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SEPARATION OF TERTIARY BUTYL ALCOHOL – WATER SYSTEM BY USING LITHIUM BROMIDE

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Abstract: Extractive distillation is used for the separation of azeotropic mixture of tertiary butyl alcohol and water. Tertiary butyl alcohol is used as a solvent, ethanol denaturant, paint remover ingredient and also used as gasoline octane booster. Tertiary butyl alcohol makes an azeotrope at 79.9 °C, containing 11.8% water. In this work addition of salt helped to break the azeotrope by changing the relative volatility of the mixture facilitating separation effectively than the conventional method. Extractive distillation at 80°C, was carried out by varying the concentration of salt LiBr (10, 15, 20, 25, 30 & 35 g.) in TBOH-Water azeotropic mixture and it was found that 88.98 (wt. %) separation of TBOH was achieved for (35 g.) salt concentration.

Keywords: Azeotrope, Lithium bromide, Relative volatility, Extractive distillation.

I. Introduction

Extractive distillation is basically used to separate azeotropes and other mixtures that have key components with a relative volatility below about 1 over an appreciable range of concentration. The conventional method for separation of azeotropic composition is by using extractive distillation addition of solvent to break the azeotrope with an extra separation step is needed to recover the solvent which adds extra cost to the separation. A separation solvent is used in the method of extractive distillation. It is being chosen depending upon various factors that is it should be non-volatile, has a high boiling point and is miscible with the mixture, but doesn't form an azeotropic mixture with any of the component. [1]

Ivan D. Gil et al. (2012) studied separation of ethanol-water using glycerol as solvent in stage-1 and solvent recovery in stage II. [2] M.A.S.S. Ravagnani et al. (2010) investigated that tetra ethylene glycol was more reliable but requires more energy than ethylene glycol to separate ethanol-water azeotrope. [3] Yi-Feng Lin studied the separation of 2-propanol+water azeotropic mixture, using 1, 3-propanediol as a potential agent. [4] For separation of TBOH-water; Lloyd berg et al. (1992) used some conventional solvents like dimethyl adipate, 1, 4-butanediol, dipropylene glycol, tetraethylene glycol, methyl benzoate, dimethyl formamide including di methyl phthalate (DMP) which is used in this work and also entails the use of some organic compounds as agents in azeotropic and extractive distillation [5]. Ionic liquids (ILs) are also used for separations of azeotropic systems and are usually composed of heterocyclic organic cations and various anions and have unique properties such as non-volatility, non-flammability and a wide temperature range for liquid phase. [6-8] Despite these merits, ionic liquids showed high viscosities that could reduce separation efficiency as studied by E.Quijada Maldonado et al. (2013). E.Quijada Maldonado et al. (2013) compared the performance of 1-ethyl-3-methylimidazolium dicyanamide [emim][DCA] and ethylene glycol for the separation of ethanol-water mixture. [9-11]

Few researchers have studied a new method which could be adopted as extractive distillation in which solid salt or its aqueous solution was added to the mixture in place of liquid solvent as in salts its own vapor pressure is absent. 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. [12, 13] 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. In the case of, isopropanol-water [14], acetic-acid-water [15], ammonia-water [16] systems, LiBr salt is used for separation. Various studies have also been done to predict the salt effect on alcohol-water-salt systems. [17] In some systems, salt is added to the solvent to enhance the separation ability of the solvent as investigated in ethylene glycol-ethanol-water system potassium acetate salt (KAC) is added to enhance the separation ability of ethylene glycol because the interaction between water and KAC are stronger than that between alcohol and KAC. [18, 19]

II. Azeotropic Condition & Basic Properties

At atmospheric conditions, a binary mixture of tertiary butyl alcohol (TBOH)-water forms an azeotrope at 88.2wt.% and 79.9-80°C. But it forms an azeotrope at 74.51-75.10 wt.% (boiling point 80°C) in Vinati organics Ltd. Lote, India.

Table I Basic properties of system components

Component	Density(g/cc)	Molecular Weight (g.)	Boiling Point(°C)
Tertiary Butyl Alcohol	0.79	74	82.4
Water	1	18	100
LiBr	3.464	86.84	1265

III. Experimental

A. Materials

Tertiary butyl alcohol (TBOH) (LR grade, 98% purity) was purchased from Fisher Scientific, Mumbai [India] and Lithium bromide (LiBr) (LR grade, 98% purity) was purchased from Hyderabad [India] and Dimethyl Phthalate (DMP) was purchased from MCC Laboratory Chemicals, Pune [India] of 100% purity. LiBr solution was made with distilled water (40%). Sample of azeotropic mixture was procured from Vinati Organics Ltd, Lote [India].

B. Methods

Reactor (three necked flask) with Dean stark apparatus and condenser assembly was used for distillation in which provision was made for measuring temperature as shown in figure 1. For the experimentation 150 ml of azeotropic mixture of known composition was taken with different solvents viz.

DMP, LiBr and DMP + LiBr.

The liquid mixture was heated up to 80°C with the help of heating mantle (0-100°C) by slowly increasing the heat input, through variac. When the steady state was achieved, the bottoms and distillate collected into the sample bottles with respect to time and analysed.

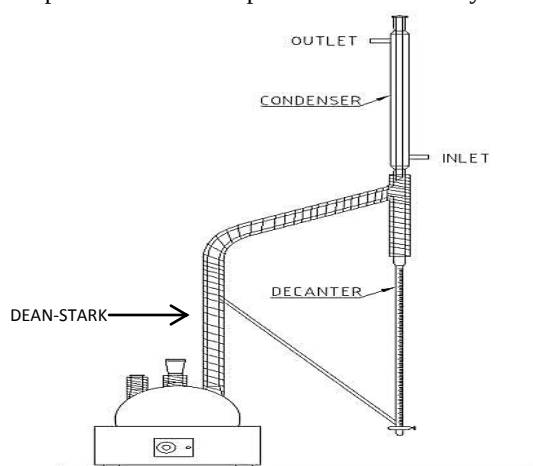


Figure 1: Schematic diagram of Extractive Distillation

C. Analysis of the Sample

Original sample was analysed (74.51 wt. % TBOH, 25.49 wt. % Water). Composition of the liquid and vapour samples were analysed by gas chromatograph (Perkin Elmer, USA).

1V. Results and Discussion

Figure 2 illustrates the effect of LiBr loading (10, 15, 20, 25, 30 & 35 g) on TBOH concentration. It was found that use of LiBr eliminates the azeotrope formation and relative volatility changes from 1 to 2.426 in that particular range of azeotropic composition. Increase in LiBr loading showed the increase in concentration of TBOH up to a certain limit and after 25 g. of loading there was minute change in the TBOH concentration as shown in figure 2 and figure 3. The separation from 74.51 wt.% to 88.98 wt.% was achieved by this method. Those results obtained are in agreement with Vora *et al.* (2013). Addition of salt increased the boiling point of water as lithium bromide (LiBr) has high boiling point and it is also hygroscopic in nature that causes its use in this application.

It was observed that for the same azeotropic composition using dimethyl phthalate (DMP), as solvent maximum up to 79.38 % purity of TBOH was obtained whereas using DMP+LiBr, there was slight increase in purity of TBOH (81.99%) was achieved. The same phenomenon was observed by Lei *et al.* (2002) and Ligerio *et al.* (2003) in the separation of ETOH –Water system. Experimental results are summarized in Table II and III. The Comparison of effect of LiBr-35, DMP & DMP+LiBr on TBOH concentration was shown in Figure 4.

Table II: Experimental data for purity of TBOH by using DMP & DMP+ LiBr

Sample+ DMP (60 g.)		
S.NO.	Time (min.)	%Purity of TBOH in distillate (wt.%)
1.	30	79.38
2.	60	78.31
Sample+ DMP (60 g.)+ LiBr (25 g.)		
1.	30	81.85
2.	45	81.99
3.	60	72.81

Table III: Experimental data for purity of TBOH by using different grams of LiBr

LiBr (g.)	%Purity of TBOH in distillate (by wt.%)
10	85.38
15	86.09
20	87.10
25	87.71
30	88.69
35	88.98

Figure 2: Effect of LiBr loading on TBOH concentration (wt.%) with time

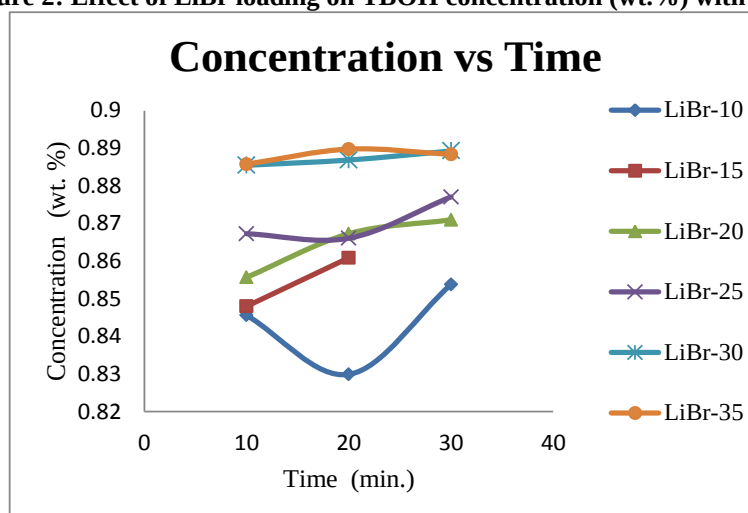


Figure 3: Variation in different grams of LiBr and concentration of TBOH in the distillate

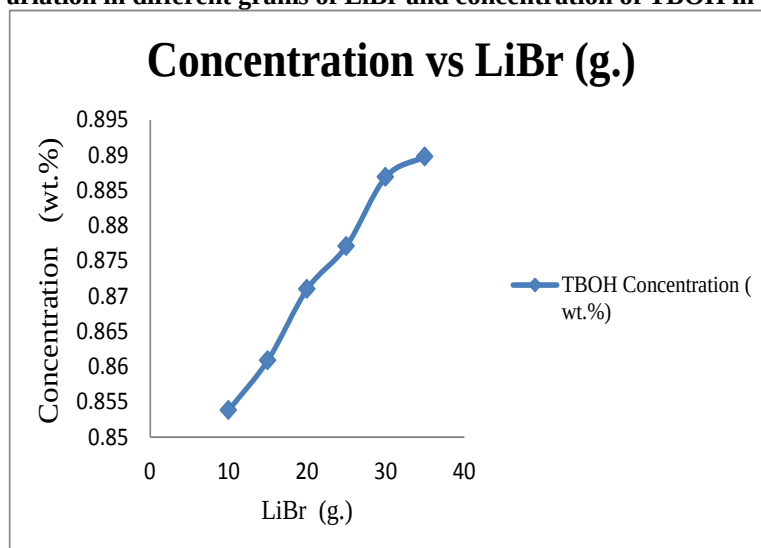
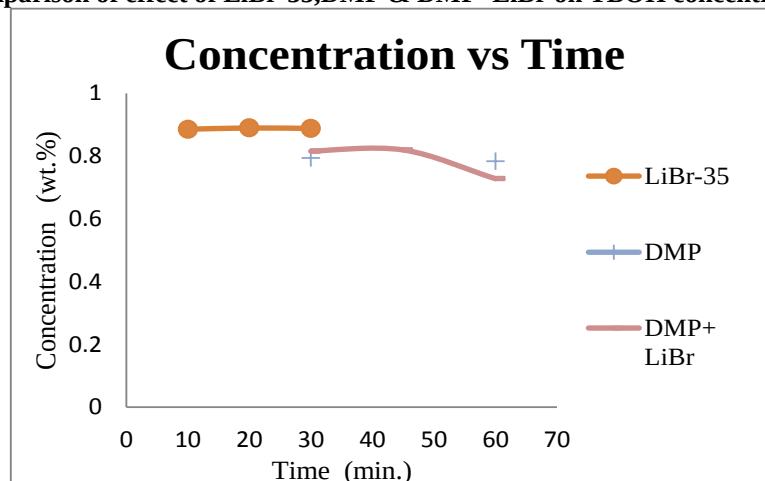


Figure 4: Comparison of effect of LiBr-35,DMP & DMP+LiBr on TBOH concentration with time



V. Conclusion

It can be concluded that extractive distillation with LiBr is more effective as compared to use of conventional solvent (DMP) and also better than the use of (salt + solvent). The salt recovery and reuse can be done more economically and efficiently. However there is need to refine the technique using the salt for separation of TBOH and to improve the results up to 99% so as to apply the method on full scale in industry.

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