

Effect of Li-Br salt on azeotropic mixture of formic acid-water by extractive distillation

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ABSTRACT

Separation and purification are an integral part and a major cost factor in the chemical industry. Distillation is a very commonly used for solvent separation and purification process. It is neither cost effective nor process efficient when dealing with close-boiling and azeotropic solvent mixtures without modifying the relative volatility of the solvent components with an extraneous solvent or a non-volatile solute electrolyte or nonelectrolyte. The selection of a suitable modifier generally depends on the experimental determination of its effect on the Vapour Liquid Equilibrium (VLE) of the solvent mixture. Formic is most widely used preservative and antibacterial agent in livestock feed. Aqueous Formic acid is obtained during these processes and recovery of which is of great significance. We would then require towers with large number of stages which would be operated with high reflux ratio and required high energy costs and operating costs. In practice extraction with suitable solvent is carried out before pure recovery occurs during the rectification of azeotropic mixture. An alternative separation process is the addition of Lithium Bromide (Li Br) salt into Formic acid water solution. Lithium bromide is largely soluble in water. Addition of salt will increase the boiling point of salt-water solution, there by separating comparatively pure Formic acid as overhead product. Li Br-water solution remains as residue from which Li Br can be readily separated by evaporation and reused. Experiments are carried out in laboratory with different concentrations of Formic acid-water, in Othmer still which is vapor-liquid equilibrium apparatus. An Extractive distillation column will be designed based on experimental results. Cost analysis of this new separation technique will be carried out. The experimental data will be correlated to any model to calculate activity co efficient

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

1. INTRODUCTION

Separation and purification are an integral part and a major cost factor in the Chemical industry. Distillation, a very commonly used solvent separation and purification process is neither cost effective nor process efficient when dealing with close boiling and azeotropic solvent mixtures. The conventional method for separating these types of mixtures is to shift the azeotropic composition by altering column pressure or by using extractive distillation by addition of solvent to break the azeotrope. Separation by altering the column pressure is possible only if the pressure has a considerable effect on azeotropic composition. Moreover the extra separation step is needed to recover the solvent or to adjust the pressure which adds extra cost to the separation. Instead of adding a solvent a nonvolatile salt could be used as a separating agent to alter the VLE of a given mixture. It is envisioned that the ions of the added salt form association complexes more with the molecules of one of the components to be separated than with the other components. This association complex phenomenon may result in altering the vapour and partial pressures, solubility, thermal conductivity, density, surface tension etc. These changes may result in altering the VLE of the system, thus altering the ease of separation and shifting or eliminating the azeotropic point of a given mixture.

2. PROJECT OBJECTIVE

The objective is to study the effect of addition of Li Br on separation of Formic acid – water mixture and to find out the possibility of the use of concentrated solution of Li Br as a solvent for separating the formic acid from Formic acid-water mixture by extractive distillation process.

3. 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

4. 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.

5. OTHER SEPARATION TECHNIQUES:

Though Distillation is the most widely used separation technique, energy consumption is very high. Replacing distillation partially or completely by other separation technique may result in considerable savings in energy. The Techniques are listed as follows:

1. Super critical extraction
2. Reactive distillation
3. Membrane separation
4. Molecular sieve adsorption
5. Freeze crystallization
6. Addition of salt
7. Pressure swing adsorption
8. Pervaporation

6. EXPERIMENTAL STUDIES

6.1 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

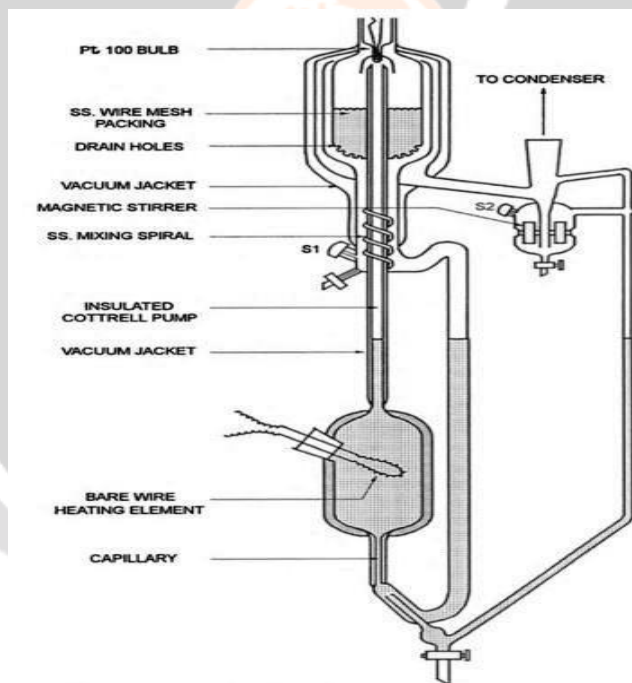


Figure 2. Raal's apparatus

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.

5.1 RESULT TABLE AND DISCUSSION

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

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

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	K	α
20%	104.2	0.13	0.078	1.66	1.76
30%	104.8	0.32	0.1787	1.79	2.16
40%	105	0.36	0.19	1.89	2.39
50%	105.9	0.4	0.212	1.88	2.47
60%	106.8	0.54	0.3	1.8	2.73
77.5%	107	0.636	0.38	1.6	2.85
90%	104.2	0.73	0.4	1.82	4.05

Where, X= mole fraction of formic acid in distillate

Y= mole fraction of formic acid in residue

K= Separation factor

α = Relative volatility

Design data of distillation column for 77.5% formic acid and water and 50grams of Li-Br

Table 4. Design data require for Distillation column

Mole fraction of formic acid in Feed(x_F)	0.57
Mole fraction of formic acid in Distillate(x_D)	0.99
Mole fraction of formic acid in Residue(x_W)	0.01
q-line	1.227
Minimum reflux ratio R_m	0.83
Actual reflux ratio ($R= 2R_m$)	1.6
No. of stages require for separation	12
Tower diameter at top of column	1.32m
Tower diameter at bottom of the column	1.45m

➤ **x-y diagram of Formic acid water Li-br at different composition of formic acid**

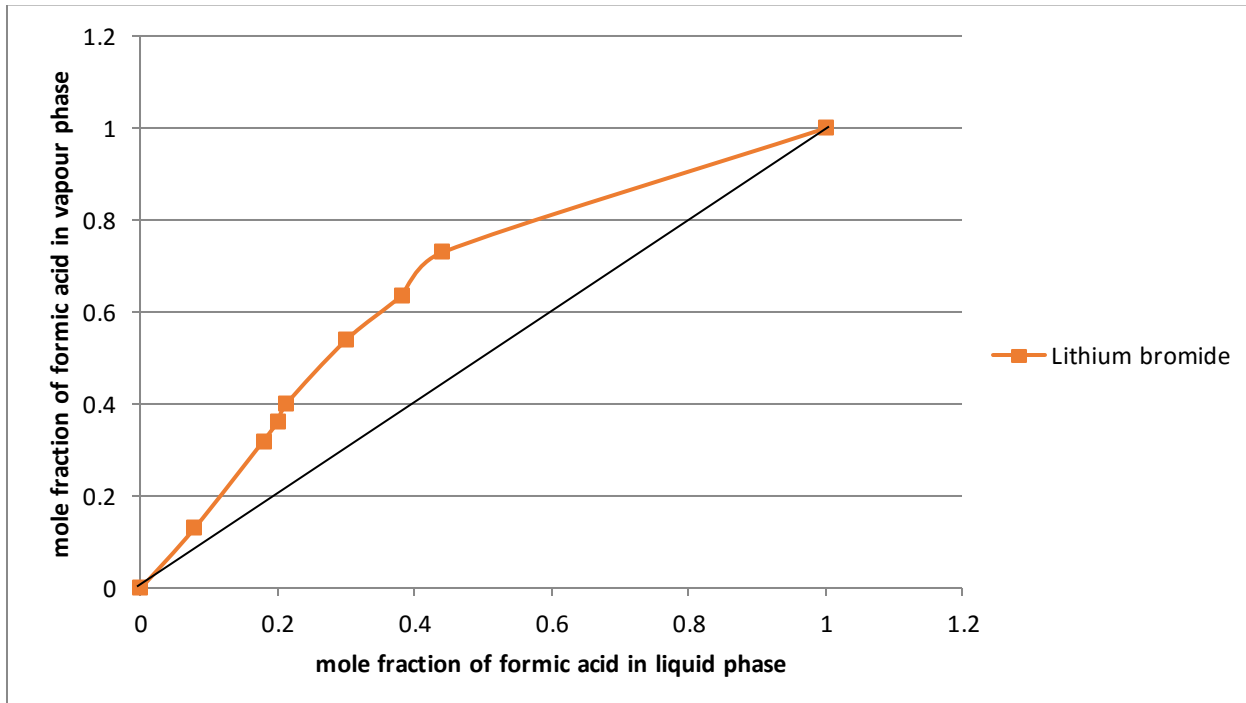


Chart 1. Comparison of x-y Diagrams of formic acid –water and Li-Br

6. CONCLUSION

From the above experiment we may conclude that separation of pure Formic acid is possible using concentrated Li Br solution, as a solvent in extractive distillation process. From the experimental data and results, no. of theoretical stages required for desired separation is coming 12 and reflux ratio is $1.86 \cong 2$ which is very low. A distillation column can be design based on this system and activity coefficients can be calculated.

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.

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