCTION:-

The study of influence of salt on vapour liquid equilibrium of solvent mixture is of interest, because addition of salt to a mixed solvent will enhance the relative volatility and break azeotrope of the mixture. Salt-Effect distillation is a method of Extractive distillation in which salt is dissolved in the mixture of liquids to be distilled. The salt acts as a separating agent by raising the relative volatility of the mixture and by breaking any azeotropes that may otherwise form. Extractive distillation is defined as distillation in the presence of miscible, high boiling, relatively non-volatile component, the solvent, that no forms azeotropes with other component in the mixture.<sup>[1]</sup> The Extractive distillation method is used for mixtures having a low value of relative volatility, nearing unity. Such mixtures cannot be separated by simple distillation, because the volatility of the two components in the mixture is nearly the same, causing them to evaporate at nearly the same temperature at a similar rate, making normal distillation impractical. Extractive distillation with salt and salt containing distillation have been used in practice due to their low energy consumption high efficiency, reduced capital costs, higher yield of product, higher quality and less pollution. Vapour-liquid equilibrium (VLE), is a condition where a liquid and its vapour (gas phase) are in equilibrium with each other or more precisely a state where the rate of evaporation equals the rate of condensation on a molecular level such that there is no overall vapor-liquid inter-conversion.<sup>[1,4]</sup> There are many advantages of adding salts instead of liquids in an extractive distillation process.

1. lower energy consumption since salts are non volatile and do not evaporate or condense in the distillation process
2. Purity of the overhead product from the extracting agent is high since the salts are non volatile.
3. Sometimes a small amount of salt will facilitate required separation.

### ❖ OBJECTIVE OF EXPERIMENT/WORK:-

The objective is to study the effect of addition of  $\text{CaCl}_2$  on separation of Acetic acid – water mixture and to find out the possibility of the use of concentrated solution of  $\text{CaCl}_2$  as a solvent for separating dilute solution of acetic acid in water by extractive distillation process.

### ❖ EXPERIMENTAL :-

**1. Material:-** Calcium Chloride ( $\text{CaCl}_2$ ), Acetic Acid ( $\text{C}_2\text{H}_4\text{O}_2$ ) and Water ( $\text{H}_2\text{O}$ ).

#### **2. Method<sup>[5,7]</sup>:-**

Equilibrium apparatus used for measuring vapor-liquid equilibrium data was developed by Othmer. The still is classed as a circulating still. Circulation method was used to find VLE data for acetic acid - water – calcium chloride. The main features of the still are boiling chamber/ section, condensation section, reflux section, heating media. Heating coils are provided inside the boiling section. The schematic diagram of the apparatus assembly is shown in figure 1. It consists of a boiling pot (A), central and outlet vapor tubes (B), thermocouple (C), condenser (D), pot sampling cock (E), and interchangeable receiver with liquid sampling cock (F). The interchangeable receiver holds approximately 15 mL of distillate.

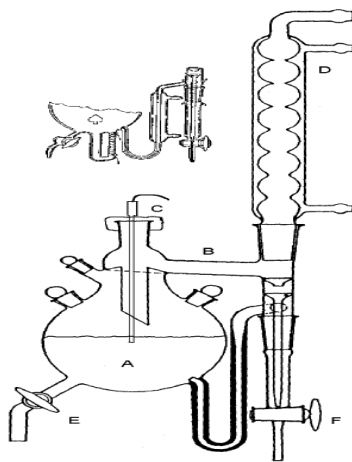


Fig 1:-Othmer Equilibrium still

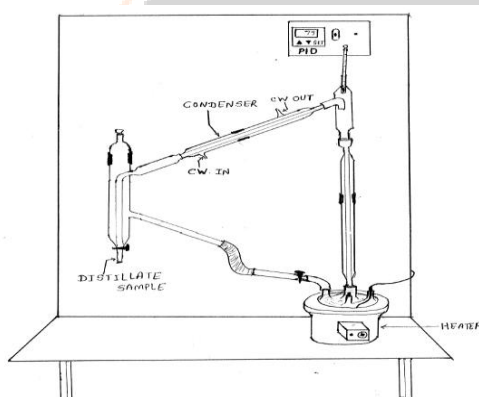


Fig 2:- Sketch of Othmer Still

In this experiment one will generate vapor-liquid equilibrium data at each of the points. Make sure there is no liquid in the boiling tube (tube wound with external resistance wire). [Note: The small amount that cannot be removed with the syringe is ok.]. Acetic acid –water mixture along with measured quantity of  $\text{CaCl}_2$  is added to the still. Heating is given through the electric heater. The funnel can be used to ensure there is no spillage during filling. Connect the digital thermometer to the thermocouple and turn on. Make sure the thermocouple is immersed in the liquid. Plug in the rheostat, turn the switch to 120 volts, and increase the power on the rheostat to approximately 70. It will take time to heat the mixture at the beginning. When the liquid is boiling and the vapor is condensing it will take 6 to 8 minutes to fill the interchangeable receiver. When the receiver is full, it will overflow into the return line. Start the stopwatch when liquid begins to overflow into the return line. Let the mixture reflux for a minimum of 30 minutes. At the end of the reflux period record the temperature of the liquid in the pot and collect a sample of the pot and the distillate liquid in marked sample vials. Only a small amount has to be collected (2 to 3 mL) because the

samples will be analyzed using a refractometer. Once the samples have been collected, turn off the rheostat. Let the liquid cool a few minutes. Add water to the pot and/or remove distillate from the receiver in order to bring the mixture in the pot to the next sample point concentration you want to analyze. [Note: distillate removed from the receiver should be put in the waste bottle.] Turn on the rheostat and repeat the procedure. Normally 3 to 4 sample points can be done in a 3 hour lab period. After the last sample point is analyzed for the lab period, turn off the rheostat and let the solution cool so it is warm to the touch. Drain the pot into the labeled one liter bottle provided in the equipment box. Remove the remainder of the liquid in the heating tube with the syringe and add to the one liter bottle. This will be saved for the next lab period. At the next lab period, transfer the mixture in the one liter bottle to the sample pot and continue with the experiment.

At the end of the experiment let the mixture in the pot cool, then remove and put in the waste bottle. Because of the addition of  $\text{CaCl}_2$  in water, the boiling point of  $\text{CaCl}_2$ -water mixture will increase, i.e. boiling point elevation takes place. The lower boiling point component Acetic acid will be vaporized. The vapors generated are sent into the condenser and condensed. The condensed liquid is collected from the outlet of the condenser. In the residue,  $\text{CaCl}_2$ -water mixture is collected. When the temperature stabilizes, indicating thermal equilibrium, a sample of distillate collected is withdrawn and analyzed. The pressure in the still is atmospheric pressure. PID controller is installed to control and measure the temperature. The analysis of distillate and residue is carried out by simple titration with standard solution of sodium hydroxide to calculate the mole fraction of acetic acid and water.

❖ **Effect of addition of calcium chloride in water or boiling point elevation after addition of calcium chloride in water.**<sup>[3,4]</sup>

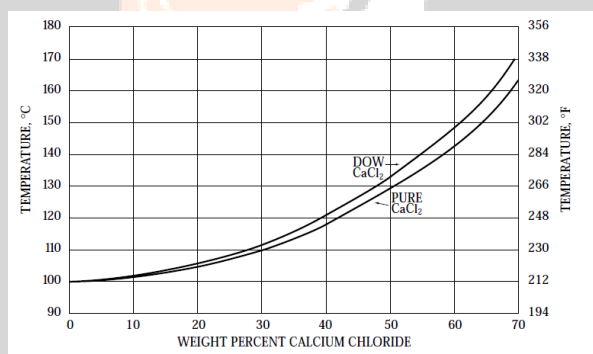


Fig 3:- Boiling Points of Calcium Chloride Solutions

Figure 3 shows the boiling points of 0–70% aqueous solutions of pure and DOW commercial calcium chloride. Solutions of pure calcium chloride above 69% cannot be prepared by boiling at 760 mm pressure because dihydrate begins to separate as a solid phase and the solution composition remains constant. Boiling points of commercial calcium chloride vary with the amount and the kind of impurities present. The curve shown (in Figure 3.7.1) represents an average Dow material from which any individual sample should not be expected to deviate by more than  $1^\circ\text{C}$  ( $2^\circ\text{F}$ ).

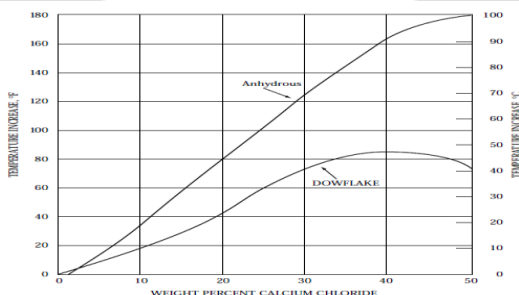


Fig 4 :- Theoretical Temperature Increases in Preparing Aqueous Solutions of DOWFLAKE or Anhydrous (94%)

When DOWFLAKE or Anhydrous calcium chloride is dissolved in water, considerable heat is liberated. This temperature increase is shown in Figure 4 for concentrations up to 50% calcium chloride. For example, the heat generated in preparing a 40% calcium chloride solution with DOWFLAKE would result in a temperature increase of approximately 47°C (84°F). With Anhydrous, the temperature increase would be approximately 91°C (164°F). Thus, if the temperature of the water is 23°C (74°F), the final solution temperature will exceed 68°C (155°F) for DOWFLAKE and 114°C (238°F) for Anhydrous. These temperature calculations are theoretical in that they do not account for heat loss.

#### ❖ METHODS USED FOR CALCULATIONS:

##### Method used to calculate Activity Coefficient:

The activity coefficient is of special importance because of its application in phase equilibrium calculations. There are many equations for activity coefficient:-

1. Wohl's three-suffix equations.
2. Margules equation.
3. vanLaar equation.
4. Wilson equation.
5. Non-random two-liquid (NRTL) equation.
6. Universal quasi-chemical (UNIQUAC) equation.
7. Universal functional activity coefficient (UNIFAC) method.

#### ❖ EXPERIMENTAL PROCEDURE:-

First make 1 N NaOH solution which is standardised with 1 N Oxalic acid solution. Now, make 100 ml of 10% concentrated acetic acid and water mixture and for that we have to add 9.54 ml of acetic acid and add 90.46 ml water. Now take calcium chloride and it is 50% of the water present in the 10% acetic acid –water mixture, and mix well calcium chloride in mixture. After that measure the volume of the feed mixture and add it to the flask of Modified othmer still. Heating the feed mixture causes acetic acid to vaporize as an over head product leaving calcium chloride -water solution as residue. Volume of Distillate collected is measured and is titrated with 1N NaOH solution. Similarly volume of residue is measured and is titrated with 1N NaOH solution. Mole fraction of Acetic acid in distillate and residue is calculated.

#### ❖ EXPERIMENT RESULTS:-

VLE data for acetic acid-water- calcium chloride system:-

S.r No.	Temp °C	x(1)	y(1)	x(2)	y(2)	K=y/x	$\alpha$	$\gamma(1)$	$\gamma(2)$	A	B
1	100	0.0104	0.0384	0.9895	0.9615	3.6951	3.8029	6.5611	0.97181	1.4840	-0.00024
2	101	0.0136	0.063	0.9862	0.9332	4.6391	4.8861	7.9575	0.91327	9.7824	-0.04253
3	102	0.0112	0.0537	0.9887	0.9478	4.7946	5.0099	7.967	0.89312	30.0664	-0.07090
4	102	0.0226	0.0966	0.9773	0.9039	4.2743	4.6244	7.1026	0.86169	10.1517	-0.07183
5	103	0.0286	0.0803	0.9713	0.9196	2.8076	2.9658	4.5121	0.85156	10.3594	-0.08419
6	103	0.0543	0.1669	0.9456	0.833	3.0736	3.489	4.9396	0.79233	3.7771	-0.08546

Where, x(1,2) = mole fraction of A.A in liquid & mole fraction of water in liquid.

y(1,2) = mole fraction of A.A in vapour & mole fraction of water in vapour.

$K = y/x =$  Separation factor.

$\alpha = \frac{y(1-x)}{x(1-y)}$  = Relative Volatility.

$\gamma(1) = \frac{P y_1}{P_{v1} x_1}$  &  $\gamma(2) = \frac{P y_2}{P_{v2} x_2}$  = Activity coefficients.

$A = \ln \gamma_1 \left[ 1 + \left\{ \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1} \right\} \right]^2$  &  $B = \ln \gamma_2 \left[ 1 + \left\{ \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2} \right\} \right]^2$  = Vanlaar Constants.

## ❖ SCOPE OF EXPERIMENT / WORK:

Acetic acid is the most widely used aliphatic carbonic acid. An acetic acid and water, do not form an azeotrope. Despite this it is very difficult to separate pure acetic acid (boiling point: 118.1°C) from a dilute solution of acetic acid and water by distillation alone. As progressive distillations produce solutions with less and less water, each further distillation becomes less effective at removing the remaining water. Distilling the solution to dry acetic acid is therefore economically impractical. One would then need towers having a large number of stages, which would have to be operated with a high reflux ratio. This would necessarily involve high costs for energy and high operating costs, if rectification with vapor condensation is not used. Conventionally, for solutions of higher concentrations of acetic acid i.e. 50-70 %, this problem is solved by adding ethyl acetate as an entrainer, which forms an azeotrope with water that boils at 70.4°C. By adding ethyl acetate as an entrainer, it is possible to distill away the azeotrope and leave nearly pure acetic acid as the residue. For concentrations of less than 40%, solvent extraction followed by extractive distillation is carried out. But this would require separation of entrainer and solvent from the remaining mixture. A dilute solution of Acetic acid –water is prepared and to this mixture, a measured quantity of  $\text{CaCl}_2$  is added. This mixture is heated in Modified othmer still. Heating is given through the electric heater. Because of the addition of  $\text{CaCl}_2$ , the boiling point elevation takes place, i.e. the boiling point of  $\text{CaCl}_2$  -water mixture will increase. The lower boiling point component Acetic acid will be vaporized first, leaving  $\text{CaCl}_2$  -water solution in the residue. This dissertation covers increasing boiling point of  $\text{CaCl}_2$  -water solution and there by separating nearly pure acetic acid at the over head.  $\text{CaCl}_2$  is chosen because it do not react with acetic acid and mainly because of its hygroscopic nature and its boiling point elevation is very high.

## ❖ FUTURE SCOPE:

From VLE data first we can find activity coefficient using suitable model. And based on experimental data one can design distillation column by finding number of theoretical stages and reflux ratio and compare the result with conventional technology like liquid-liquid extraction and azeotropic distillation. One can carry out detailed cost analysis to check economical viability of this new technology compare to conventional one. Similarly  $\text{CaCl}_2$  can also be used to break the azeotropic mixture like ethanol water, IPA-water by addition of small amount of  $\text{CaCl}_2$ , since in these cases water is less volatile component and hence small amount of salt will be sufficient to break azeotrope.

## ❖ CONCLUSION:

During experimental work we use different concentration of acetic acid ranging from 10-30 with different concentration of  $\text{CaCl}_2$ . During experimental work it was found that by addition of 40-60 % of  $\text{CaCl}_2$  Resulted in separation of acetic acid as overhead product. It was found from experimental VLE data that as concentration of  $\text{CaCl}_2$  increases salting out effect on acetic acid increases which is shown by separation factor and relative volatility. From the above experiment we may conclude that separation of pure acetic acid from its dilute solution in water is possible using concentrated  $\text{CaCl}_2$  solution, as a solvent in extractive distillation process.

## ❖ ACKNOWLEDGEMENT:

I would like to express my respect and sincere gratitude to my thesis supervisor, **Prof. Rajul P. Bhatt**, for giving me an opportunity to work under her supervision for my Master degree program at the L. D. College of Engineering. I am indebted to Prof. Bhatt for her invaluable supervision and esteemed guidance. As my supervisor, her insight, observations and suggestions helped me to establish the overall direction of the research and to achieve the objectives of the work. Her continuous encouragement and support have been always a source of inspiration and energy for me. I could not have imagined having a better advisor and mentor for my Dissertation project.

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