

Extractive Distillation of Acetic Acid from its Dilute Solution using Lithium Bromide

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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 non-electrolyte. 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. Acetic acid is most widely used as aliphatic carbonic acid. It is frequently used as a solvent like in manufacture of cellulose acetate or in manufacture of many pharmaceutical products. Aqueous acetic acid is obtained during these processes and recovery of which is of great significance. Separation of pure water from dilute solution of Acetic acid –water mixture in the concentration range of 1 % to 30 % Acetic acid by simple rectification is almost impossible as relative volatility of the mixture in this range approaches unity. 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(LiBr) salt into acetic-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 acetic acid as overhead product. LiBr–water solution remains as residue from which LiBr can be readily separated by evaporation and reused. Experiments are carried out in laboratory with different concentrations of Acetic 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 coefficients.

Words: Vapor liquid Equilibrium, Lithium bromide, Extractive distillation, recovery of acetic acid, Othmer still

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 type 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 non volatile 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.

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) Some times a small amount of salt will facilitate required separation.

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:

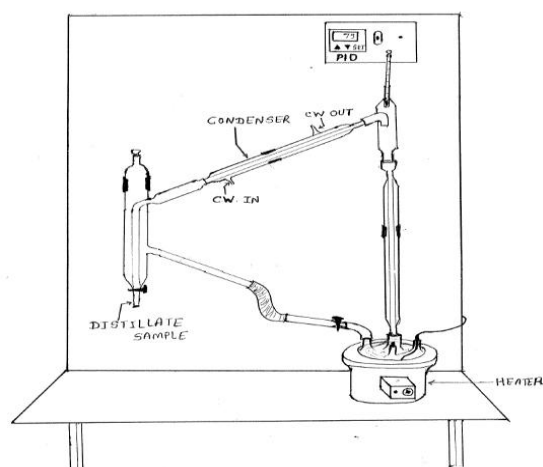
1. Super critical extraction
2. Reactive distillation
3. Membrane separation
4. Molecular sieve adsorption
5. Freeze crystallization
6. Addition of salt
7. Pressure swing adsorption
8. Pervaporation

Project Objective:

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

Procedure:

These experiments are performed using Othmer Still It is vapour- liquid equilibrium apparatus. Experimental set-up is shown in the following figure.



Still is mounted over a heater. The condenser is mounted over the distillation unit. The condensate from the condenser is collected in the receiver. Acetic acid – water mixture along with measured quantity of LiBr is added to the still. Heating is given through the electric heater. Because of the addition of Li-Br in water, the boiling point of Li-Br-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. When the temperature stabilizes, indicating thermal equilibrium, a sample of distillate collected is withdrawn. The pressure in the still is atmospheric pressure. PID controller is installed to control and measure the temperature. In the residue, LiBr-water mixture is collected which can be recirculated. 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.

LiBr is chosen because,

- ▶ It do not react with acetic acid.
- ▶ It is very hygroscopic in nature.
- ▶ Its boiling point elevation is very high.

Properties of LiBr :

1. Molarmass : 86.84g/mol
2. Appearance : White solid
3. Density : 3.464 g/m³
4. M.P. : 552 °C
5. B.P. : 1265 °C
6. Solubility in water : 145g /100ml at 4 °C,
166.7g/100ml at 20 °C,
254g /100ml at 90 °C

Soluble in methanol, ethanol, ether and slightly in pyridine, hygroscopic in nature.

Uses:

Its extreme hygroscopic character makes LiBr useful as a desiccant in certain air conditioning systems. Otherwise the salt is useful as a reagent in organic synthesis. For example it reversibly forms adducts with some pharmaceuticals. Previously it was used as sedative in the treatment of bipolar disorder.

Hazards:

Lithium salts are psychoactive and somewhat corrosive. When lithium bromide is dissolved into water, the reaction is very exothermic.

According to Perry's hand book:

Sr. No.	Conc. of LiBr %	Absolute Pressure, in mm Hg	Boiling point of LiBr solution °C	Boiling point of pure water °C	Boiling point elevation °C
1	59.5	76.2	88.88	46.11	42.77
2	59.5	7	40.00	5.56	34.44
3	50	38.1	60	33	27

From the above data it can be concluded that increase in operating pressure, increases boiling point elevation of LiBr-water solution .

Scope of Thesis Work :

Acetic acid is the most widely used aliphatic carbonic acid. Apart from its use as a reaction partner, e.g. during the production of acetic-acid esters, it is frequently also employed as a solvent, for instance, during the production of cellulose acetate or during the manufacture of pharmaceutical products. Aqueous acetic acid is obtained as a rule during the foregoing processes. In most cases its recovery is of great economic significance.

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. You 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 LiBr is added.This mixture is heated in Othmer still. Heating is given through the electric heater. Because of the addition of Li-Br, the boiling point elevation takes place, i.e. the boiling point of Li-Br-water mixture will increase. The lower boiling point component Acetic acid will be vaporized first,leaving LiBr-water solution in the residue.

Experimental procedure and data:

300 ml of water+300 g of LiBr solution was prepared.(conc. of LiBr =50%w/v)In this solution 72 ml of glacial acetic acid (conc. of A.A.=20% approx) is added and the feed mixture is added to the flask of Othmer still. Heating the feed mixture causes acetic acid to vaporize as an over head product leaving LiBr-water solution as residue. Volume of Distillate collected is measured and is titrated with 0.1N NaOH solution(previously standardised with 0.1 N Oxalic acid solution)Similarly volume of residue is measured and is titrated with 0.1N NaOH solution.Mole fraction of Acetic acid in distillate and residue is calculated.

Experimental results:

VLE data for Acetic acid-water – LiBr system*

Sr.No.	Temp. °C	y	x
1	107	0.6859	0.38153
2	105	0.5957	0.3225
3	104	0.5674	0.2828
4	101	0.116	0.033
5	100	0.09843	0.01806
6	100	0.06205	0.0069
7	100	0.033	0.000542

*Here y and x are mole fractions of more volatile component (i.e.acetic acid) in distillate and residue respectively.

Determination of No.of theoretical stages:

x_F = mole fraction of more volatile component in feed mixture

x_W = mole fraction of more volatile component in residue

x_D = mole fraction of more volatile component in distillate

$$x_F = \frac{20/60}{(20/60) + (80/18)} = 0.069$$

$$x_W = 0.01$$

$$x_D = \frac{(70/60)}{(70/60) + (30/18)} = 0.4117$$

$$q = \frac{H_G - H_F}{H_G - H_L} = \frac{(H_G - H_L) + (H_L - H_F)}{H_G - H_L}$$

$$q = \frac{\lambda + C_L(t_b - t_f)}{\lambda}$$

$$t_b = 101^\circ\text{C}$$

$$t_f = 25^\circ\text{C}$$

$$\lambda = \lambda_{AA}x_F + (1 - x_F)\lambda_W$$

$$\lambda_W = 40572 \text{ kJ/kmol} \quad (\text{from steam table})$$

$$\lambda_{AA} = 25116 \text{ kJ/kmol} \quad (\text{from Perry's Chemical Engineers Hand-book, 4th edition})$$

$$\lambda = 25116 \times 0.069 + 40572 \times 0.931 = 39,505 \text{ kJ/kmol}$$

$$C_L = C_{LAA} \times x_F + (1 - x_F) \times C_{LW} = 0.069 \times 128 + 0.931 \times 75.348$$

$$= 78.98 \text{ kJ/kmol}^\circ\text{C}$$

(C_{LAA} and C_{LW} are determined at 63°C)

$$q = \frac{39505 + 78.98(101 - 25)}{39505} = 1.1519$$

$$y = \frac{q}{q-1} \times x - \frac{x_F}{q-1}$$

$$= \frac{1.1519}{0.1519} \times x - \frac{0.069}{0.1519}$$

From which at $y=0.4$, $x=0.116$

At $x_D = 0.4117$

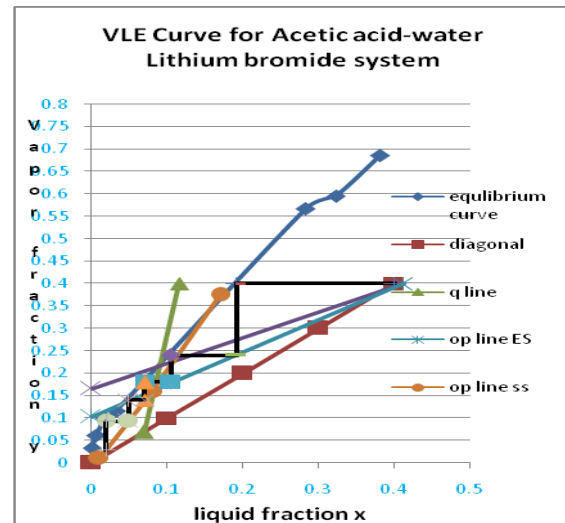
$$\frac{x_D}{R_m + 1} = 0.165$$

$$R_m = 1.495$$

Taking $R = 2 \times R_m$,

$$R = 2 \times 1.495 = 2.99 \cong 3$$

$$\frac{x_D}{R + 1} = \frac{0.4117}{3 + 1} = 0.103$$



ES=enriching section

SS=stripping section

Conclusion:

From the above experiment we may conclude that separation of pure acetic acid from its dilute solution in water is possible using concentrated LiBr solution, as a solvent in extractive distillation process.

From the experimental data and results, no. of theoretical stages required for desired separation are coming 5.5 and reflux ratio is $2.99 \cong 3$ which is very low.

A distillation column can be design based on this system and activity coefficients can be calculated.

Future scope :

Considering above calculations, number of theoretical stages are found ,which is equal to five and a half and reflux ratio is coming approx.equal to 3 which is very less, based on this it seems that this technology may prove more economical than conventional technology like liquid-liquid extraction

and azeotropic distillation. Similarly LiBr can also be used to break the azeotropic mixture like ethanol-water, IPA-water by addition of small amount of LiBr, since in these cases water is less volatile component and hence small amount of salt will be sufficient to break azeotrope.

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