

SEPARATION OF PROPIONIC ACID – WATER AZEOTROPE USING CaCl_2 SALT

Chauhan Kajol¹, Bhatt Rajul P.²

¹ P. G. Student, Chemical Engineering Dept., L. D. College of Engineering, Gujarat, India

² Asst. Professor, Chemical Engineering Dept., L. D. College of Engineering, Gujarat, India

ABSTRACT

The study of effect 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. 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. The measurement of vapour liquid equilibrium of Propionic acid + water + calcium chloride at different concentrations of salt below saturation level is done. The addition of calcium chloride to this solvent mixture increases the water concentration in liquid phase at equilibrium. The objective is to study the effect of addition of CaCl_2 on separation of propionic acid – water mixture and to find out the possibility of the use of concentrated solution of CaCl_2 as a solvent for separating dilute solution of acetic acid in water by extractive distillation process.

Keyword:- Azeotropic Separation, Propionic Acid Water, CaCl_2 Salt

1. INTRODUCTION^[1,2]

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 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:

- (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

1.1 Solute-addition Distillation Methods^[5]:

A Physiochemical change of the VLE behaviour of an azeotropic mixture by the addition of an extraneous liquid component offers a number of possibilities. We name the mixture to be separated as the original mixture, and the added component that facilitates the separation the Solute. For the purpose of ease of visualization, we limit our considerations to binary homo-azeotropic original mixtures and one component entrainers. The same separation techniques apply to multi-component mixtures where the key components form characteristic mixtures falling into the, categories discussed, and the entrainer may be a mixture of components. We distinguish between three different conventional entrainer-addition based distillation methods depending on the properties and role of the entrainer and the organization (scheme) of the process:

1. Homogeneous azeotropic distillation (ordinary distillation of homoazeotropic mixtures):

The entrainer is completely miscible with the components of the original mixture. It may form homoazeotropes with the original mixture components. The distillation is carried out in a conventional single-feed column.

2. Heteroazeotropic distillation (decanter-distillation hybrids that involve heteroazeotropes):

The entrainer forms a heteroazeotrope with at least one of the original mixture components. The distillation is carried out in a combined column and decanter system.

3. Extractive distillation:

The solute has a boiling-point that is substantially higher than the original mixture components and is selective to one of the components. The distillation is carried out in a two-feed column where the solute is introduced above the original mixture feed point. The main part of the solute is removed as bottom product.

1.2 Other Separation Techniques^[3,5]

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 techniques
4. Molecular sieve adsorption
5. Freeze crystallization
6. Addition of non-volatile solute electrolyte or non-electrolyte
7. Pressure swing adsorption

1.2 Reason for choosing CaCl_2 as a salt^[6]

- Calcium chloride is cheap and easily available in market approximately 25rs/kg

- Calcium chloride is hygroscopic and has a good characteristic to give higher boiling point elevation.
- And during literature survey I have observed results of calcium chloride for separation of other azeotropic mixture are very good .

2. EXPERIMENTAL WORK

At azeotropic composition experiments are performed using different concentration of lithium bromide and it was observed that azeotrope is completely eliminated at even lower concentration of both the salts.

2.1 Experimental set up and Procedure:

Modified VLE still consists of a flat bottom two neck flask of 250 ml capacity. Side neck is small, from which sample is charged and neck in the centre of flask is comparatively larger in diameter and long. Centre neck consists of a small tube concentric with the neck. Centre neck is connected horizontally with a receiving chamber, top of which is connected with condenser and bottom is connected via a small capillary tube to bottom of flat bottom flask. This capillary tube is fitted with three way cock. Liquid phase temperature is measured by a thermometer immersed in thermo well at the side neck. Vapor phase temperature is measured by a thermometer immersed in thermo well in the centre neck. Flat bottom flask is equipped with a magnetic stirrer and is kept over heating mantle. Chilled water is circulated through tubes of condenser. Flat bottom flask is covered with a wide stripe which is heated by separate electric source which acts as heating medium and insulation both.

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Feed is charged through small neck to flat bottom flask and the neck is closed using thermo well. Charge is heated and stirred continuously using magnetic stirrer cum heater. Vapour liquid mixture will rise and it will be continuously heated by heater as well heating stripe. Vapour will rise through the small concentric tube and send to the condenser where it condenses in to the receiver. Equilibrium is allowed to reach i.e. when the temperature remains constant for 25-30 minutes, equilibrium temperature is noted.

Condensate is collected in the receiver and re circulated back to the main flask. Recirculation was carried out three times and after that equilibrium temperature was noted down. Vapor phase sample is collected from receiver and liquid phase sample is collected from main flask for analysis with standard NaOH solution. Condenser is kept open to atmosphere to ensure atmospheric pressure. Because of the addition of Lithium Bromide in water, the boiling point of salt -water mixture will increase, i.e. boiling point elevation takes place and azeotrope is broken.

3. RESULTS

3.1 VLE data: Experimental data of addition of CaCl_2 in azeotropic mixture of P.A-Water.

Composition (% of acid)	Amount of salt(CaCl_2),	Temp($^{\circ}\text{C}$)	Mole fraction of PA in distillate	Mole fraction of PA in residue	Mole fraction of water in distillate	Mole fraction of water in residue
17.7%	10%	95.2	0.0664	0.0543	0.9339	0.9457
17.7%	20%	92.6	0.0744	0.042	0.9256	0.958

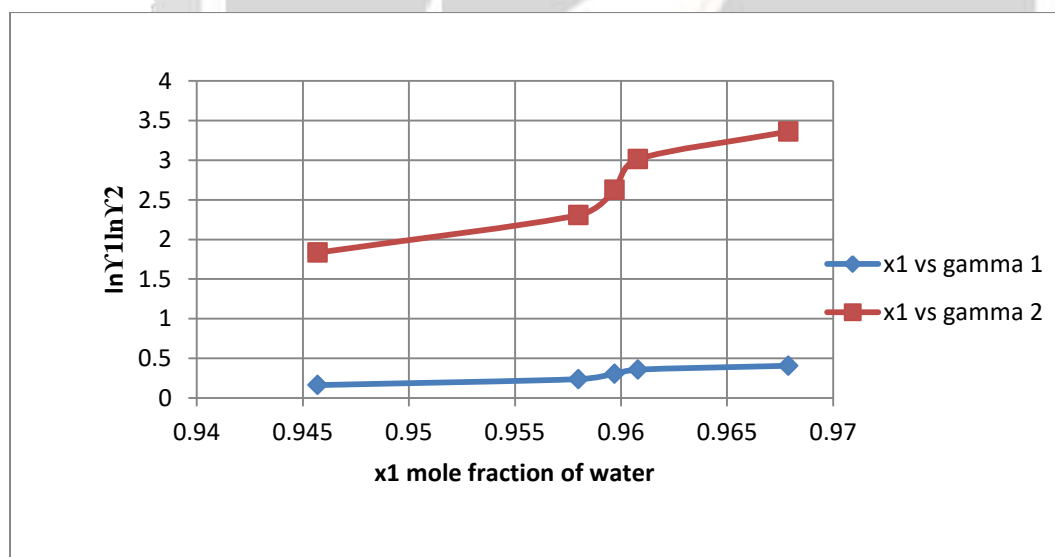
17.7%	30%	90.3	0.0894	0.0403	0.9106	0.9597
17.7%	40%	88.1	0.117	0.0392	0.883	0.9608
17.7%	50%	86.4	0.1258	0.0321	0.874	0.9679

3.2 Calculation for activity coefficient for propionic acid – water & CaCl₂ at different composition of CaCl₂

Sr.No	Temp (°C)	P1 for Water (mmHg)	P2 for P.A (mmHg)	Y1 for water	Y2 for P.A	lnY1	lnY2
1	95.2	638.263	148.593	1.175874	6.254369	0.162012	1.83328
2	92.6	579.428	133.967	1.267278	10.04938	0.236871	2.307511
3	90.3	531.251	121.814	1.357394	13.84041	0.305567	2.627592
4	88.1	488.314	111.473	1.430349	20.34903	0.357919	3.013033
5	86.4	457.193	103.371	1.501049	28.81313	0.406164	3.360831

3.3 Graphs

lnY1, lnY2 vs x1 for different composition of CaCl₂



4. CONCLUSION

Experiments are performed at azeotropic composition using different concentration of CaCl₂ and it was observed that azeotrope is completely eliminated at even lower concentration of salt.

It was observed that as concentration of salt increases, concentration of propionic acid in vapour phase increases.

Experiments were performed using different concentration of salt and it was found that at 20% salt concentration, there is a sharp increase in concentration of propionic acid in vapor phase, after that the increase in concentration of propionic acid is comparatively less.

It can be concluded that CaCl_2 can be used as salt to break the azeotrope of acid –water and the minimum salt concentration for breaking azeotrope is 10 % salt solution which is cheaper than the solvents used in industry for extractive distillation, because salt can be recovered and reused also.

5. REFERENCES

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