SEPARATION OF PROPIONIC ACID – WATER AZEOTROPE USING LiBr SALT

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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 + Lithium Bromide at different concentrations of salt below saturation level is done. The addition of Lithium bromide to this solvent mixture increases the water concentration in liquid phase at equilibrium. 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 dilute solution of acetic acid in water by extractive distillation process.

Keyword:- *Azeotropic Separation, Propionic Acid Water, LiBr Salt*

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1. INTRODUCTION [3, 4]

The study of influence of salt on vapour liquid equilibrium of solvent mixture is of interest, because addition of salt on mixed solvent will enhance the relative volatility and break azeotrope of the mixture. 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 vapour phases are identical, these kinds of mixtures are known as the azeotropes.

Extractive distillation with salt 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.
Concentration of aqueous nitric acid using magnesium nitrate are some of the application of the salt effect on vapour-liquid equilibrium.

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.

In many branches of science, the phase equilibrium thermodynamics is of fundamental importance. In chemical engineering almost all the manufacturing processes involve mass and energy transfer between phases. Processes such as: gas–liquid absorption, adsorption, leaching, refrigeration and distillation, liquid–liquid extraction etc., are some of important are where mass transfer and heat transfer between phases are taken very effectively into account to get desired result.

The present work involves the measurement of vapour - liquid equilibrium of Propionic acid + water + salt.

The addition of salt to this mixture increases the propionic acid concentration in vapour phase at equilibrium. This indicates a preferential association of salt with less volatile component i.e. propionic acid in the propionic acid-water mixture. Most of the Salt effect studies were carried out at saturated level of salt.

The separation of azeotropic systems (which have low relative volatility) is either difficult or un economical, by using convention al methods like fractional distillation. To overcome such difficulties in industries a third component is added in order to alter the system properties. If the third component is liquid then in that case the molecules of the liquid component forms an association or complex with the molecule of the less volatile component to the feed as compared to that of the more there by increasing the relative volatility of the more volatile component and thus the azeotrope can be eliminated. This process however requires an additional column to recover the separating agent from the product stream.

Due to this difficulty, the solid salts are considered better than the liquid separating agents as they produce a solvent– free extract and require no other separating column. The salt dissolved in a mixed solvent may affect the boiling point, the mutual solubility of the two liquid components, and the equilibrium vapour phase composition. Generally, the ions of the dissolved salt tend to attract the molecules of the more polar component by the electrostatic field of the ions and there by enriching the vapour composition of the less polar solvent, in which the salt is less soluble.

If the dissolved salt associates, preferentially, with the molecules of one component of the solvent compared with those of the other, then in that case one component is "salted out" in respect to the other. In such a case, the activities and the solubility relationship between the two volatile components of the liquid solution are altered relative to each other in a manner which results in a change of composition of the equilibrium vapour-phase, even if no salt is present in the vapour phase.

Various predictive and correlative models were proposed to calculate the vapour liquid equilibrium of the mixed solvent– salt systems. The experimental data are correlated using following models based on the local composition concept:

1. The electrolytic NRTL model of Mock et al. (1986)
2. The modified UNIQUAC model of Sander et al. (1986)
3. Modified Wilson and modified NRTL models of Tan (1985), Tan (1987)

The results of correlation were compared with those obtained through data prediction using the modified Wilson and the modified NRTL predictive models of Tan. The new set of ion-solvent and salt-solvent interaction parameters obtained from the data correlation with the extended UNIQUAC model of Sander et al.(1986) and salt– solvent inter action parameters obtained from the data correlation with the electrolyte NRTL.

There are many advantages of adding salts instead of liquids in an extractive distillation process:

1. Lower energy consumption sins alts 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 Production of Propionic Acid [5]

Propionic acid is mainly produced by the Hydrocarboxylation of ethylene using nickel carbonyl as the catalyst:

$$H_2C = CH_2 + H_2O + CO \rightarrow CH_3CH_2CO_2H$$

It is also produced by the aerobic oxidation of Propionaldehyde. In the presence of cobalt or manganese ions, this reaction proceeds rapidly at temperatures as mild as 40–50 °C:

$$CH_3CH_2CHO + 0.5\ O_2 \rightarrow CH_3CH_2COOH.$$
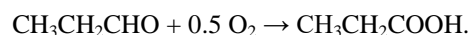
Large amounts of Propionic acid were once produced as a byproduct of acetic acid manufacture.

1.2 Reason for choosing Li-Br as a salt [6]

The various reasons for choosing Li-Br as salt are as follows:

- Li-Br salt is hygroscopic.
- It has a good characteristic to give higher boiling point elevation with water.
- Li-Br is having high boiling point too, so it will not vaporize during distillation and can be recovered easily from water by evaporation.
- Use of Li-Br may shift the azeotrope.

1.3 Effect of Salt on Vapor - Liquid Equilibrium [2]

The addition of a dissolved salt is generally known to further complicate the vapour liquid equilibrium relationships in a system of two volatile components, since the liquid phase then becomes a concentrated solution of an electrolyte whose degree of dissociation is a function of the relative proportions of the other two components. The salt may affect the activities of the volatile components either through form at ion an association complex or alternatively altering the structure of the binary solvent mixture.

Generally, the particles (molecules or ions or both) of dissolved salt end to attract the molecules of one component of the binary more strongly than those of the other, tending to form association complexes preferentially, but not necessarily solely, with the former. Usually, the added component is more likely to associate preferentially with the chemically similar binary system, thus affecting the volatilities of the two original components by differing amounts.

Electrostatic fields by preferential attraction of the salt ions would apply for the more polar component of the binary solvent. Since the added agent is likely to complex to a certain extent with both liquid components, the volatiles of both will most likely tend to be lowered, but by differing amounts depending on how selective the agent is, if the association preference of the salt is for the less volatile of the two liquid components, then its volatility will be reduced by volatile component, resulting in an increase in the value of relative volatility and enrichment of the equilibrium vapour in the more volatile component.

Also, the value of relative volatility will be decreased and the vapour composition will be enriched in the less volatile component if the association preference of the salt is for the more volatile component.

A general rule of thumb used often in Physical Chemistry states that like dissolves like. That is, the things tend to be most soluble in those solvents with which they are most similar to in terms of their molecular nature and structureif the salt more soluble in the less volatile component, the salt will increase the value of relative volatility.

Conversely, if the salt is more soluble in the more volatile component, relative volatility will be decreased. In the former case, the more volatile component is said to be salted out by the salt, and in the latter, to be salted-in.

Kablukov and Miller were amongst the first to study the ethanol – water system with various salts added. Gross and Halpern refined the liquid phase model relating salt effect on vapour composition to association in the liquid phase. Empirically, it has been concluded that the magnitude of salt effect on the activity coefficients of the volatile components, for a given salt in a given system, will depend on the concentration of salt present in solution, and on salt effect parameter (Further, Johnson and Furter) which is a function of such degree of difference of solubility of the salt in the two pure components, degree of dissociation of the alt in solution, ion charge, ion radius, and others.

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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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.

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.

Figure 1: Experimental Set - up for vapour - liquid equilibrium in laboratory

Figure 2: Experimental Set - up for vapour - liquid equilibrium in laboratory

2.2 Data from Literature

Table 1: VLE data of Propionic acid - Water from literature [1]

Sr.No.	T(°C)	Yw	Xw	ypa	Xpa
1	141.2	0	0	1	1
2	131.8	0.252	0.04	0.748	0.96
3	121.1	0.471	0.115	0.529	0.885
4	113.2	0.633	0.232	0367	0.786
5	107.3	0.733	0.382	0.267	0.618
6	101	0.882	0.758	0.118	0.242
7	99.9	0.925	0.892	0.075	0.11
8	99.8	0.95	0.95	0.05	0.05
9	99.9	0.974	0.979	0.026	0.21
10	100	1	1	0	0

Table 2: Antonie Constants

Components	A	B	C	Temp ℃
Propionic acid	7.99064	1929.306	236.430	25℃ - 141℃
Water	8.14019	1810.94	244.485	99℃ - 374℃

2.3 Graphs

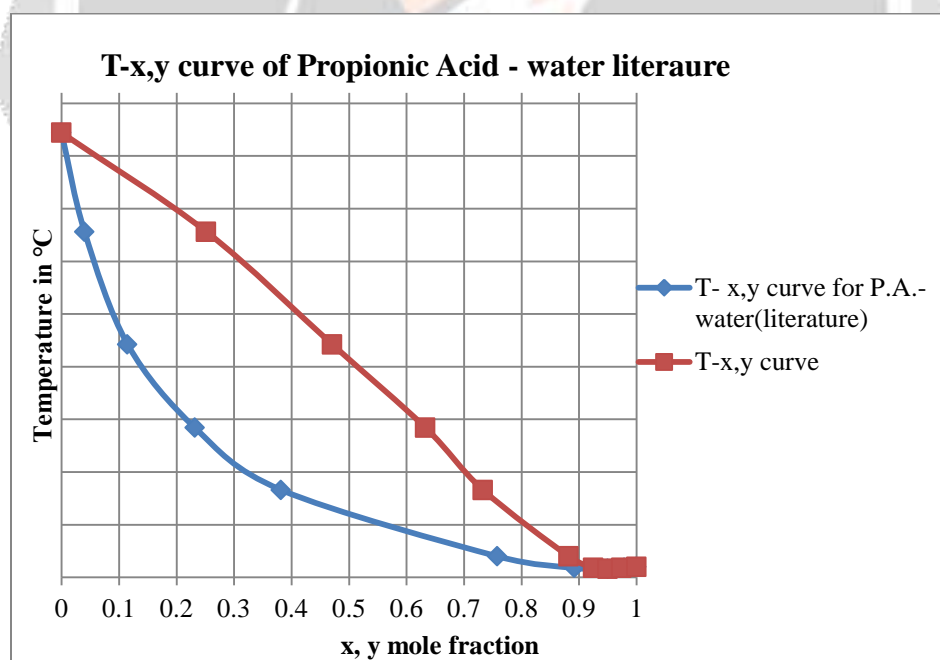**Figure 3:** T-x, y curve of Propionic Acid - water (literature)

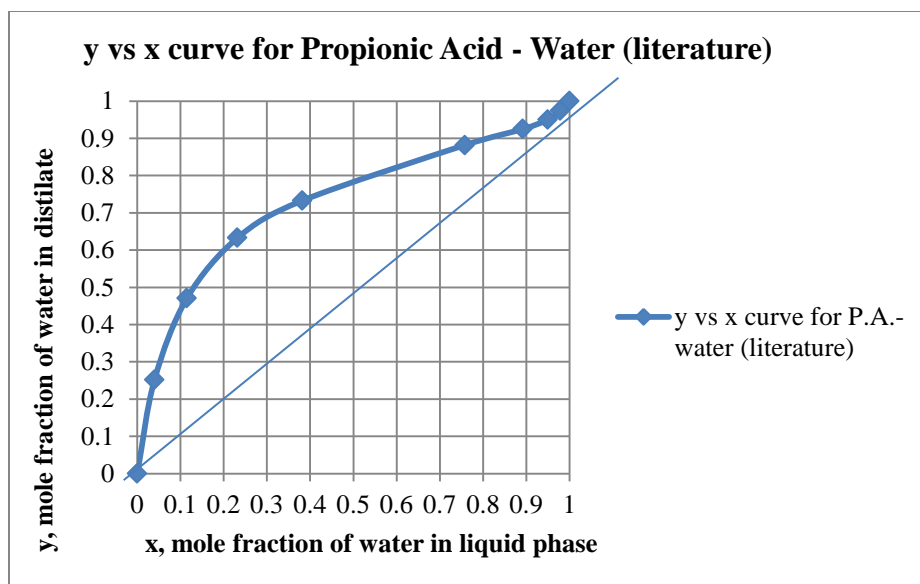**y vs x curve for Propionic Acid - Water (literature)**

Figure 4: y v/s x curve for Propionic Acid - Water (literature)

3. RESULTS

VLE data: Experimental data of addition of LiBr2 in azeotropic mixture of P.A-Water.

Composition (% of acid)	Amount of salt (Li-Br),gm.	Temp(°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
7.7%	10%	97.3°C	0.05047	0.0445	0.9495	0.9555
17.7%	20%	95.6°C	0.0678	0.0392	0.9322	0.9608
17.7%	30%	93.7°C	0.0682	0.0331	0.9318	0.9669
17.7%	40%	92.1°C	0.0691	0.0281	0.9308	0.9719
17.7%	50%	90.8°C	0.0735	0.0231	0.9265	0.9768

4. CONCLUSION

Experiments are performed at azeotropic composition using different concentration of Li-Br 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 Lithium Bromide can be used as salt to break the azeotrope of acid –water and the minimum salt concentration for breaking azeotrope is 20 % 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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