

Effect Of Addition Of LiBr Salt In Iso-Propanol - Water Binary Azeotropic Mixture

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Abstract

Isopropanol is a very useful solvent for many industries and it requires in pure form for specific applications. It makes an azeotrope with water at 80.3 °C having composition of 87.4 % by weight. It is seen that conventionally methods used are not much effective or large energy consuming. Another alternative is to add salt which is helpful in changing the relative volatility of the mixture and separation gets is much more easier. In this paper the effect of addition of Lithium Bromide salt in isopropanol -water binary azeotropic mixture using extractive distillation is discussed. As LiBr is a high boiling point salt, it will not appear in the distillate and moreover LiBr is hygroscopic and has a characteristic to give higher boiling point elevation with water which is main cause of its use in this application. Addition of salt (40% of water) eliminates azeotrope formation and purity of 99.74% (by wt.) is achieved.

Key words – Extractive distillation, VLE apparatus , LiBr salt, Karl-fischer method

1. Introduction

Distillation process is a method for separating the various components of a liquid solution depending upon the distribution of these components between a vapour phase and a liquid phase based on their boiling points. In the world of Chemical Engineering, solvent recovery is important to reduce the number of hazardous waste and pollutions. In the industries, IPA (Isopropyl Alcohol) is known as rubbing alcohol used as a cleaner and solvent. It is miscible with water, thus forming azeotrope with water at certain temperature.

An azeotrope cannot be separated by ordinary distillation since no enrichment of the vapour phase occurs at this point. Therefore, in most cases, azeotropic mixtures require special methods to facilitate their separation such as a mass separating agent like a membrane-material for pervaporation or an entrainer /solvent for azeotropic and extractive distillation. Extractive and heteroazeotropic distillation are the most common methods to break this azeotrope behaviour.

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 without modifying the relative volatility of the solvent components with an extraneous solvent or a non-volatile solute electrolyte or non-electrolyte. 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.

- Lower energy consumption since salts are non volatile and do not evaporate or condense in the distillation process
- Purity of the overhead product from the extracting agent is high since the salts are non volatile
- Some time a small amount of salt will facilitate required separation.

2. Azeotropic condition and basic properties

At atmospheric condition, a binary mixture of 2-propanol (isopropyl alcohol, IPA)–water forms a homogeneous minimum-boiling azeotrope at 87.4–87.7 mass% and 80.3–80.4 °C.

Table 1. Basic properties of system component

Component	Density(g/cc)	M.W	B.P (°C.)
IPA	0.777	60.10	82.3
Water	1	18	100
LiBr	3.464	86.84	1265

3. Reason for choosing LiBr as a salt

LiBr salt is hygroscopic and has a good characteristic to give higher boiling point elevation with water and it is used in vapour absorption cycle because of this characteristic. 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 chance that azeotrope will not occur or salt may break the azeotrope.

4. Extractive distillation

Extractive distillation is defined as distillation in the presence of a miscible, high boiling, relatively non-volatile component, the solvent, that forms no azeotrope with the other components in the mixture.

The 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.

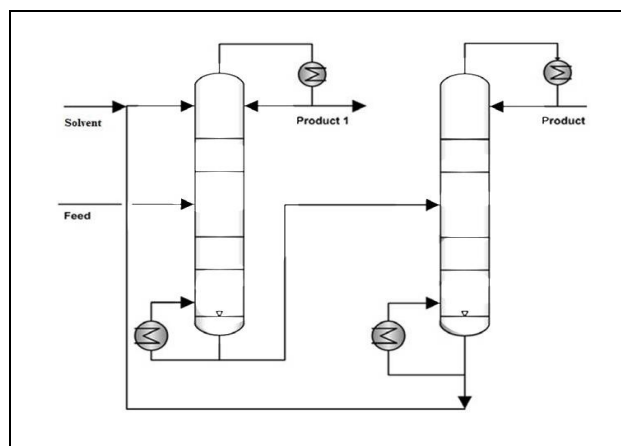


Figure 1. Flow diagram for Extractive Distillation

The method of extractive distillation uses a separation solvent, which is generally nonvolatile, has a high boiling point and is miscible with the mixture, but doesn't form an azeotropic mixture. The solvent interacts differently with the components of the mixture thereby causing their relative volatilities to change. This enables the new three-part mixture to be separated by normal distillation. The original component with the greatest volatility separates out as the top product. The bottom product consists of a mixture of the solvent and the other component, which can again be separated easily because the solvent doesn't form an azeotrope with it. The bottom product can be separated by any of the methods available.

It is important to select a suitable separation solvent for this type of distillation. The solvent must alter the relative volatility by a

wide enough margin for a successful result. The quantity, cost and availability of the solvent should be considered. The solvent should be easily separable from the bottom product, and should not react chemically with the components or the mixture, or cause corrosion in the equipment.

The newest type of extractive distillation uses ionic liquids as an entrainer. The main advantage of ionic liquids is the absence of its own vapor pressure, so it is easy to separate them from vaporizable liquids. Because of their saline character, they have a big influence on the phase equilibrium. It is much easier to shift azeotropic points or create miscibility gaps.

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

VLE apparatus at IIT, Gandhinagar has been used to carry out the experiments. The setup has round bottom flask in which feed is to be inserted. The round bottom flask is surrounded by heater to heat the feed. There are four annular section/pipes in the centre portion of the setup. The most inside one pipe carry the vapour which is caused by heating the feed, the next one carry the condensed vapour part of the first which will be re-circulated to the feed for proper temperature distribution of liquid and to increase the purity of distillate. In the third annulus section the crystals of silica gel are provided to absorb the moisture present inside the column and thus increasing distillate purity. The fourth annular part is provided to have insulation effect to reduce the heat loss to atmosphere. The air inside the annulus acts as insulator and helps in preventing heat loss.

The condenser is provided at the top of the column. Small container is kept at the bottom of the condenser to collect the distillate. One re-circulation pipe is also provided with the small container for reflux and proper temperature distribution. At the bottom, valve is provided to collect liquid from bottom (residue). PID controller is provided to monitor and measure the temperature of both vapour and liquid.

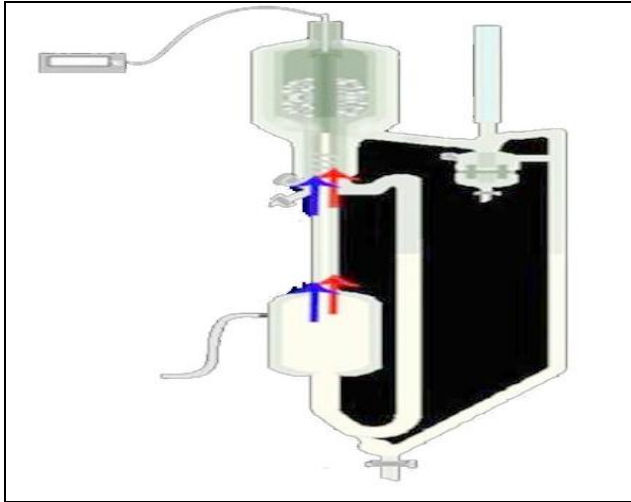


Figure 2. VLE Apparatus

Procedure:

- Step1: Measure the feed volume and component composition. Add LiBr of known grams to solution and dissolve it.
 Step 2 : Insert the feed into round bottom flask and start heating. Meanwhile start water flow in condenser.
 Step 3 : After some time vapour will start condensing in the distillate collector. Let it be filled till re-circulation starts from the container.
 Step4: Measure liquid and vapour temperature continuously and allow both temperature to reach the same value.
 Step 5 : When steady state is achieved and value of both temperature remain same for a long time take the sample from distillate and bottom.
 Step 6 : Measure its composition and repeat the step 6 for different compositions of IPA.
 Step 7 : Plot T-x-y graph and x-y graph and Calculate remaining quantities.

5.2. Sample analysis

The sample analysis is carried out by measuring the density of distillate and the % IPA is found out from "Perry's handbook" (IPA-Water density data). The results are verified by performing Karl-Fischer test (measuring quantity of water in distillate).

5.3. Results and discussion

Experiments are performed taking azeotropic composition and different quantity of LiBr salt to find out how much quantity of LiBr is highly effective. Results are shown below.

Table 2. Purity of IPA for different grams of LiBr for azeotropic composition

LiBr (g)	% Purity of IPA in distillate (by wt.)
5	91.72
10	93.65
15	94.91
20	96.68
25	97.40

We fix the satisfactory amount of LiBr needed for separation as 20 g (40% of water present). Now, we have generated the x-y data for the different composition of IPA taking 20g of LiBr fix for all. Results are shown below.

Table 3. x-y data for 20g LiBr in solution

x	Y
0	0
0.02341	0.041
0.08148	0.3248
0.16765	0.42438
0.23994	0.49798
0.462	0.6766
0.6278	0.8976
0.77165	0.99138
1	1

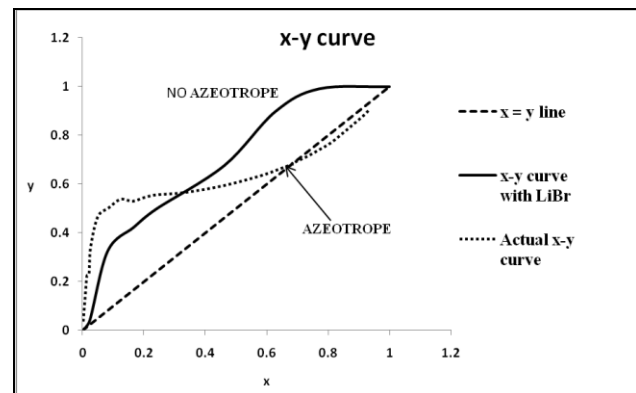


Figure 3. x-y curve comparison

It is found that use of LiBr eliminates the azeotrope formation and relative volatility changes from 1 to 2.4363 in that particular range of azeotropic composition. The separation is achieved from 87.4 % to 99.74 % (by wt.).

Proposed Flowsheet:

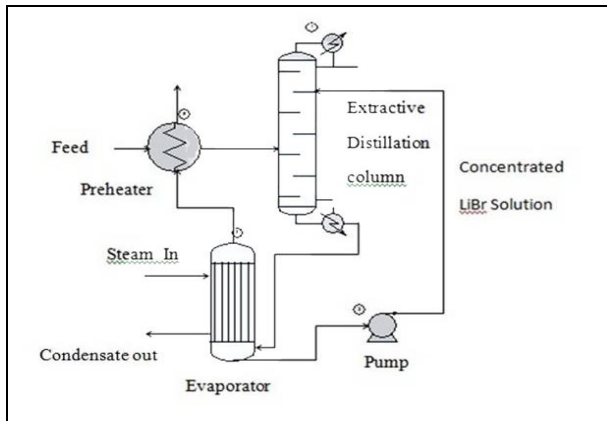


Figure 4. Flow diagram for entire operation

6. Conclusion

It can be concluded that extractive distillation of IPA-water binary azeotropic mixture by the use of LiBr salt is much more cost effective than conventional azeotropic distillation. It removes the use of auxiliary column (2nd column) which will save the fixed cost of that column as well as its operating cost and its reboiler duty. Use of evaporator will concentrate the dilute solution of LiBr-water and that can be recycled and reused in the column. The change in relative volatility is significant and will reduce the overall no. of stages required for the separation in the column. So it can be concluded that this technology is more efficient and cost effective compared to conventional azeotropic distillation.

7. Future scope

This separation method can also be used with other systems also in which water is one of the components and makes minimum or maximum boiling point azeotrope.

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