



APPLICATION OF CLOUD POINT EXTRACTION METHODOLOGY FOR THE INTENSIFIED REMOVAL OF PHENOL

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ABSTRACT

The surfactant-based separation technologies based on the clouding phenomenon of non-ionic surfactants is gaining importance in the removal of phenolic components from wastewater. Cloud point extraction is one such methodology used to effectively remove the impurities selectively. The experiments are carried out to study the effect of non-ionic surfactant concentration and additives concentration on cloud point of non-ionic surfactant which is one of the design parameter for the cloud point extraction system. The effect of surfactant concentration, solute concentration, electrolytes concentration and operating temperature on the vital parameters of the system such as phase volume ratio (RV), pre-concentration factor (fC), solute distribution coefficient (Kd) and extraction efficiency (η %) has been studied. In the present study, Triton X-100 and phenol are used as surfactant and solute respectively. In order to study the electrolyte effects, NaCl and Na₂SO₄ are used for salting-out effect and NaI and NH₄SCN are used for salting-in effect.

Keywords: Non-Ionic Surfactants, Cloud Point, Cloud Point Extraction.

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1. INTRODUCTION

Recently, more emphasis is shown on health and environment by many a agencies across the globe. The contamination of earth's environment by wastewater discharges containing huge traces of aromatic compounds can cause severe problems. Phenol is one of the major pollutants which have toxic effects on human health. The ingestion of phenol polluted water in the human body causes proteins degeneration, tissue erosion and paralysis of the central nervous system and also damages the kidney, liver and pancreas [1]. The industrial effluent standard value of phenol is 1mg/l [2]. Hence, it is necessary to remove the phenol from

industrial effluents before discharging into the water stream as it may prone to several bound diseases.

For removal of aromatic compounds, extraction technique has been used. This process is applicable for various process industries, such as petroleum industries, coal tar industries, biological material separations, pharmaceutical industries and removal of pollutants from wastewater stream. The disadvantages of this separation processes are the requirement of more organic solvent, time, cost, sensitivity, solution stick on the wall of column and safety hazard considerations [3]. Hence, it is necessary to identify the new separation technique. Even there are different separation techniques are available, recently the cloud Point Extraction (micelle mediated separation process systems) is identified as one of the potential separation system. These are several advantages in surfactant-based separation (or CPE) technologies, process is reversible, flexibility of the process, easy phase separation, availability of various surfactants, low amount of surfactant is needed, possibility of designing a desirable surfactant, nontoxicity and biodegradability of most surfactants, achievement of high values of concentrating factor, decrease the dissolve oxygen in water atmosphere inter phase, modest energy consumption, high extraction efficiency, no fouling, safety and low cost.

The clouding phenomenon is the attractive feature of non-ionic surfactants. When the aqueous solution of nonionic surfactant is heated, it turns cloudy at a definite temperature and this temperature is referred as the Cloud Point (CP). Due to heating, the weakening of hydrogen bonding between a water molecule and the hydrophilic moiety of the surfactant leads to the decreased solubility of a surfactant and clouding phenomena occurs [4]. The clouding may be also due to change in balance of hydrophilic and hydrophobic interactions. By allowing the solution to settle at a temperature above the cloud point, phase separation takes place. The smaller phase contains most of the surfactant and usually sinks to the bottom, some cases at the top called as surfactant rich phase or coacervate phase. The more voluminous aqueous supernatant has surfactant content approximately equal to the CMC also called as dilute phase. This is known as Cloud Point Extraction (CPE) [5-7].

The first step in the design of cloud point extraction is determination of CP. The cloud point of a non-ionic surfactant is can be altered with the additives such as organic compounds, alcohols, salts and operating conditions like temperature and pressure [3]. Since the cloud point extraction is to be carried out above the cloud point temperature, the cloud point of non-ionic surfactants play a vital role in separations based on non-ionic surfactants.

Hence in this study, the effect of concentration of surfactant and additives on cloud point temperature are studied and also the phase volume ratio, pre-concentration factor, solute distribution coefficient and extraction efficiency of the cloud point extraction have been studied with the influence of the concentration of surfactant, solute, electrolytes and operating temperature. Triton X-100 is used as non-ionic surfactant and phenol is used as solute (organic additive). In order to study the electrolyte effects, NaCl and Na₂SO₄ are used for salting-out effect and NH₄SCN and NaI are used for salting-in effect.

2. EXPERIMENTAL

2.1. Reagents

Triton X-100 (purchased from Fluka) is used as non-ionic surfactant. It is an octylphenol ethoxylate consisting of 9 to 10 moles of ethylene oxide and abbreviated as TX-100. It is a high purity and water-soluble liquid. Phenol (purchased from Ranbaxy) is used as solute. The electrolytes used are Sodium chloride and Sodium sulfite (purchased from Paxmy),

Ammonium thiosulphate (purchased from Reachem) and Sodium iodide (purchased from s d fine-chemicals ltd).

2.2. Apparatus

The determination of the cloud points was carried out in a water-bath with a good temperature control within $\pm 0.1^\circ\text{C}$. The phase separation can be achieved using centrifugation for 15 min at 3000 rpm. After centrifugation, both phases become transparent with a clear phase boundary. The phenol concentration in the dilute phase was measured using UV-visible spectrophotometer at the wavelength of 520 nm.

2.3. Determination of Cloud point

The cloud point of aqueous surfactant solution is determined by heating 10 ml of such micellar solution in graduated glass tubes. The rate of temperature increase in the water bath is set at 1°C per min. The cloud point is determined by visual observation at the temperature at which the solution became obviously turbid. The measurement of cloud point temperature is reproducible within $\pm 0.2^\circ\text{C}$. The same procedure is repeated for aqueous nonionic surfactant micellar solution with addition of phenol and electrolytes. When the solution is heated above the cloud point temperature, it will accelerate the phase separation. After centrifugation, the volumes of both phases have been noticed. The amount of phenol in the dilute phase can be determined by 4-aminoantipyrene methods using UV-visible spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Effect of Cloud point

The variation of cloud point with the surfactant concentration is studied. The cloud point temperature of aqueous solutions of TX-100 decreases up to 3.5% (by wt) and then increases with increases in TX-100 concentration. At higher surfactant concentration, the cloud point continues to increase due to the presence of structured water-surfactant system and the water molecules might act as buffers between micelles [8]. Koshy et al also observed the same trend. The change in cloud point temperature for different concentration of Phenol also studied. M.H.J.Weiden [9] and William.N.Maclay observed the similar results [10].

In order to study the effect of electrolytes on cloud point, four different salts were used for the present study to consider both salting-in and salt out effect. In salting out effects, the salts can promote the dehydration process and the cloud point will decrease. In salting in effect, the salts can inhibit the dehydration process and the cloud point will increase. When small amount of salt is added to nonionic surfactant solutions, the cloud point remains constant. Salting in effect salts (NH_4SCN , NaI) increase the critical micelle concentration and raise the cloud point. In contrast, salting out salts (NaCl , Na_2SO_4) can decrease the cloud point. The cloud point changes of the aqueous TX-100 solution in presence of electrolytes are observed. The cloud point changes of the aqueous TX-100 solution in presence of solute and electrolytes are also observed. The same trend is observed [11, 12].

3.2. Effect of concentration of surfactant, solute, electrolyte and operating temperature on CPE

In this section, the effects of surfactant concentration, solute, electrolyte concentration and operating temperature on CPE are discussed. For without electrolytes, the concentration of surfactant is varied from 0.5 to 2.5% (by wt), solute concentration is varied from 0.1 to 0.5% (by wt). The experiments without electrolytes have been conducted at three different temperatures such as 50, 60 & 70°C . The experiments with the electrolytes are conducted for the surfactant concentration and solute concentration 2.5% (by wt) and 0.1% (by wt) respectively. NaCl and Na_2SO_4 are used as salting-out effect salts and all the experiments

have been conducted at three different temperatures. For NaCl, the experiments are conducted at 50, 60 & 70°C. For Na₂SO₄, the experiments are conducted at 50, 55 & 60°C. NaI and NH₄SCN are used to study the salting-in effect and all the experiments have been conducted at three different temperatures i.e. 80, 82.5 & 85°C. These operating temperatures have been selected based on the cloud point temperatures.

3.3. Phase volume ratio

The phase volume ratio, R_V , is defined as the ratio of the volume of the surfactant-rich phase to that of the volume of the aqueous phase. The volumes of the two phases are measured using graduated centrifuged tubes.

$$R_V = V_S / V_W \quad (1)$$

where V_S and V_W are the volumes of the surfactant-rich phase and the aqueous phase respectively.

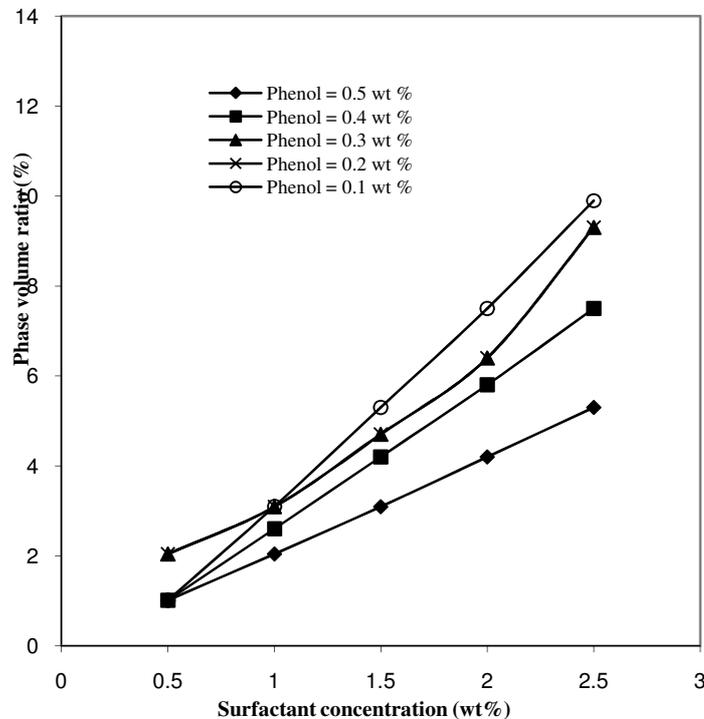


Figure 1. Effect of solute and surfactant in phase volume ratio

Figure 1. shows the effect of surfactant and solute concentration in phase volume ratio. From the figure it is observed that the phase volume ratio increases with increase in surfactant concentration and it decreases with increase in solute concentration. The phase volume ratio increases because of increase in the volume of surfactant rich phase. This may be due to the large amount of surfactant present in the surfactant rich phase. The low phase volume ratio for higher concentration of solute shows that the amount of phenol in surfactant-rich phase would be high [13].

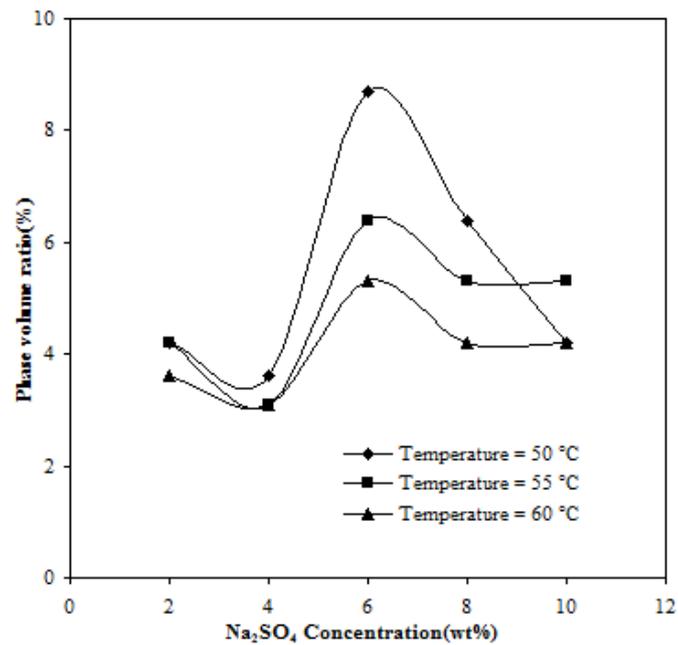


Figure 2. Effect of Na₂SO₄ and operating temperature on phase volume ratio

The effect of Na₂SO₄ concentration and operating temperature on the phase volume ratio is shown in Figure 2. The phase volume ratio increases with increase in Na₂SO₄ concentration and it decreases with increase in operating temperature. The addition of electrolyte would compress the volume of surfactant-rich phase from 0.9 ml to 0.25 ml because of the dehydration process.

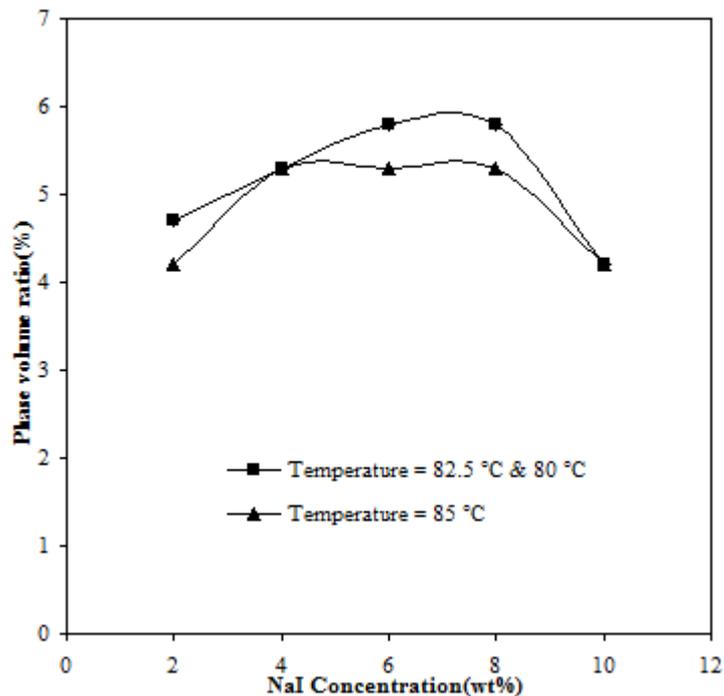


Figure 3. Effect of NaI and operating temperature on phase volume ratio

The influence of NaI concentration and operating temperature on phase volume ratio is shown in Figure 3. In this case the phase volume ratio attained high value such as salting-out at 6% (by wt) of electrolyte concentration and then decreases with increase in electrolyte concentration.

3.4. Pre-concentration factor:

The pre concentration factor, f_c , is defined as the ratio of the volume of bulk solution before phase separation to that of the surfactant-rich phase after phase separation.

$$f_c = V_t/V_s \quad (2)$$

where V_t and V_s are the volumes of the bulk solution before phase separation and the surfactant-rich phase respectively.

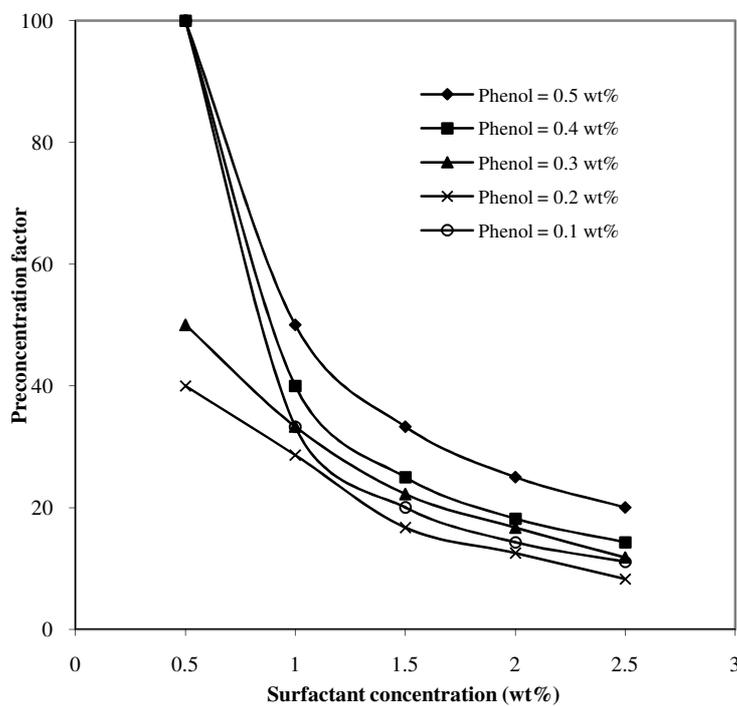


Figure 4. Effect of solute and surfactant in pre-concentration factor

Figure 4. shows the effect of surfactant and solute concentration on pre-concentration factor. It is observed that the pre-concentration factor decreases with increase in surfactant concentration and decreases with solute concentration. The solute is more hydrophobic, it has less solubility because of that pre-concentration decrease with increase in solute concentration. Bingjia yao et al. (2008) and D.Sicilia et al. (2002) also observed the similar result.

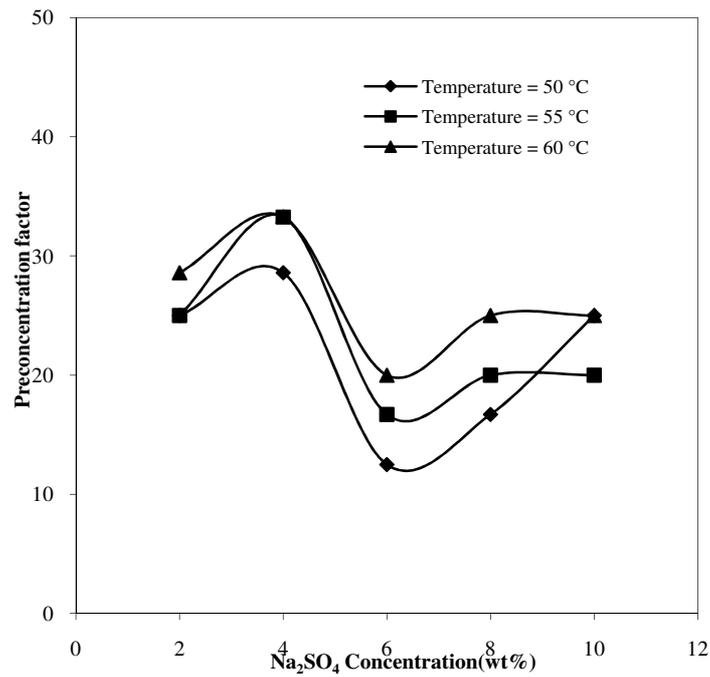


Figure 5. Effect of Na₂SO₄ and operating temperature on pre-concentration factor

The effect of Na₂SO₄ concentration and operating temperature on the pre-concentration factor is shown in Figure 5. The pre-concentration factor was obtained in the CPE process for 0.1% (by wt) of phenol and 2.5% (by wt) of TX-100 without any electrolyte is 11. The addition of electrolyte may compress the surfactant-rich phase volume [13] and the pre-concentration factor for the same concentration of solute and surfactant in presence of salt fall down from 40 to 10.

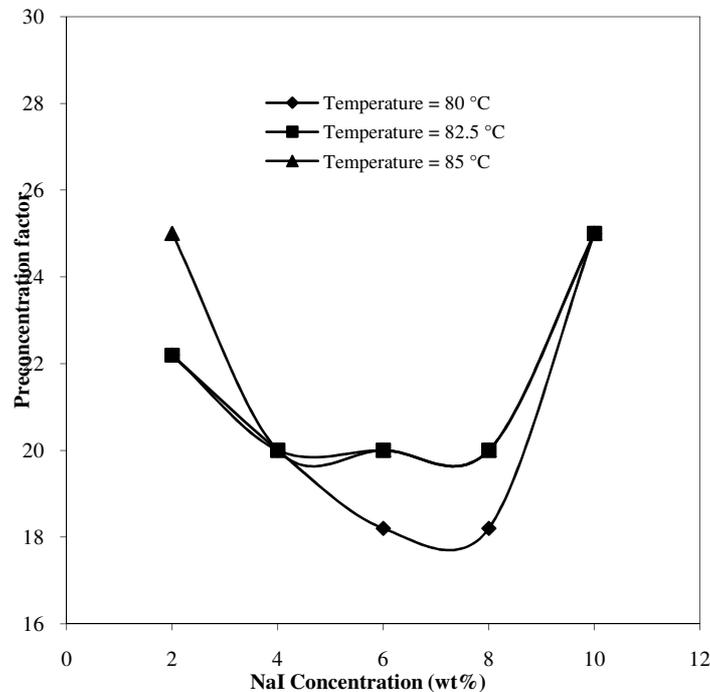


Figure 6. Effect of NaI and operating temperature on pre-concentration factor

The effect of NaI concentration and operating temperature on the pre-concentration factor is shown in Figure 6. The pre-concentration factor decreases up to 6% (by wt) of NaI concentration and then increases with increase in salt concentration. The pre-concentration factor is obtained as high as 67, because of added electrolytes would compress the V_S .

3.5. Distribution Coefficient:

The distribution coefficient or equilibrium partition coefficient, K_d or K_p , is defined as the ratio of the concentration of solute in surfactant-rich phase to that of the concentration of solute in dilute phase.

$$K_d = C_s / C_w \tag{3}$$

where C_s and C_w are the concentration of solute in the surfactant-rich phase and the dilute phase respectively.

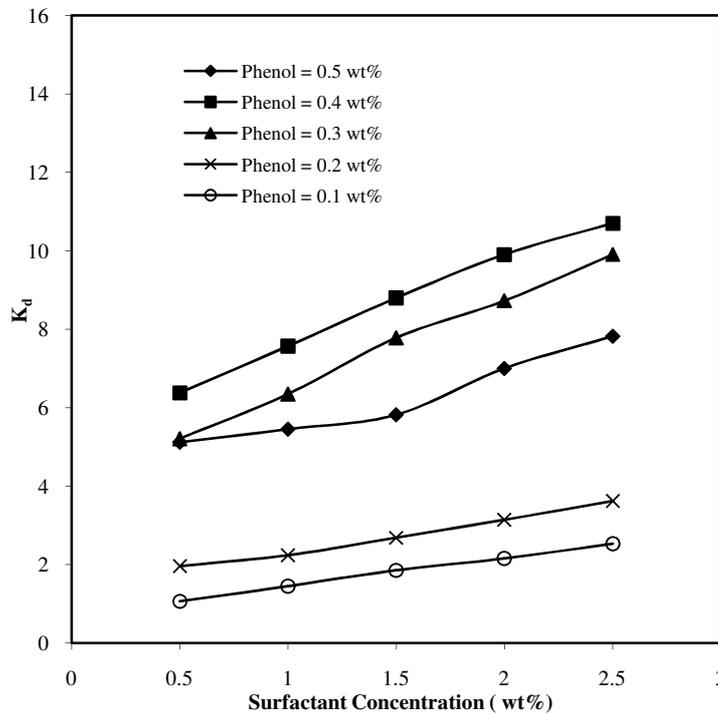


Figure 7. Effect of operating temperature at 60°C on distribution coefficient

Figure 7. shows the effect of operating temperature at 60°C on distribution coefficient. The same pattern is observed for 50°C & 70°C. It increases with increase in both surfactant and solute concentration. The distribution of solute depends on the specific solute-water interaction. If the interaction is more, then distribution coefficient will be high. The distribution coefficient increases with increase in operating temperature is shown in Figure 8. for the phenol concentration of 0.4% (by wt) and three different temperatures. The observations made by B.H.Chen et al. (2003) and D.Sicilia et al. (2002) are similar to the present experimental observation.

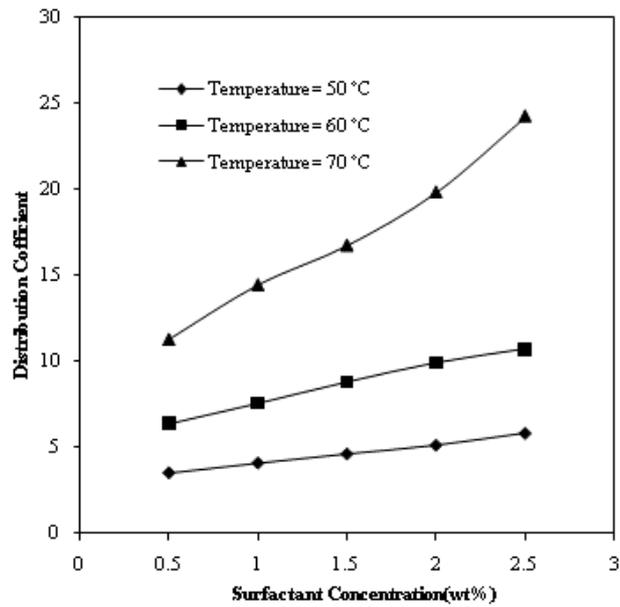


Figure 8. Effect of operating temperature at Phenol concentration = 0.4% (by wt) on distribution coefficient

The effect of Na_2SO_4 concentration and operating temperature on distribution coefficient is shown in Figure 9. The distribution coefficient increases with increase in Na_2SO_4 concentration and also it increases with increase in operating temperatures. The addition of electrolyte would compress the volume of surfactant-rich phase (V_S); due to low V_S , the amount of solute in surfactant-rich phase is very high. Because of high C_S , distribution coefficient also found as high value [13].

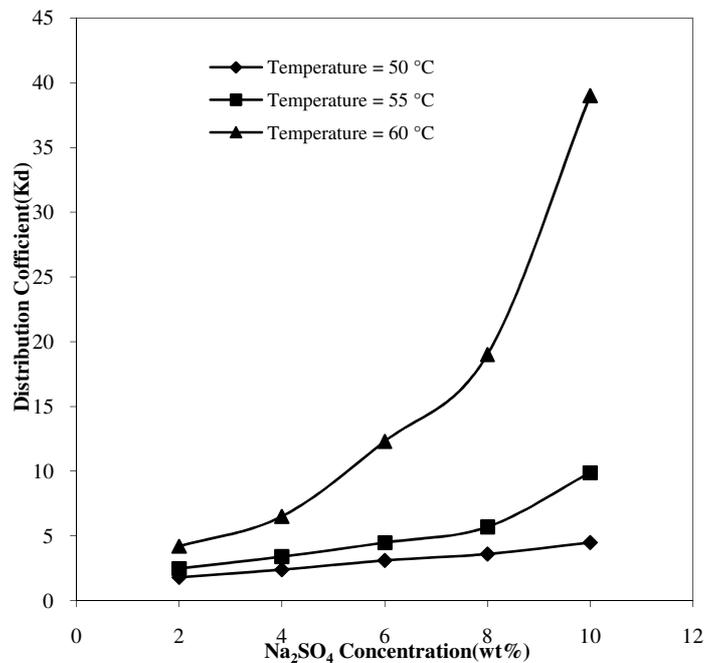


Figure 9. Effect of Na_2SO_4 and operating temperature on distribution coefficient

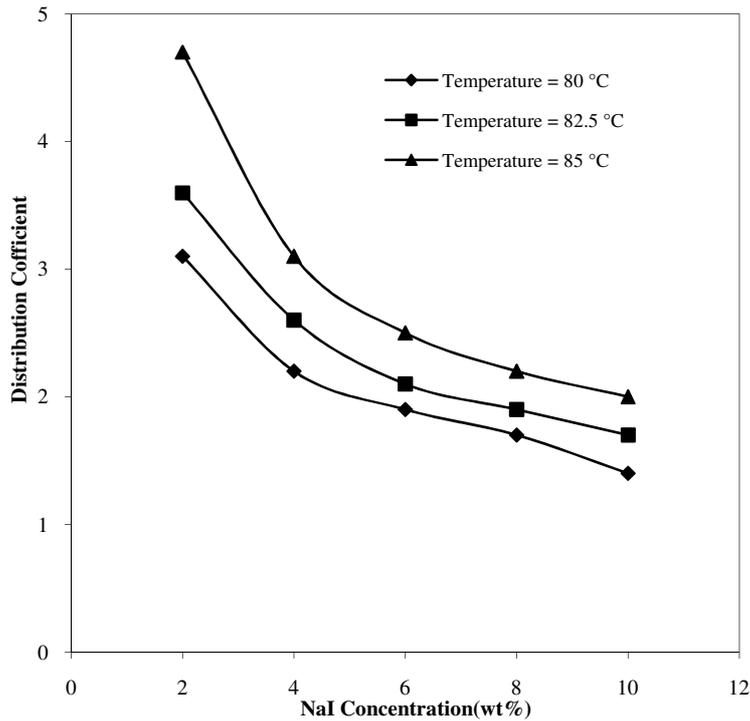


Figure 10. Effect of NaI and operating temperature on distribution coefficient

The effect of NaI concentration and operating temperature on distribution coefficient is shown in Figure 10. The distribution coefficient decreases with increase in concentration of NaI and it increases with increase in operating temperatures. The distribution coefficient decreases because of hydrophobic nature of the solute. Hydrophobicity is probably due to the increase in the water solubility of the hydrocarbon compounds.

3.6. Extraction Efficiency:

The recovery efficiency of solute, η , can be characterized as the percentage of solute extracted from the bulk solution into the surfactant-rich phase.

$$\eta\% = \frac{C_0V_t - C_w(V_t - V_s)}{C_0V_t} * 100 \quad (4)$$

where C_0 is the initial concentration of solute in the micellar solution and C_w is the concentration of solute in dilute phase.

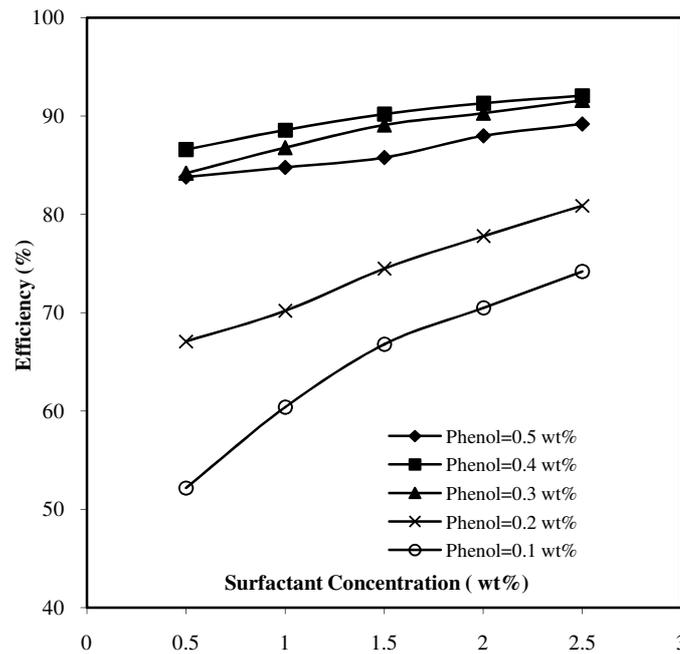


Figure 11. Effect of operating temperature at 60°C on Efficiency (%)

Figure 11. shows the effect of temperature at 60°C on the extraction efficiency. For temperature 50 and 70°C, the observed trend is similar to 60°C. It increases with increase in surfactant concentration and also increases with increase in operating temperatures. The nature of solute is more hydrophobic and then the extraction efficiency is low at 50°C. The extraction efficiency is high, when the system is at higher operating temperature. The increase in recovery at elevated temperatures may be due to an increase in solubility of the solutes in the micellar phase [15].

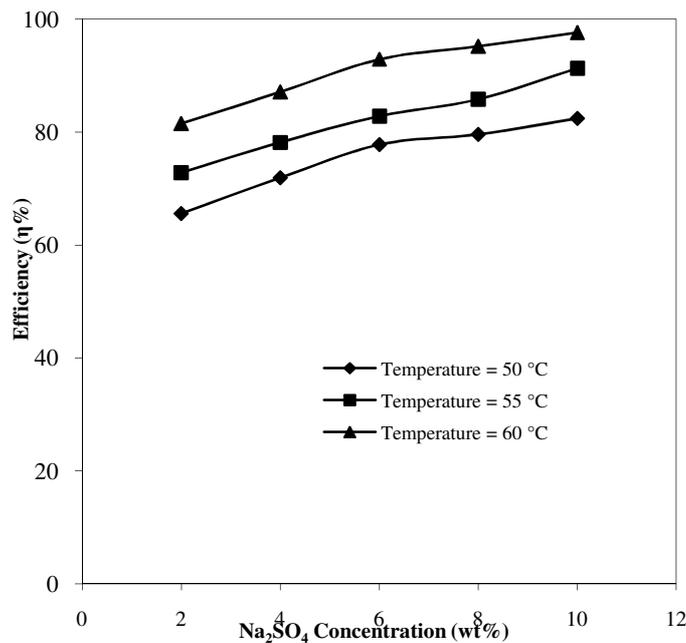


Figure 12. Effect of Na₂SO₄ and operating temperature on extraction efficiency

Figure 12. illustrates the effect of Na_2SO_4 concentration and operating temperature on the recovery of phenol. The efficiency increases with increase in concentration of Na_2SO_4 and operating temperature. An efficient change in the recovery is observed at the different salt concentrations. Recovery of phenol depends on the micellar concentration. Increasing salt concentration could lead to greater recovery efficiency. For example, the recovery of phenol for sodium sulfate increases up to 98% at the operating temperature of 60°C. At the higher operating temperature, the recovery of phenol increases due to an increase in solubility of the analytes in the micellar phase [16]. The above said parameters are studied for NaCl at the three different temperatures such as 50, 60 & 70°C and the similar trend is observed.

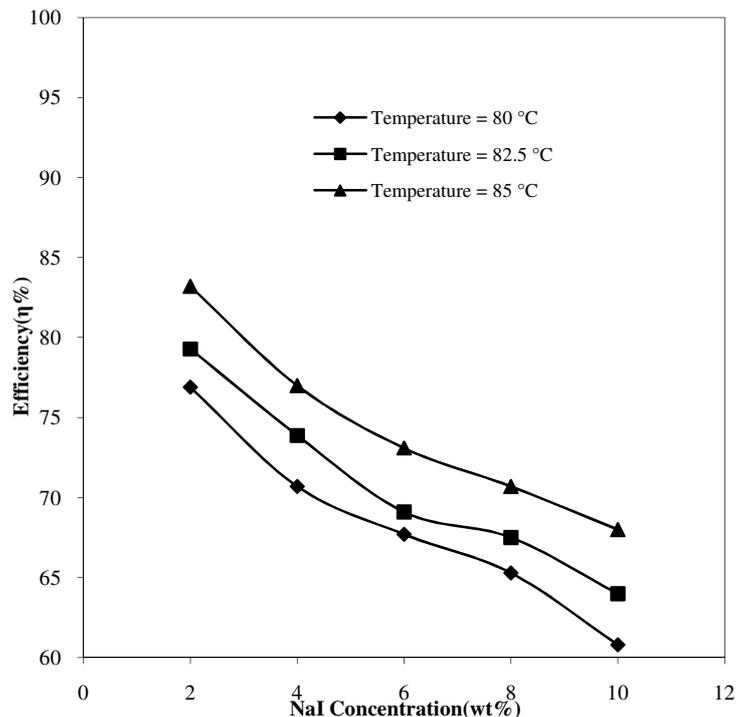


Figure 13. illustrates the effect of NaI concentration and operating temperature on the recovery of phenol. The recovery of phenol decreases with increase in concentration of NaI and it increases with operating temperatures. The recovery of solute decreases, because of solute hydrophobicity. The above said parameters are studied for NH_4SCN at the same set of temperature conditions.

4. DEVELOPMENT EMPIRICAL MODELS

In the cloud point extraction study, the effect of concentration of surfactant, solute and operating temperature are studied on the various parameters such as phase volume ratio, pre concentration factor, the concentration of phenol in surfactant-rich phase and dilute phase, distribution coefficient and efficiency. In order to develop empirical models to predict the pre concentration factor, distribution coefficient and efficiency, the correlations are developed by considering the variables, concentration of surfactant, solute, operating temperature and phase volume ratio that affect the above mentioned design parameters. Different combinations of dimensionless groups are analyzed, the following correlation is proposed. The constants and absolute arithmetic relative deviations for efficiency, distribution coefficient and pre-concentration factor are given in Table: 1.

Table 1. Constants and absolute arithmetic relative deviations for empirical equation.

Parameters	Constants				AARD (%)
	a	n_1	n_2	n_3	
η	39.994	-0.239	3.55	0.281	3.6
K_d	0.039	-1.513	24.196	1.771	21.2
f_c	99.63	0.005	0.001	-0.973	6.5

$$\eta, K_d \text{ \& } f_c = a \left(\frac{C_{\text{surfac tan t}}}{C_{\text{solute}}} \right)^{n_1} \left(\frac{\text{Operatingt emperature}}{273} \right)^{n_2} \left(\frac{V_s}{V_w} \right)^{n_3} \quad (5)$$

5. CONCLUSIONS

CPE using Triton X-100 as non-ionic surfactant can extract phenol without using organic solvents. The effect of nonionic surfactant concentration (TX-100) on cloud point was studied. The cloud point temperature decreases up to 3.5% (by wt) with the increase in Triton X-100 concentration and then it increases with increase in concentration. The cloud point temperature of Triton X-100 decreases with increase in phenol concentration. As NaCl and Na₂SO₄ concentration increases, the cloud point temperature decreases because of salting out effect and the cloud point temperature increases for NH₄SCN and NaI due to its salting-in effect. The design parameters such as phase volume ratio, pre-concentration factor, distribution coefficient and extraction efficiency are studied with respect to the effect of surfactant, solute and electrolyte concentration and for different set of operating temperatures. The distribution coefficient and extraction efficiency are increases with increase in surfactant and solute concentration for without electrolytes. For added electrolytes, Phase volume ratio decreases with increasing operating temperature and it is attained high value at 6 wt% Na₂SO₄ and NaI concentrations. The Distribution coefficient and extraction efficiency increases with increasing in operating temperature and NaCl and Na₂SO₄ concentration for salting-out effect. The Distribution coefficient and extraction efficiency decreases with increasing in NH₄SCN and NaI concentration and it increases with increasing in operating temperature. Based on experimental data correlation is proposed.

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