

Separation of azeotropic mixture of formic acid-water by using Li-Br as a salt by extractive distillation

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ABSTRACT

Formic acid is a very useful solvent for many industries and it requires in pure form for specific applications. It makes an azeotrope with water at 107.5°C having composition of 77.5% of formic acid by weight. It is seen that conventional methods used are not much effective or large energy consuming. Another alternative is by adding salt which is helpful by altering the relative volatility of the mixture and separation gets easier. In this paper the effect of addition of Lithium Bromide salt in Formic acid -water binary azeotropic mixture using extractive distillation is discussed. As Lithium bromide is a nonvolatile salt, it will not appear in the distillate and moreover Lithium bromide is hygroscopic in nature so it gives higher boiling point elevation with water which is main cause of its use in this application. Addition of salt eliminates formation azeotrope

Keywords:- VLE, Extractive Distillation, Formic acid + water + Li-Br system

1. INTRODUCTION

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. If we add lithium bromide in mixture of formic acid and water solution then lithium bromide increase the concentration of water in liquid phase because Li-Br has high boiling elevation with water and from top of the column we can get formic acid. Whenever a mixture of liquids is boiled, the composition of the vapor phase is usually different from that in the liquid phase. For some mixtures there is a unique point or rather composition where the liquid and vapor phases are identical, that point is known as the azeotrope.

The present work involves the measurement of vapour liquid equilibrium of Formic acid + water + lithium bromide at different concentrations of salt below saturation level. The addition of lithium bromide to this solvent mixture increases the water concentration in vapour phase at equilibrium. This indicates a preferential association of salt with less volatile component, formic acid in the formic acid-water mixture. Most of the Salt effect studies were carried out at saturated level of salt

There are some advantages adding salt in extractive distillation over the adding a solvent

- Less energy consumption since salts are non-volatile and doesn't evaporate or not condense in the distillation
- Purity of the overhead product from the extracting agent is high since the salts are non-volatile
- In Some cases a small amount of salt will facilitate required separation.

2. AZEOTROPIC CONDITION AND PROPERTIES

At atmospheric condition, a binary mixture of formic acid (Methanoic acid)–water forms a homogeneous minimum boiling azeotrope at 77.5 mass% of formic acid and 107.5 °C

Table 1. Properties of component

Component	Density($\frac{g}{cm^3}$)	Molecular weight(g/mole)	Boiling point(°C)
Formic acid	1.220	46.03	100.8
Water	1	18	100
Lithium bromide	3.464	86.84	1265

3. REASONS FOR SELECT LITHIUM BROMIDE AS A SALT FOR THIS SYSTEM

Lithium bromide salt is hygroscopic in nature and it provides high characteristic to give higher boiling point elevation with water. It is used in vapour absorption cycle because of this property. Though it is little bit costlier, salt is having high boiling point too, so it can be recovered easily from water. So use of salt may shift the azeotrope to other point or there may be a chance that azeotrope will not occur or salt may break the azeotrope.

4. EXTRACTIVE DISTILLATION

This is a multicomponent rectification method similar in purpose to azeotropic distillation. To a binary mixture which is very difficult or impossible to separate by ordinary means a third component, termed as a solvent is added, which changes the relative volatility of the original mixture, and hence separation is possible. The added solvent is of low volatility and is itself not appreciably vaporized in the fractionator. The main conclusions drawn from the study were as follows:

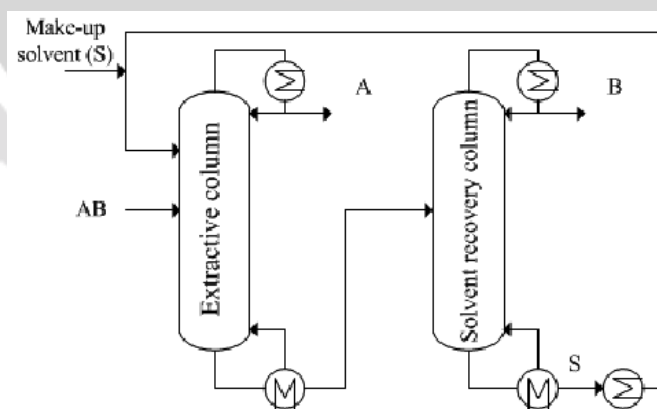


Figure 1. Schematic diagram of extractive distillation

A new method can be adopted as extractive distillation in which solid salt or its aqueous solution is added to the mixture in place of liquid solvent. Due to addition of salt, the boiling point elevation of the mixture takes place and azeotrope can be broken or shifted, and separation of components can be achieved. The selection of salt should be done properly so as to ease the separation. Specific salt can be used for specific system.

5. EXPERIMENTAL STUDIES

5.1 Apparatus and Experimental procedure:

Equilibrium apparatus used for measuring vapor-liquid equilibrium data was developed by J.D.Raal., and we are using modified Raal's apparatus

Vapor bubbles generated in magnetically stirred boiling chamber propel two phase mixture through a Cottrell tube surrounded by a vacuum jacket. The two phase mixture rises upwards and forced to pass downwards co-currently through a loosely packed section where vapor phase separates from liquid. The vapor flows downwards through a tube that is concentric with the inner tube, conveying return liquid to the reboiler and bubbles through liquid in the inner equilibrium chamber from small holes at the bottom of vapor down comer. Vapor is passed through a separate tube and sent to condensate chamber where it condenses. Condensate sample is collected from condensate chamber which is also magnetically stirred.

Temperature is measured above equilibrium chamber. Liquid phase sample is collected from boiling chamber

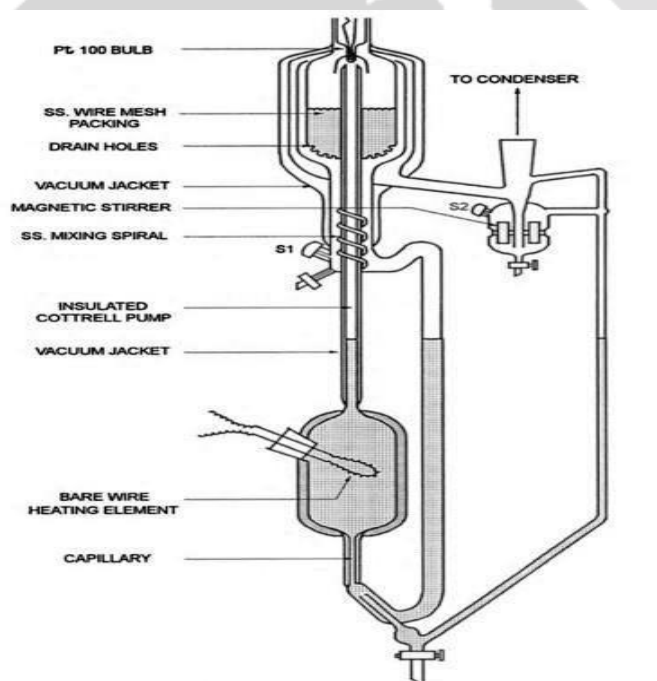


Figure 2. Raal's apparatus

1. Measure the feed volume and component composition. Add Li-Br of known grams to solution and dissolve it.
2. Insert the feed into round bottom flask and start heating. Meanwhile start water flow in condenser
3. After some time vapour will start condensing in the distillate collector. Let it be filled till re-circulation starts from the container.
4. Measure liquid and vapour temperature continuously and allow both temperature to reach the same value.
5. When steady state is achieved and value of both temperature remain same for a long time take the sample from distillate and bottom.
6. Measure its composition and repeat the step 6 for different compositions of Formic acid
7. Plot T-x-y graph and x-y graph and Calculate remaining quantities.

5.2 RESULT TABLE AND DISCUSSION

Table 2.VLE data of formic acid-water at different concentration of Li-Br

Composition(% of formic acid)	Amount of salt(gm)	Temp(°C)	Mole fraction of FA in distillate	Mole fraction of FA in residue
77.5%	15	103.4	0.27	0.58
77.5%	40	104	0.45	0.27
77.5%	50	105	0.63	0.38
77.5%	72	107	0.42	0.34
77.5%	100	108	0.48	0.27

Where, X= mole fraction of Formic acid in distillate
 Y= mole fraction of formic acid in residue

Table 3. VLE data of Formic acid-water at 50grams of Li-Br

Composition	Temp(°C)	y	x
20%	104.2	0.13	0.078
30%	104.8	0.32	0.1787
40%	105	0.36	0.19
50%	105.9	0.4	0.212
60%	106.8	0.54	0.3
77.5%	107	0.636	0.38
90%	104.2	0.73	0.4

Where, X= mole fraction of formic acid in distillate
 Y= mole fraction of formic acid in residue
 K= Separation factor
 α = Relative volatility

Table 4. VLE data of Formic acid-water at 50grams of CaCl₂

Composition	Temp	y	x
20%	101.3	0.13	0.089
30%	102	0.22	0.13
40%	102.8	0.378	0.195
50%	103.4	0.49	0.26
60%	104.2	0.58	0.31
77.5%	105.5	0.67	0.39
90%	106	0.84	0.48

Where, X= mole fraction of formic acid in distillate
 Y= mole fraction of formic acid in residue
 K= Separation factor
 α = Relative volatility

➤ **x-y diagram of Formic acid water and $CaCl_2$ at different composition of formic acid**

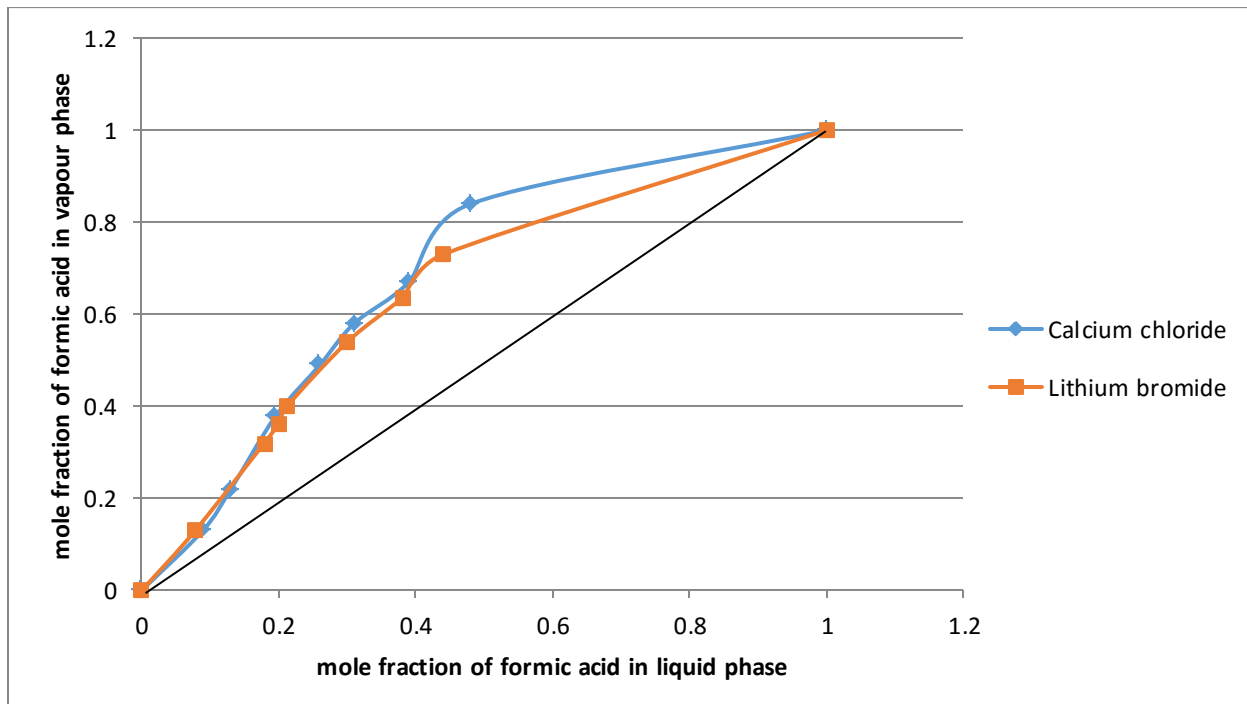


Chart 1. Comparison of x-y Diagrams of formic acid and water for both salts Li-Br and $CaCl_2$

6. CONCLUSION

After performing above experiments of formic acid-water using Li-Br, we are able to eliminate the azeotrope of by using both salts by extractive distillation, and 50grams of Li-Br is optimum concentration of salt at azeotropic composition. If we increase the concentration of Li-Br above optimum quantity than the separation of formic acid is decrease.

By performing experiment at different composition of formic acid-water and fixed quantity of Li-Br and $CaCl_2$ separation is somewhat higher in calcium chloride.

7. REFERANCES

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