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Separation of Isomeric Butanol Mixture Using Hydrotropes, Plots Using Matlab

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Abstract. This work is mainly concerned with a typical study on the effect of hydrotropes such as sodium benzoate, nicotinamide and tri-sodium citrate on the separation of isomeric butanol mixture (n-butanol and iso-butanol) under a wide range of hydrotrope concentrations (0 to 3.00 mol/L) and different system temperatures (303 to 333K). From this experiment, it was found that the separation of n-butanol increases with increase in hydrotrope concentration and also with system temperature. A Minimum Hydrotrope Concentration (MHC) in the aqueous phase was found essential to initiate significant separation of n-butanol from isomeric mixture (n- butanol and iso butanol). The performance of hydrotropes towards separation of n-butanol was measured in terms of Setschenow constant 'Ks' and reported for all hydrotropes used in this study. Similarly, response surface methodology plot was drawn for best hydrotrope concentration.

Keywords: Hydrotropes, Separation technique, Mat lab approach

1. Introduction

Hydrotropy is a unique process different from simple phase mixing, co-solvency or salting in. Intermolecular complex formation between the hydrotrope and the solubilization may occur in some instances but is not the general rule. The field of separation assumes greater significance in chemical and petrochemical industries. It appears to be a collective molecular phenomenon that operates above a characteristic concentration of the hydrotrope in water. Above this concentration, this is termed as the Minimum Hydrotrope Concentration (MHC**)**, the hydrotrope molecules self- aggregate into loose non-covalent assembly which offers a microenvironment of lowered polarity that aids the solubilization of the hydro phobic solute molecule. Neuberg (1916) was the first identify this innovative technique. It is the phenomenon by which certain organic compounds can be used to effect a several fold increase in the solubility of solutes that are sparingly soluble in water under normal conditions[1],[3]. This increment in solubility of water is probably due to the formation of organized assemblies in hydrotrope molecules at minimum hydrotrope concentration (MHC). Similarly the increasing trend reaches certain values beyond which there is no appreciable change in solubility. This is referred to as the Maximum Hydrotrope Concentration (Cmax).

Selective solubilization of o/p-chloro benzoic acid and o/p-nitro aniline in sodium butyl mono glycol sulfate solution [6] and separation of o/p xylene mixture using different hydrotropes nicotinamide, sodium slycilate [9] were studied previously. Hydrotropes normally comprise of hydrophilic and the hydrophobic moiety being typically too small to induce micelle formation. Each hydrotrope has a selective ability towards a particular component in a mixture, which facilitates easy recovery of hydrotropes by controlled dilution water. Generally most compounds when dissolved in water decrease the solubility of second component. Some present opposite behavior leading to considerable solubility increases. The occurrence of such phenomena leads to the terminologies 'salting out', referring to reduced solubility and 'salting in' for the

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reverse effect. The compounds that cause increase in the aqueous solubility are sometimes called hydrotropes [8], [7], [10] and [2]. Response surface methodolgy is statistical method, which uses quantitative data from appropriate experiment to design data. This method was introduced by Box and Wilson (1951). Using central composite design, surface plot was drawn.

Central composite design is one of the models in response surface (RSM) plot. Matlab 7.01 was used for the various hydrotrope concentration Vs % extraction of normal butanol.

2. Materials and Methodology

Materials such as sodium benzoate, nicotinamide and tri-sodium citrate were of very high purity grade and procured from S.D. Fine Chemicals, Mumbai with a manufacturer's stated purity of 99.9%.

The separation of isomeric mixture by thermostatic bath was method used for different hydrotropes such as sodium benzoate, nicotinamide and tri sodium citrate. The hydrotrope solutions of different concentration were prepared by dilution with distilled water. About 100 ml of n- butanol and isobutanol was taken and equal amount of hydrotrope solution was added and mixed for 180mins. The mixture was then transferred to a separating funnel which was immersed in a constant temperature bath fitted with a temperature controller that could control the temperature within 303 to 333K. The setup was kept at over night for attaining equilibration. After equilibrium was attained, the aqueous phase and organic phase were carefully separated and analyzed to quantify the concentration using High Performance Liquid Chromatography (HPLC). Duplicate runs were conducted and found that the error was < 2%.C-18 columns are used. The column was packed with silica gel.

3. Results and Discussion

Experimental data on the effect of hydrotropes, i.e., sodium benzoate, nicotinamide and tri sodium citrate on the percentage extraction of n-butanol are plotted in Figures 1, 2 and 3. Percentage extraction ($E1$) is the ratio of number of moles of n-butanol extracted in the presence of hydrotrope to number of moles of n-butanol initially present. It was observed that the percentage extraction of n-butanol did not show any appreciable increase until 0.40 mol/L of sodium benzoate was added in the aqueous phase. But upon subsequent increase in the concentration of sodium benzoate the percentage extraction of n-butanol was found to increase significantly. This concentration of n-butanol in the aqueous phase, i.e., 0.50mol/L, is termed the Minimum Hydrotrope Concentration (MHC), which is the minimum required amount of sodium benzoate in the aqueous phase to initiate significant increase in the percentage extraction of n-butanol. It was observed that the MHC value of sodium benzoate in the aqueous phase does not vary even at increased system temperatures, i.e., 313, 323, and 333 K. A similar trend in the MHC requirement was observed for nicotinamide. Therefore, it is evident that hydrotropic separation was displayed only above the Minimum Hydrotrope Concentration (MHC), irrespective system temperature Hydrotropy technique did not seem to be operative below MHC which may be a characteristic of a particular hydrotrope with respect to each solute. The percentage extraction effect varies with concentration of the hydrotropes. At 2.50 mol/lit the extraction of n-butanol using sodium benzoate was 64.61%. This concentration is known as Maximum Hydrotrope Concentration (C_{max}). Beyond this concentration there is no appreciable extraction of n-butanol from the mixture. The maximum percentage extraction of n-butanol was obtained 64.61% for the corresponding value of 3.00mol/lit of sodium benzoate concentration at 333K. In concentration range of sodium benzoate between 0 and 3.00mol/L, three different regions were obtained Region I, 0.00 to 0.50 mol/L, Region II, 0.50 to 2.50 mol/L and Region III, 2.50 to 3.00 mol/L). It was observed that sodium benzoate was inactive below in Region I. There was an appreciable increase in percentage extraction of n-butanol in Region II and there was no further increase in the percentage extraction of n-butanol in Region III. Therefore sodium benzoate was found to be an effective hydrotrope concentration in the range between 0.50and 2.50mol/L towards n-butanol. The insignificant extraction of n- butanol below MHC may be due to the inability of hydrotropes to form aggregates with required number of hydrotrope molecules in the aqueous phase .Similarly beyond Cmax values there is no water molecules to form more aggregates. The effective separation of sodium benzoate increases with hydrotrope concentration and also with system temperature. Similar trend was observed for nicotinamide (MHC [0.5mol/lit]), C_{max}[2.4mol/lit] and tri sodium citrate (MHC [0.4mol/lit]), (C_{max} [2.4mol/lit])

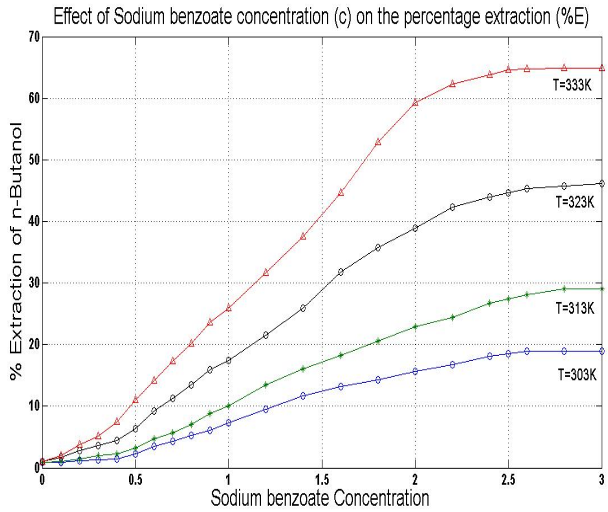

Fig. 1: Effect of Sodium benzoate concentration (C) on the percentage extraction (% E) of n-butanol

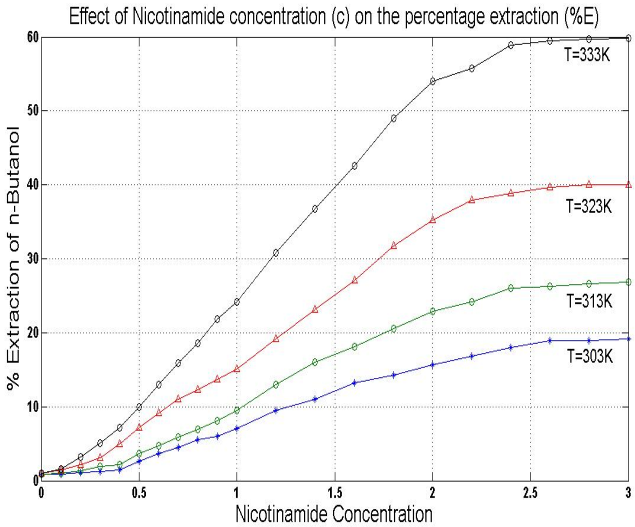

Fig. 2: Effect of Nicotinamide concentration (*C*) on the percentage extraction (% *E*) of n-butanol

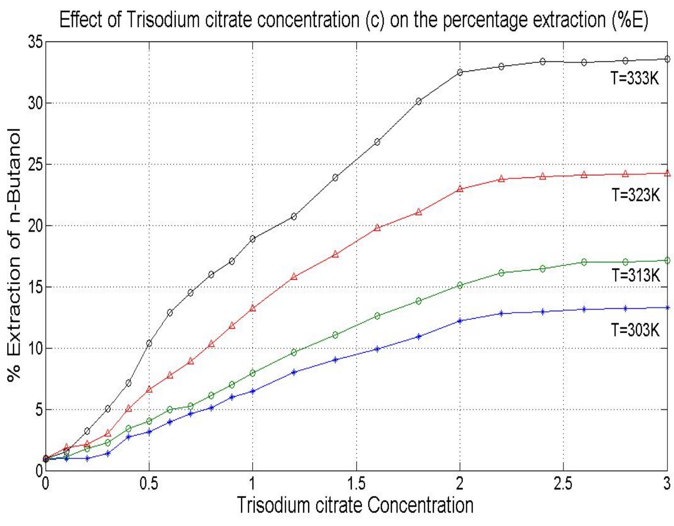

Fig. 3: Effect of Tri sodium citrate concentration (*C*) on the percentage extraction (% *E*) of n-butanol

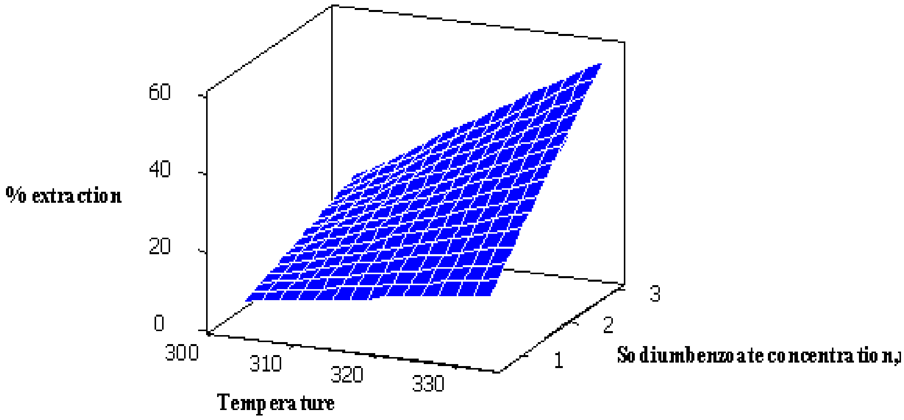

Fig. 4: Best Hydrotrope (Sodium benzoate)

Table 1: MHC and C_{max} Values of Hydrotropes

Hydrotropes	**MHC**	C_{max}
Sodium Benzoate	0.5	2.5
Nicotinamide	0.5	2.4
Tri sodium citrate	0.4	2.4

Table 2: Setschenow constants (Ks) values of hydrotropes with respect to n-butanol

Hydrotropes	K_s			
	303K	313K	323K	333K
Sodium Benzoate	0.452	0.463	0.482	0.502
Nicotinamide	0.435	0.442	0.475	0.487
Tri sodium citrate	0.338	0.356	0.369	0.373

3.1. Effectiveness of Hydrotropes

The effectiveness factor of each hydrotrope at different system temperatures has been determined by analyzing the experimental percentage extraction data for each case, applying the model suggested by Setschenow and later modified by Gaikar for percentage extraction studies as given by

$$\log [E/E_m] = K_S[C_S - C_m]$$

Where E and E_m are the percentage extraction values of n-butanol at any hydrotrope concentration (C_S) and Minimum Hydrotrope Concentration (MHC or C_m) respectively. The Setschenow constant (K_S) can be considered as a measure of the effectiveness of a hydrotrope at any given conditions of hydrotrope concentration and system temperature.

4. Conclusions

This study involves the separation of close boiling isomeric mixture n-butanol and isobutanol was carried out selectively with aqueous solutions of three hydrotropes namely, Sodium benzoate, nicotinamide and tri sodium citrate. The effect of temperature and the hydrotrope concentration has been studied. The highest percentage extraction of 64.61 was observed in the case of sodium benzoate at a temperature of 333 K. The unprecedented increase in the percentage extraction by the effect of hydrotropes is attributed to the formation of organized aggregates of hydrotrope molecules at a critical concentration. Mat lab 7.5.0 is used for all the hydrotrope concentration vs. percentage extraction of n- butanol. It was used for plotting the hydrotropic concentration. Also, from the Response Surface Methodology plot, the optimum temperature value for sodium benzoate (hydrotrope) was 330K.

5. Acknowledgement

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6. References

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