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Equilibrium in the Reactive Extraction of Aqueous Phenol Using Tributyl Phospate in n-Hexane

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Phenol is a hazardous chemical which usually contained in the wastewater from some industries, such as oil refineries, coal processing, and plastics. Phenol is dangerous substance to a microorganism although in low concentration in wastewater. According to the United State Environmental Protection Agency, the maximum concentration of phenol in wastewater is 1 ppm. This requirement is lower than the concentration of phenol in normal wastewater discharged from industries that is 100 to 1000 ppm. Phenolic substances are very difficult to be destroyed by oxidation in the present of microorganism. Chemical oxidation of phenolic substance using ozone or combination between the ozone and UV irradiation is impossible to handle huge amount of wastewater due to the expensiveness of ozone production and also its low solubility in water. The prospective method to recover of phenol from wastewater is reactive extraction in which phenol makes a complex with the extractant.

This research investigated the equilibrium of the reactive extraction of phenol from water using tributyl phosphate (TBP) in n-hexane. An equilibrium model has been developed in this research and the laboratory experiments have been carried out. The parameters of the laboratory experiment are the initial concentration of phenol in water, initial concentration of TBP in n-hexane, and the extraction temperature.

The experimental results showed that the higher the TBP concentration in n-hexane, the higher the amount of phenol which can be extracted to the organic phase. The correlation between the distribution coefficients (K_c) with the ratio of TBP concentration (Co_{TBP}) to the initial TBP concentration (Coi_{TBP}) in n-hexane can be formulated by $K_C = 11.59 - 12.002 Co_{TBP} / Coi_{TBP}$ with the sum of square of error of 10.87%. The lower the extraction temperature, the higher the amount of phenol extracted to the organic phase. The correlation between the distribution coefficients with the temperature (T) can be approached by $K_c = 1505.45(1/T) - 4.06$ with the sum of square of error of 2.63%. The value of distribution coefficient of physical equilibrium (K_p) decreases with the increase of temperature, meanwhile the value of the equilibrium constant of solvation reaction (K_r) is increase with increasing the temperature. The expression of K_r as a function of temperature is $K_r = -2.8636(1/T) + 0.0133$ with the sum of square of error of 0.04%.

Keywords: Equilibrium, Reactive Extraction, Phenol, Tributyl Phosphate, n-Hexane.

INTRODUCTION

Phenol is one of the major pollutants in wastewater generated in various industrial processes such as petroleum refineries, coal conversion, and plastic production plants. They are harmful to organisms even at low concentration (Igarashi *et al.*, 2004). Removing phenol and its derivatives from aqueous solution is not easy because of the following two main reasons: 1) Phenol is not easily oxidized by oxygen/ozone direct flushing and 2) Biological decomposition of phenol can never avoid the disposal of excess bioactive slurry generated during the main oxidation process (Kurumada *et al.*, 2004). The prospective method to recover of phenol from wastewater is reactive extraction in which phenol makes a complex with the extractant. Separation of phenols from dilute aqueous solution by use of tri-*n*-octyl phosphine oxide as extractant has been reported by MacGlashan *et al.* (1985). Urtiaga and Ortiz (1997) have studied the extraction of phenol using trialkylphosphine oxides (cyanex 923) in kerosene. Removal of phenol from an aqueous solution using hydrogel incorporated with extractant tributyl phosphate has been investigated and reported by Igarashi *et al.* (2004).

This research investigated the equilibrium of the reactive extraction of phenol from water using TBP in n-hexane. An equilibrium model has been developed in this research and the laboratory experiments have been carried out. The parameters of the laboratory experiment are the initial concentration of phenol in water, initial concentration of TBP in *n*-hexane, and the extraction temperature. In this experiment, TBP was used as extractant because it is a superior extractant species of phenol (Kurumada *et al.*, 2004). In the extraction process, TBP reacts with phenol to form a complexe, while *n*-hexane functions to dilute TBP. TBP has an advantage as extractant for use in aqueous extraction due to its negligible solubility in water (Shah and Tiwari, 1981). TBP in *n*-hexane has been used as extractant by some investigators. Matsumoto *et al.* (1998) has investigated synergistic extraction of lactic acid with tri-n-octylamine and TBP as extractants. In his research, *n*-hexane has been used as diluent. The recovery of acetic acid from dilute aqueous streams using liquid-liquid extraction with TBP has been studied by Shah and Tiwari (1981). Mulyono and Pardah (2008) has investigated the equilibrium on reactive extraction of lactic acid with TBP in *n*-hexane.

EXPERIMENTAL

Reagent and Solutions

Distilled water with the density of 0.9959 g/cm^3 and viscosity of 0.0089 g/(cm·s) was used in this experiment. Phenol, TBP, *n*-hexane, and other chemicals were supplied by Merck Co. as analytical reagent grade, and all were used without further purification.

Experimental Procedure

The experiments were done for the extraction of phenol with pure *n*-hexane and for the extraction of phenol with TBP diluted by *n*-hexane. For measuring the equilibrium distribution coefficient of phenol in *n*-hexane, the aqueous solution of phenol with a fixed concentration and *n*-hexane of equal volume of 50 cm^3 were mixed in a flask and shaken at a fixed temperature for one hour to attain the extraction equilibrium. After equilibrium condition was attained, the solution was then settled for one hour in a separatory funnel to separate the extract (organic) phase and the raffinate (aqueous) phase. Phenol concentration in the aqueous phase was determined by titration with known concentration of $Na_2S_2O_3$ solution using amylum as indicator. The concentration of phenol in organic phase was calculated by total mass balance of the phenol. The experimental parameters were phenol initial concentration (150, 200, 250, 300, and 350 ppm) and temperature (283, 293, 303, and 313 K).

The experiments for the extraction of phenol with TBP in *n*-hexane were carried out by shaken of equal volume (50 cm^3) of aqueous solution of phenol with solution of TBP in *n*-hexane. The experimental procedure was similar to that explained above, with the experimental parameters of phenol initial concentration (150, 200, 250, 300, and 350 ppm), temperature (283, 293, 303, and 313 K), and TBP concentrations in *n*-hexane (150, 200, 250, 300, and 350 ppm).

Theoretical Background

The mechanism of the reactive extraction of phenol using TBP in *n*-hexane is shown in Fig. 1. Phenol in aqueous phase is in equilibrium with the phenol in TBP-*n*-hexane phase. Phenol in the organic phase is also in chemical equilibrium with the complex of phenol·TBP which is produced from the solvation reaction between phenol and TBP. At the equilibrium between phenol in organic phase and in aqueous phase, the concentration-based equilibrium distribution coefficient (K_c) can be calculated by Eq. (1) as follows (MacGlashan *et al.,* 1985).

$$K_c = \frac{\left(C_{wi} - C_{wf}\right)}{C_{wf}} \times \frac{O}{W} \tag{1}$$

Eq. (1) is formulated based on the assumption that during the extraction, there is no change in solution volume and complete immiscibility between aqueous and organic phases. K_c can be defined as mole ratio of phenol in extract phase to the phenol in raffinate phase. Mole number of phenol in extract phase is the sum of phenol complexed with TBP and the uncomplexed phenol present in n-hexane. The formula of K_c is expressed by Eq. (2).

$$K_c = \frac{Co_{Phenol.TBP} + Co_{Phenol}}{Cw_{Phenol}} \tag{2}$$

In the extraction of phenol using pure *n*-hexane, the physical distribution coefficient (K_p) of phenol at equilibrium is defined as the ratio of phenol concentration in extract (organic) phase to the phenol concentration in raffinate (aqueous) phase as follows.

$$K_p = \frac{Cof}{Cwf} x \frac{O}{W} \tag{3}$$

In the extraction of phenol using TBP in *n*-hexane, the physical (uncomplexed) distribution coefficient of phenol in equilibrium is defined as:

$$K_p = \frac{Co_{Phenol}}{Cw_{Phenol}} \tag{4}$$

Eq. (4) can be written by Eq. (5).

$$Co_{Phenol} = K_p \cdot Cw_{Phenol} \tag{5}$$

In this extraction, phenol is considered to form 1:1 complexes with TBP according to the following reaction (Igarashi *et al.*, 2004):

$$Phenol + TBP \leftrightarrow Phenol.TBP \tag{6}$$

The equilibrium constant (K_r) for the complexation reaction as expressed by Eq. (6) is formulated by Eq. (7).

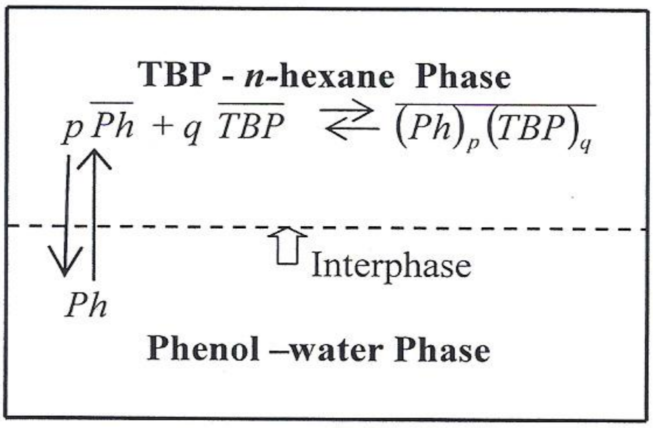

Figure 1. Mechanism of the reactive extraction of phenol using TBP in *n*-hexane.

$$K_r = \frac{Co_{Phenol.TBP}}{Co_{Phenol}.Co_{TBP}} \qquad (7)$$

Combining Eqs. (2), (4), and (7) yields (MacGlashan *et al.,*1985):

$$K_c = K_p + \left[K_p \cdot K_r \cdot Coi_{TBP} \left(\frac{Co_{TBP}}{Coi_{TBP}} \right) \right] \qquad (8)$$

At the equilibrium, the concentration of phenol in aqueous phase which is obtained by titrating raffinate solution can be used to calculated K_c using Eq. (2). Then, the values of K_p and K_r are evaluated by linear regression of Eq. (8). Coi_{TBP} in Eq. (8) is the initial TBP concentration in the organic phase, is calculated from the amout of TBP mixed with *n*-hexane. Co_{TBP} is the concentration of uncomplexed TBP in organic phase, can be calculated from the TBP mass balance as follows:

$$Coi_{TBP} = Co_{Phenol.TBP} + Co_{TBP} \qquad (9)$$

$Co_{Phenol\cdot TBP}$ is the concentration of phenol•TBP complex, is calculated from the phenol mass balance depicted by Eq. (10).

$$W\left(Cwi_{phenol} - Cw_{phenol}\right) = O\left(Co_{Phenol.TBP} + Co_{Phenol}\right) \qquad (10)$$

RESULTS AND DISCUSSION

Extraction of Aqueous Phenol with Pure *n*-Hexane

Extractions of aqueous phenol using pure *n*-hexane were done to calculate the values of K_p using Eq. (3). The values of K_p for the experiments with various initial phenol concentration at 30°C are shown in Table 1. The average value of K_p is 0.268.

Table 1. The values of K_p for the extraction of aqueous phenol with pure *n*-hexane in various initial phenol concentration at 30°C.

No.	Cwi_{Phenol} (ppm)	Cwf_{Phenol} (ppm)	Cof_{Phenol} (ppm)	K_p
1	315.56	246.10	69.47	0.28
2	276.02	231.88	44.14	0.19
3	256.64	206.15	50.49	0.24
4	195.03	165.51	29.52	0.18
5	158.31	109.10	49.21	0.45

Table 2. The values of Cw_{Phenol}, Co_{Phenol}, $Co_{Phenol\cdot TBP}$, and Co_{TBP} for the experiments using fixed Cwi_{Phenol} and Coi_{TBP}.

No.	Cwi_{Phenol} (ppm)	Coi_{TBP} (ppm)	Cw_{Phenol} (ppm)	Co_{Phenol} (ppm)	$Co_{Phenol\cdot TBP}$ (ppm)	Co_{TBP} (ppm)
1	315.56	990.44	160.54	45.32	109.71	880.74
2	276.02	849.03	141.68	26.97	107.38	741.65
3	256.64	707.45	170.70	41.81	44.14	663.33
4	195.03	565.98	110.88	19.78	64.38	501.61
5	158.31	424.46	51.29	23.14	83.89	340.57

Table 3. The values of K_c and Co_{TBP}/Coi_{TBP}.

No.	K_c	Co_{TBP}/Coi_{TBP}
1	0.97	0.89
2	0.95	0.87
3	0.50	0.94
4	0.76	0.89
5	2.09	0.80

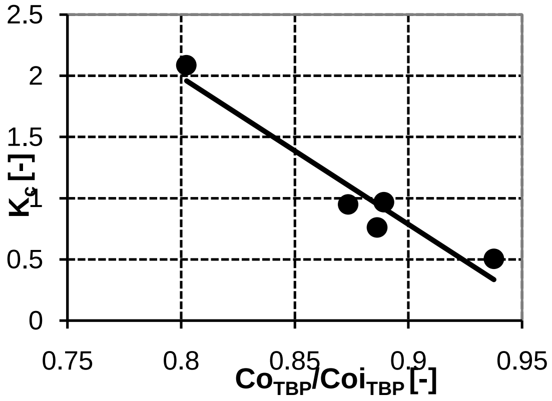

Figure 2. The values of K_c versus Co_{TBP}/Coi_{TBP}.

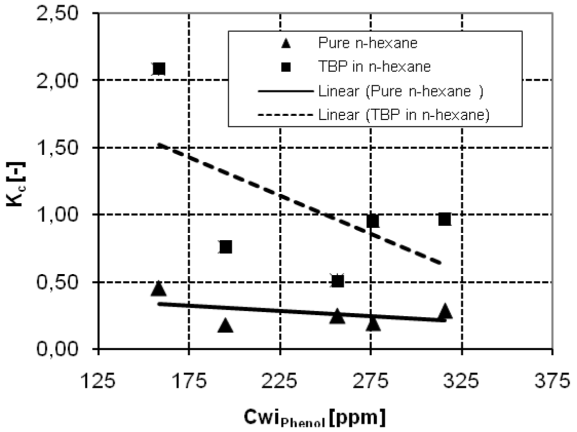

Figure 3. Values of K_c for the extraction of aqueous phenol using pure *n*-hexane and using TBP in *n*-hexane.

The Effect of TBP Concentration on Equilibrium Distribution Coefficient

The experiments were carried out at 30°C by varying TBP concentration in *n*-hexane at different initial phenol concentration in water. The calculated values of phenol concentration in raffinate phase (Cw_{Phenol}), phenol concentration in extract phase (Co_{Phenol}), concentration of phenol·TBP complex in extract phase ($Co_{Phenol \cdot TBP}$), and free TBP concentration in extract phase (Co_{TBP}) for the extraction with fixed initial phenol concentrations in water (Cwi_{Phenol}) and initial TBP concentration in *n*-hexane (Coi_{TBP}) are shown in Table 2. From the data shown in Table 2, then the values of equilibrium distribution coefficient (K_c) were calculated using Eq. (2). The values of Co_{TBP}/Coi_{TBP} were also calculated. The calculated values of K_c and Co_{TBP}/Coi_{TBP} are shown in Table 3 and plotted in Fig. 2.

The values of K_p and K_r can be calculated using linear regression based on Eq. (8) from the data in Table 3. The correlation between K_c and Co_{TBP}/Coi_{TBP} can be expressed as $K_C = 11.59 - 12.002 Co_{TBP} / Coi_{TBP}$ with sum of square of error of 10.87%. In can be seen in Fig. 2 that the higher the initial TBP concentration in organic phase, the higher the value of K_c. The higher the amount of TBP in *n*-hexane, the higher the amount of phenol reacted with TPB to form the complex of phenol·TBP. So the amount of the extracted phenol from the aqueous phase to the organic phase increased with increasing the initial TBP concentration in the organic phase.

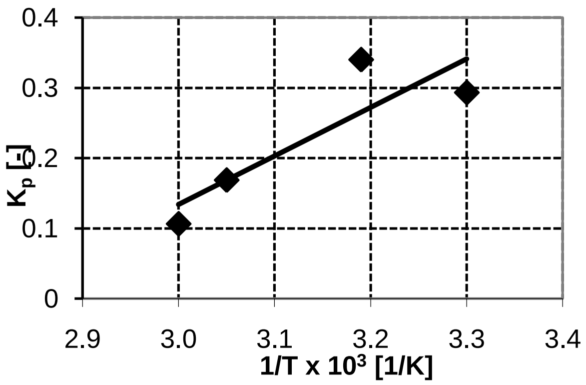

Figure 4. K_p as a function of extraction temperature.

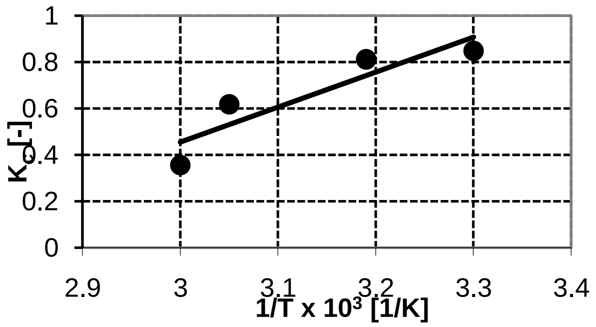

Figure 5. K_c versus *1/T* for the extraction of aqueous phenol with TBP in *n*-hexane.

The values of K_c for the extraction of aqueous phenol using pure *n*-hexane were calculated using Eq. (1), while Eq. (2) was used to calculate the values of K_c for the extraction of aqueous phenol using TBP in *n*-hexane. Figure 3 shows the comparison between the both values as a function of the initial phenol concentration in aqueous phase. It can be seen in Fig. 3 that the values of K_c for the extraction of phenol using TBP in *n*-hexane are higher than those for the extraction of phenol using pure *n*-hexane.

Effect of Temperature

The effect of temperature on the equilibrium distribution coefficient was studied by carrying out the experiments with the initial phenol concentration in aqueous phase of 350 ppm and initial concentration of TBP in organic phase of 424.5 ppm. The experiments were done at different temperatures of 303, 313, 328, and 333 K. The effect of temperature on the values of K_p was also studied by carrying out the extraction of phenol using pure *n*-hexane with a fixed initial phenol concentration at those temperatures. The values of K_p as a function of temperature is depicted in Fig. 4. It is shown in Fig. 4 that the value of K_p decreases with increasing the temperature due to increasing phenol solubility in water by increasing temperature. So the higher the extraction temperature, the lower the amount of phenol extracted to the *n*-hexane.

The values of K_c for the extraction of phenol using TBP in *n*-hexane with initial phenol concentration in aqueous phase of 350 ppm and initial concentration of TBP in organic phase of 424.5 ppm at different temperature is illustrated in Fig. 5. Figure 5 shows that the value of K_c decreases with increasing the extraction temperature. The phenol solubility in water increases with increasing the temperature, so the amount of phenol extracted to the organic phase is decreased by increasing the temperature. The expression of K_c as a function of *1/T* can be formulated by linear regression of the

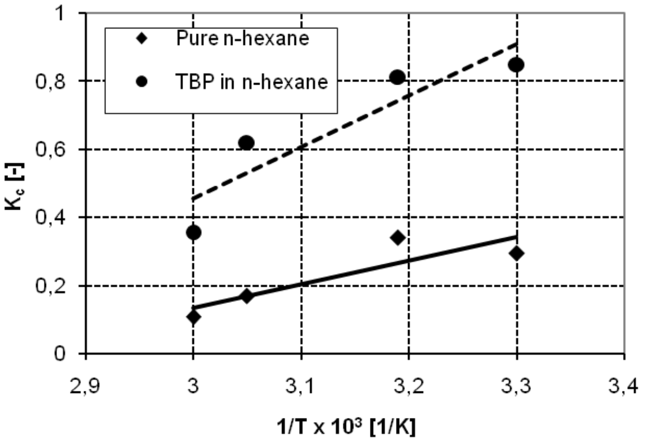

Figure 6. The comparison of K_c for the extraction of phenol with pure *n*-hexane ($K_c = K_p$) and with TBP in *n*-hexane.

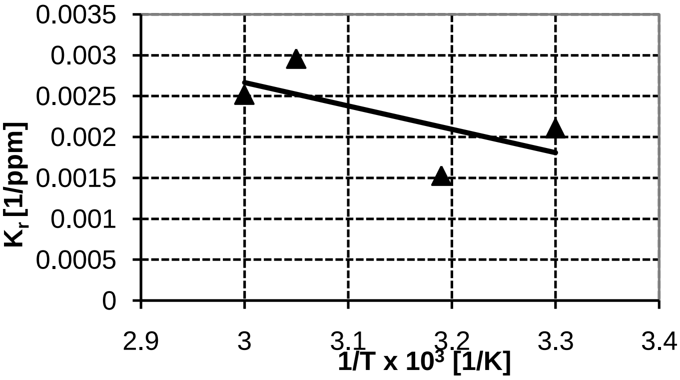

Figure 7. K_r as a function of temperature.

data, and the result is $K_c = 1505.45(1/T) - 4.06$ with sum of square of error of 2.63%.

The comparison between the values of K_c for the extraction of phenol with pure *n*-hexane ($K_c = K_p$) and that of the extraction of phenol with TBP in *n*-hexane is shown in Fig. 6. Fig. 6 reveals that for all temperatures the distribution coefficients of phenol extraction with pure *n*-hexane are lower than those of the extraction of phenol with TBP in *n*-hexane. By the presence of TBP in *n*-hexane, there is solvation reaction between phenol and TBP in organic phase to form phenol·TBP complex. So the presence of TBP in *n*-hexane increases the amount of phenol extracted from aqueous phase to the organic phase.

To measure the amount of phenol reacted with TBP to form a complex of phenol•TBP in organic phase, the K_r was calculated at different temperatures using Eq. (7) or Eq. (8). The calculated result of K_r is shown in Fig. 7. It is known from Fig. 7 that the value of K_r increased with increasing the extraction temperature. The expression of K_r as a function of temperature can be formulated as $K_r = -2.8636(1/T) + 0.0133$ with sum of square of error of 0.04%.

CONCLUSIONS

The reactive extraction of phenol from aqueous solution with TBP in *n*-hexane has been studied. Based on the results of this study, the following conclusions are made.

1. The equilibrium distribution coefficient of the extraction of aqueous phenol with pure *n*-hexane is lower than that of the

aqueous phenol extraction with TBP in *n*-hexane.

2. The equilibrium distribution coefficient for the extraction of aqueous phenol both with pure *n*-hexane and with TBP in *n*-hexane tend to decrease with increasing temperature.
3. The correlation between K_c and Co_{TBP}/Coi_{TBP} can be expressed as $K_C = 11.59 - 12.002 Co_{TBP} / Coi_{TBP}$ with sum of square of error of 10.87%.
4. The expression of K_c as a function of temperature in K can be formulated as $K_C = 1505.45(1/T) - 4.06$ with sum of square of error of 2.63%.
5. The expression of K_r as a function of temperature is $$K_r = -2.8636(1/T) + 0.0133$$ with sum of square of error of 0.04%.

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NOMENCLATURE

$Co_{Phenol.TBP}$ = Concentration of phenol•TBP complex in organic phase at equilibrium, ppm.

Co_{Phenol} = Concentration of phenol in extract (organic) phase at equilibrium, ppm.

Co_{TBP} = Concentration of free TBP in extract (organic) phase at equilibrium, ppm.

Coi_{TBP} = Initial concentration of TBP in organic phase, ppm.

Cof_{Phenol} = Concentration of phenol in extract (organic) phase at equilibrium for the extraction with pure *n*-hexane, ppm.

Cwf_{Phenol} = Concentration of phenol in raffinate (aqueous) phase at equilibrium for the extraction with pure *n*-hexane, ppm.

C_{wf} = Concentration of solute in aqueous phase at equilibrium, ppm.

C_{wi} = Initial concentration of solute in aqueous phase, ppm.

Cw_{Phenol} = Concentration of phenol in raffinate (aqueous) phase at equilibrium, ppm.

Cwi_{Phenol} = Initial concentration of phenol in aqueous phase, ppm.

K_c = Equilibrium distribution coefficient, concentration of phenol in organic phase divided by concentration of phenol in aqueous phase.

K_p = Equilibrium distribution coefficient of uncomplexed phenol.

K_r = Equilibrium constant of 1:1 solvation/complexation reaction, 1/ppm.

O = Volume of organic phase, cm^3.

W = Volume of aqueous phase, cm^3.

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