Separation of Azeotropic Solution of Ethyl Acetate-Ethanol by Cobalt Nitrate

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*Abstract—**Separation of azeotropic solution by simple distillation requires third column to remove the added entrainer, but it is not cost effective and energy effective process. Hence to overcome this difficulty, a salt effect on vapour liquid equilibrium (VLE) relationship is provided as a potential technique of extractive distillation for azeotropic system. In the present study, the comparative effect of zinc chloride and cobalt nitrate on ethyl acetate–ethanol system at atmospheric pressure of 760mmHg has been studied. Moreover, linear relationship between salt concentration and relative volatilities has been reported.***

Keywords— Vapour Liquid Equilibria; Salt Effect; Ethyl Acetate-Ethanol Azeotropic System.

I. INTRODUCTION

Concentrated ethanol of various grades is becoming an increasingly important as a fuel for vehicles and also used in adhesives, cosmetics, explosives, detergents, industrial coatings, ink, vinegar, windscreen washer fluid, heat transfer fluid and in certain process industries. Ethyl acetate is a solvent used in a wide range of applications, including printing inks, varnishes and car care chemicals and in the production of enamels, plastics and rubber and in the food industry in the production of synthetic flavoring and in the pharmaceutical industries as an extraction solvent in the production of pharmaceuticals[1]. A mixture of ethanol and ethyl acetate is produced during the separation of Fischer- Tropsch oxygenated products into different components. The azeotrope of ethanol and ethyl acetate is difficult to separate by distillation because the compounds boil within a narrow range and because of the existence of binary azeotrope of these compounds [2].In the azeotropic distillation, third liquid component is added to alter the relative volatilities. As we use solid nonvolatile salt it would not present in distilled product. Change in relative volatility by adding nonvolatile salt depends upon solubility of salt in liquid. Kablukov [3][4] [5] in 1981 reported the results of salt effect on vapour liquid equilibrium (VLE).He observed vapour pressure were proportional to salt concentration. Miller[6] in 1897 reported that the amount of salt effect would depend on difference in solubility of salt. Wright and Butler proved the same results for salt solvation [7][8]. Samaddar & Nandi compares the difference between distillation with salt and without salt [9].Furter[10]proposed a semi theoretical model to predict salt effect. J.Proszt & G.Kollar [11] also studied the effect of calcium chloride and lithium chloride on binary acetone-methanol system. Ohe, K Yokoyama and Nakamura were discussed the isobaric liquid equilibrium for six different salt [12]. The Motoyoshi, Hirata studied the Salt Effect on Vapor Liquid Equilibrium of Acetic Ester-Alcohol with Potassium Acetate and Zinc Chloride[13].

Feiyan and Yujun reported the four isobaric vapour liquid equilibrium for binary system[14].Rathand Naik studied ethyl acetate-ethanol system for lithium chloride, lithium bromide, lithium iodide salt [15]. Recently, Balakrishnan worked for the same system using inorganic salt of chloride and nitrate [16]. In the present study, the effects of cobalt nitrate and zinc chloride on ethyl acetate ethanol azeotropic system at 760mmHg were studied in detail.

II. EXPERIMENTAL

A. Details of VLE apparatus

The still used in experimental study is similar to the design of Jaques&Furter[17] with various modifications to the Othmer still as shown in Fig.1. Othmer Still apparatus contains a 500mL flat bottom glass flask; the other parts of othmer still are boiling pot, heater and condenser. The apparatus has two opening to introduced thermometer and salt. In this design the vapour line has arranged in such manner that condensate can again recirculate to the boiling liquid though condensate chamber and tree way cock.Flat plat heater is used to heat and to get equilibrium condition.

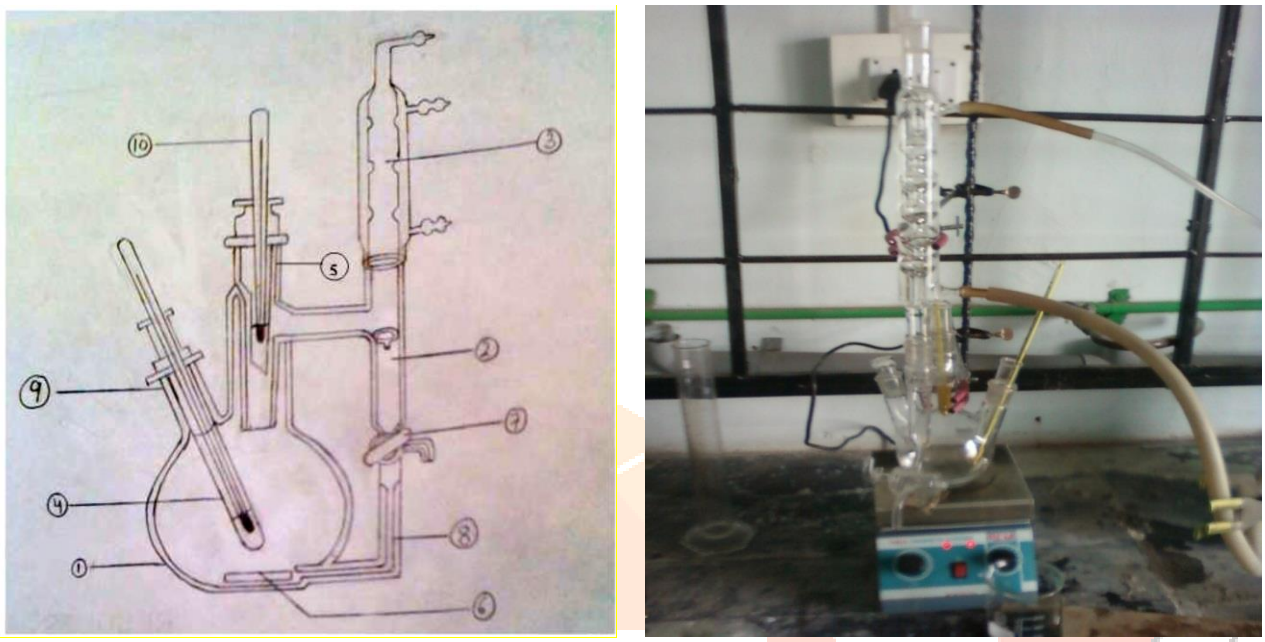

Fig. 1 Vapour liquid equilibrium (VLE) apparatus with some modification to Othmer Still. (1-500 mL flask(glass), 2-Condensate chamber, 3-Condenser, 4- Salt loading poart, 5-Second poart, 6-Magnetic stirrer, 7-Three way cock, 8-Capillary tube, 9-Thermometer for liquid phase, 10-Thermometer for vapour phase).

B. Azeotrope breaking using Cobalt Nitrate

The chemicals of analytical grade with 99 % purity were purchased from S D Finechem Ltd, Mumbai.In the present study, Zinc Chloride salt was used to verify the results reported in the literature and the Cobalt Nitrate salt was studied first time to break azeotrope of ethanol- ethyl acetate system. The different composition of ethyl acetate and ethanol was prepared with total volume of 200 mL. The salts was dried in an oven at 105 °C to remove moisture and was further added to the solution with different quantity .The heat was supplied using flat plate heating mantle. The temperature of liquid start rising slowly and finally boiling takes place after 20 min. The steady state of ethanol-ethyl acetate system was maintained after half an hour. During maintaining steady state vapour get condensed and return to boiling pot through three way cock. The samples from boiling pot and condensate were taken for analysis after maintaining equilibrium condition. Specific gravity bottle is used for the analysis. Constant temperature bath is used to maintain the temperature of sample at 25 °C. The concentration of both ethyl acetate and ethanol calculated according the mole fractions of individual component.

III. RESULT AND DISCUSSION:

The composition of solution was calculated from a calibration curve derived from measurements on standard solutions. The calibration curve is as shown in Fig. 2.The liquid composition was determined by material balance.

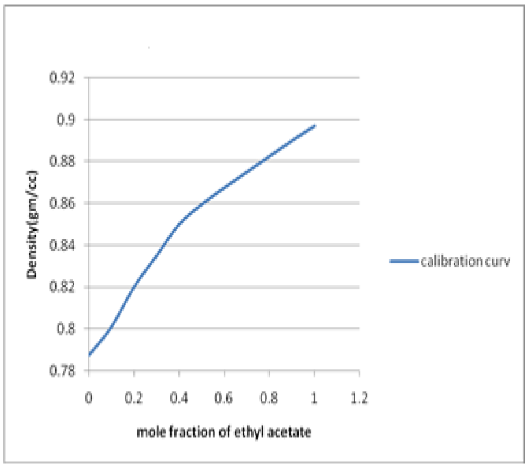

Fig. 2 Calibration curve to measure the density of binary mixture.

Fig. 3 shows minimum boiling azeotrope at 0.55 mole fraction of ethyl acetate. In this study experimental work is carried out for different concentration of zinc chloride (5% and 15%) and (9.5% cobalt nitrate)

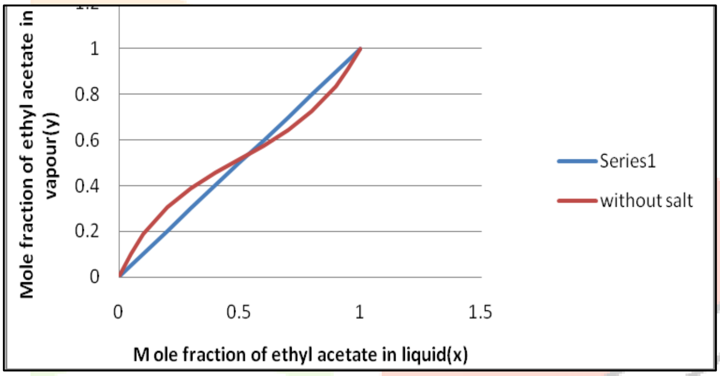

Fig. 3 VLE diagram for ethyl acetate-ethanol without salt

Selected salt for separation of azeotropic solution should have solubility in solvent .Cobalt Nitrate is dissolved in ethanol so it will change relative vitality. This is main cause of azeotropic point separation. After trying different percentage of salt from lower to higher it is reported that cobalt nitrate break azeotrop. Fig. 4 indicates that the salt cobalt nitrate has eliminated the azeotropic point of the system.

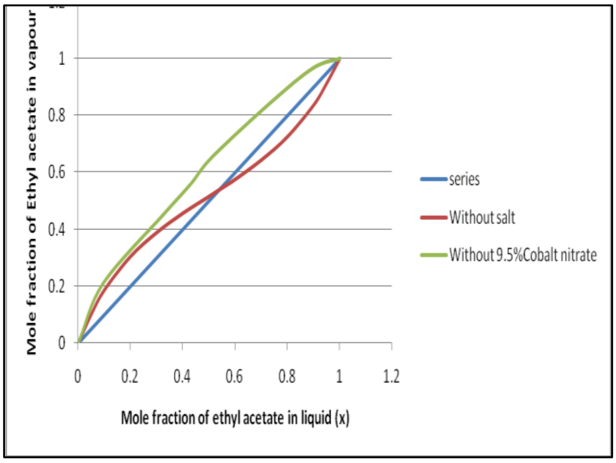

Fig. 4VLE diagram for ethyl acetate-ethanol with 9.5 % $Co(NO_3)_2$ salt.

After addition of 5% of zinc chloride the azeotropic point is shifted0.55 t0 0.8 mole fraction of ethyl acetate .However, addition of 15% zinc chloride salt eliminated the total azeotrope and successfully separated the azeotropic solution as shown in Fig. 5. It can be clearly observed that zinc chloride and cobalt nitrate both remove the azeotropic point but cobalt nitrate eliminates with smaller amount in comparison with zinc chloride. However the cost comparison indicates that both salts are of equal cost but required dosages is different. So, cobalt nitrate was found to be a good substitute to separate azeotropic point of ethyl acetate and ethanol.

(a) (b)

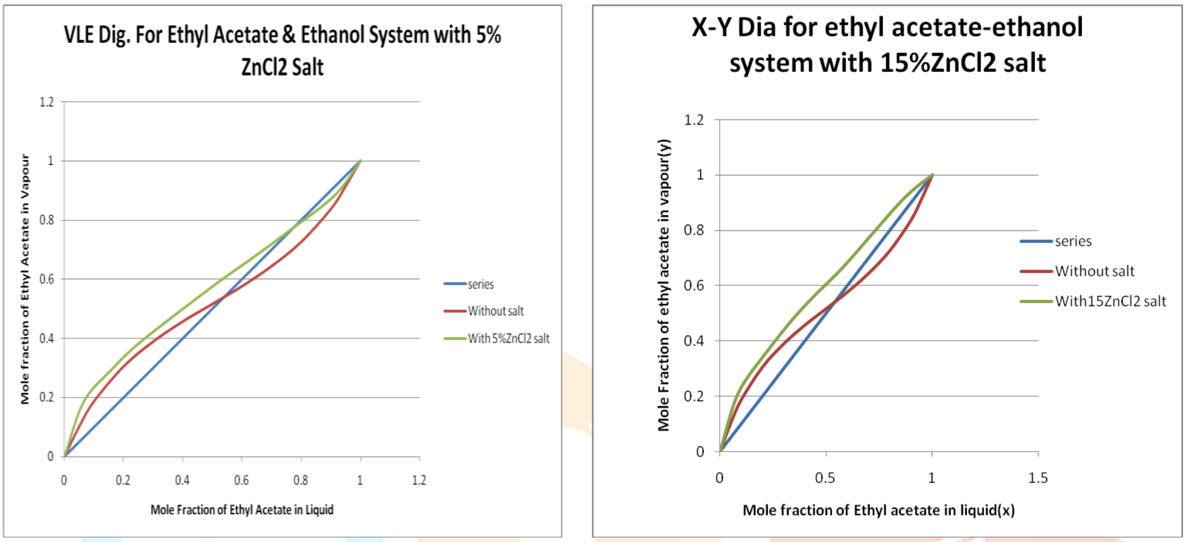

Fig. 5 VLE diagram for ethyl acetate-ethanol with (a) 5 % $ZnCl_2$ salt, (b) 15 % $ZnCl_2$ salt

IV. CONCLUSION

i. The extent of salt effect is also observed to be proportionally higher with increased concentration of the salts in the liquid mixture.

ii. Cobalt nitrate in 9.5 % (by weight) is eliminating total azeotrope of the system.

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