

CHAPTER V

RESULTS AND DISCUSSION

5.1 Test for suitable extractant and surfactant

The batch test designed for searching suitable extractants for the system could be performed by comparing percentage of zinc extraction of ten types of extractant. The results shown in figure 5.1 and table 5.1 indicated that the extractants giving percentage of extraction above 50% extraction and K value being greater than unity were ammonium persulfate and diammonium hydrogen phosphate. These extractants were used in further experiments. But the limitation of using ammonium persulfate occurred after using this extractant in continuous process. Because it could corrode metal coating agitator of equipment of the process. For this reason, diammonium hydrogen phosphate was chosen as an extractant for this system. To find the optimum concentration of extractant for using in extracting solution, the percentage of zinc extraction at various concentrations of the extractant were compared. From figure 5.2 and table 5.2, the maximum percentage of extraction and K value occurred at 8% wt/wt of diammonium hydrogen phosphate concentration. It was concluded that the extracting solution of this system was 8% wt/wt of diammonium hydrogen phosphate in aqueous solution.

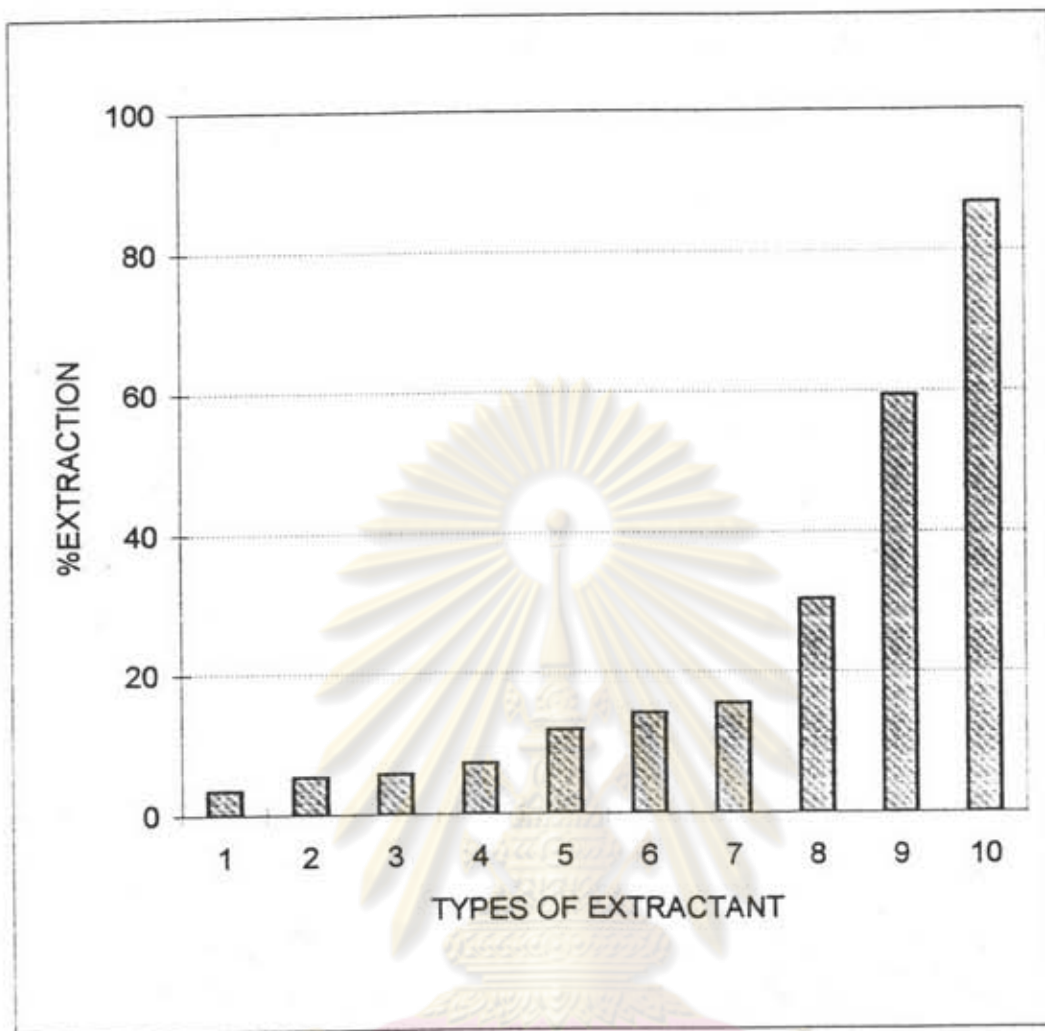


Figure 5.1 % Extraction of various types of extractant .

Note :

- | | |
|----------------------------------|-----------------------------------|
| 1 =Magnesium sulfate | 6 = Ammonium sulfate |
| 2 =Sodium thiosulfate | 7 = Sodium metasulfate |
| 3 =Sodium sulfate | 8 = Disodium hydrogen phosphate |
| 4 =Ammonium dihydrogen phosphate | 9 = Diammonium hydrogen phosphate |
| 5 =Aluminium sulfate | 10 = Ammonium persulfate |

Experimental conditions

Initial zinc concentration : 867 ppm.

Agitator speed : 600 rpm.

Phase ratio : 1:1

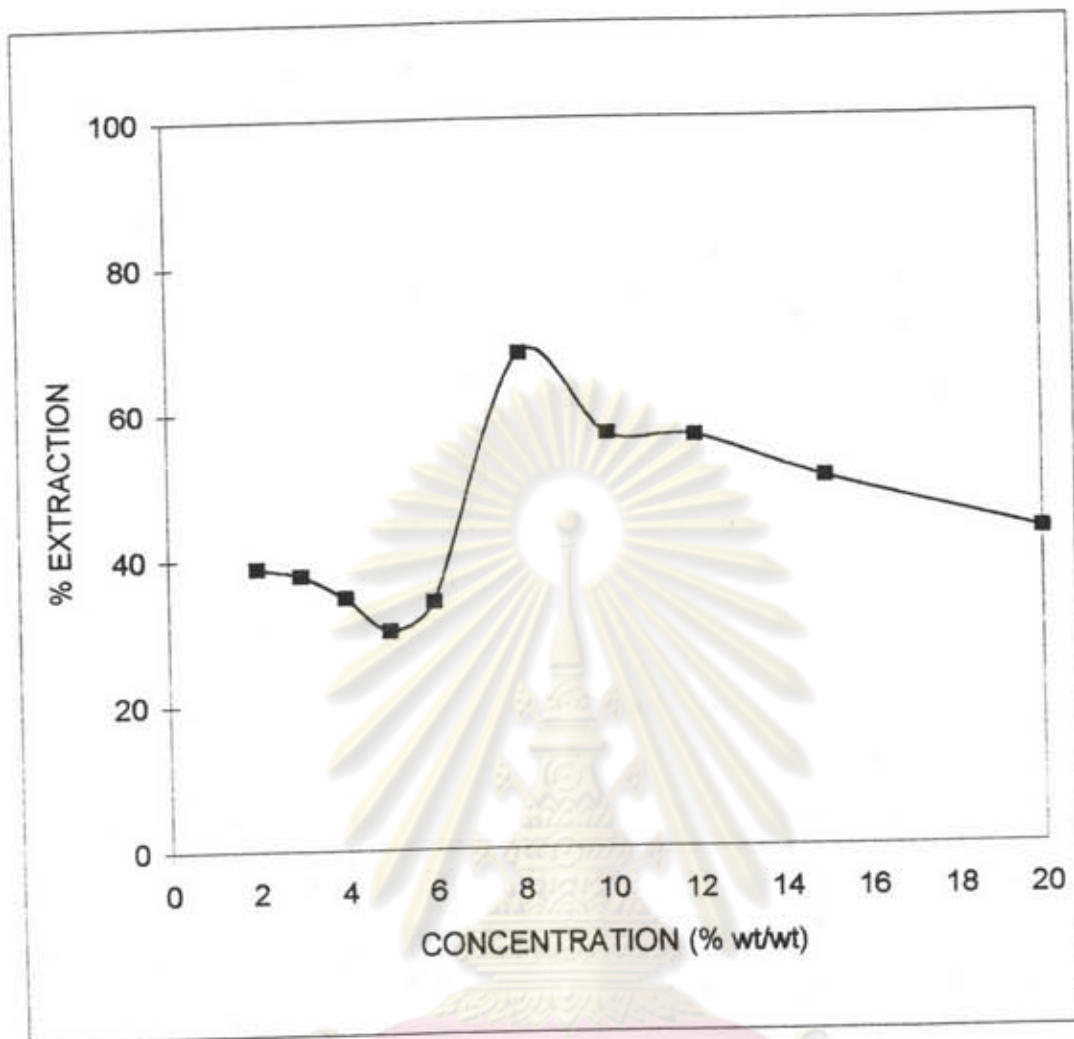


Figure 5.2 % Extraction at various concentration of diammonium hydrogen phosphate.

Experimental conditions

Initial zinc concentration : 847 ppm.

Agitator speed : 600 rpm.

Phase ratio : 1:1

Table 5.1 K value of various types of extractant.
The initial zinc concentration was 867 ppm.

Types of extractant	K value
Magnesium sulfate	0.04
Sodium thiosulfate	0.06
Sodium sulfate	0.06
Ammonium dihydrogen phosphate	0.08
Aluminium sulfate	0.13
Ammonium sulfate	0.17
Sodium metasulfate	0.19
Disodium hydrogen phosphate	0.44
Diammonium hydrogen phosphate	1.46
Ammonium persulfate	6.54

Table 5.2 K value at various concentrations of diammonium hydrogen phosphate.
The initial zinc concentration was 847 ppm.

Concentration (% wt/wt)	K value
2	0.63
3	0.60
4	0.53
5	0.43
6	0.51
8	2.11
10	1.30
12	1.29
15	1.02
20	0.75

In further study, four types of anionic surfactant such as sodium lauryl sulfate (SLS), sodium dodecyl benzene sulfonate (SDBS), Sodium diethylsulfosuccinate, and disodium laurethsulfosuccinate were performed. Owing to the micellar property, anionic surfactants had known that they gave micelles which their negative charges of hydrophilic head group directed toward the aqueous solution, so micelles of them could bind cation of metal.

From the results as shown in figure 5.3, and table 5.3, they were found that percentage of extraction of all types of the studied surfactant given approximately 15 to 20% extraction and K value were in the range of 0.16 to 0.33 when the extractant was not added in extracting solution. This indicated that using only surfactant as a extractant could extract zinc from lubricating oil in low percentage of extraction. This could explained by a assumption of electrostatic attraction between micelles and metal ions were not stable. So partial contents of metal ion could be free from micelles. It induced remaining of zinc in lubricating oil after the extraction and then decreased the percentage of extraction. Since surfactants caused emulsion suppressing phase separation of aqueous solution and oil. So SDBS being faster phase separation than other surfactant was chosen as a represent of anionic surfactants in this system. The confirmation of the extraction without extractant could be shown in figure 5.4, and table 5.4. In addition, the results from this figure also showed relationship between contact time and percentage of extraction.

From figure 5.5 and table 5.5 demonstrated that when using any types of surfactant and ammonium persulfate as extractant in extracting solution, percentage of extraction and K value were higher than those using only ammonium persulfate

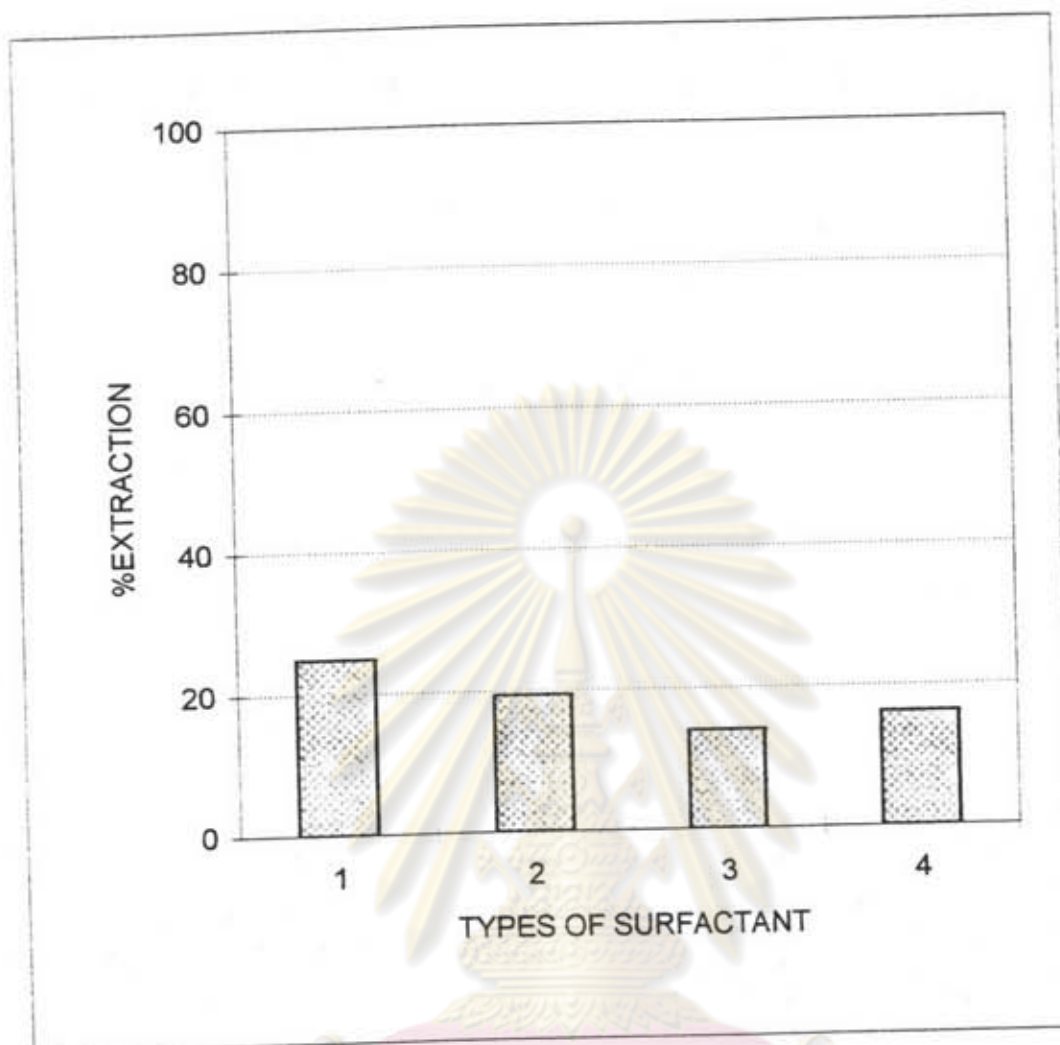


Figure 5.3 % Extraction of various types of surfactant

Note:

1 = Sodium lauryl sulfate

2 = Sodium dodecyl benzene sulfonate

3 = Sodium dioctylsulfosuccinate

4 = Disodium laureth sulfosuccinate

Experimental conditions

No extractant

Initial zinc concentration : 902 ppm.

Agitator speed : 600 rpm.

Phase ratio : 1:1

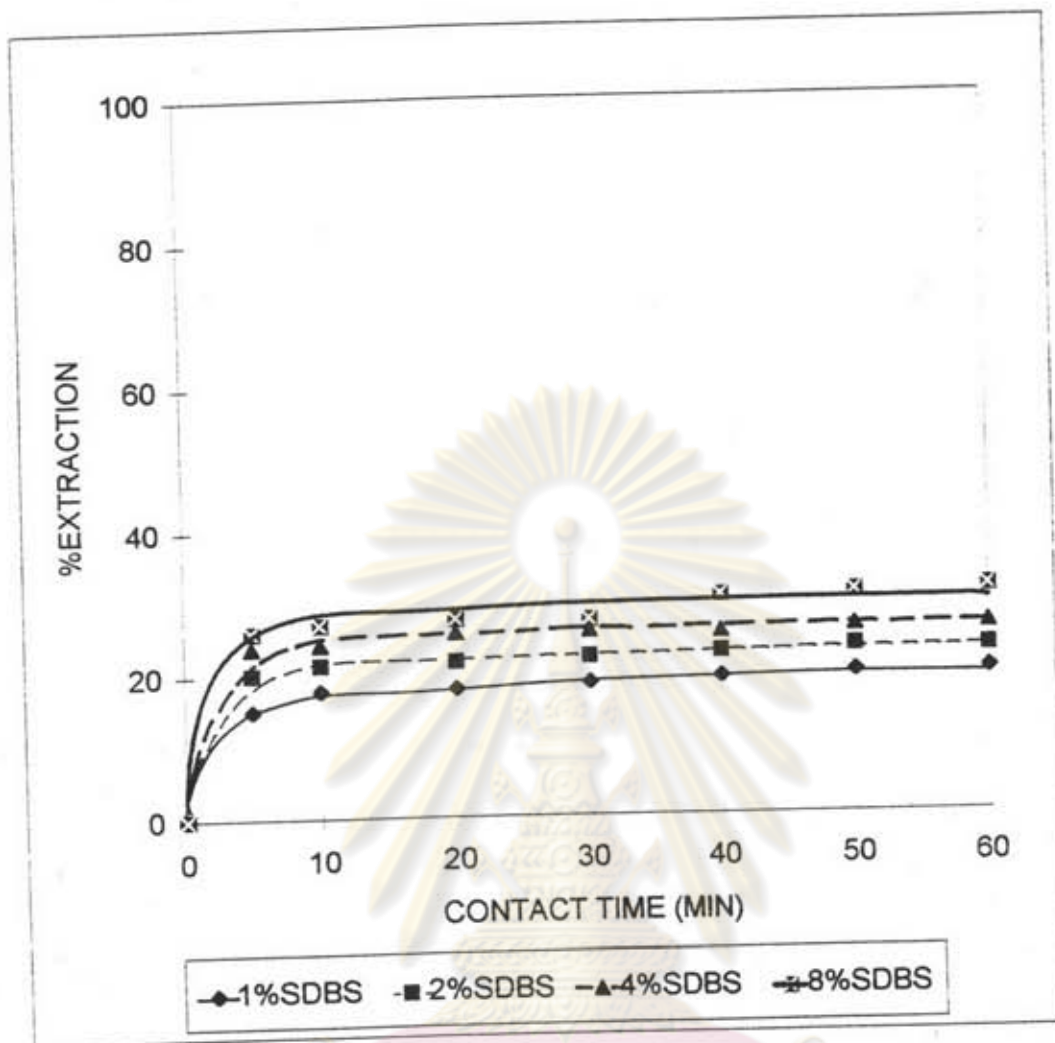


Figure 5.4 %Extraction at various SDBS concentrations

Experimental conditions

No extractant

Initial zinc concentration : 866 ppm.

Agitator speed : 600 rpm.

Phase ratio : 1:1

Table 5.3 K value of various types of surfactant.
The initial zinc concentration was 902 ppm.

Types of surfactant	K value
Sodium lauryl sulfate	0.33
Sodium dodecyl benzene sulfonate	0.24
Sodium dioctylsulfosuccinate	0.16
Disodium laurethsulfosuccinate	0.19

Table 5.4 K value at various SDBS concentration without extractant.
The initial zinc concentration was 866 ppm.

SDBS concentration (% wt/wt)	K value
1	0.25
2	0.30
4	0.35
8	0.46

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

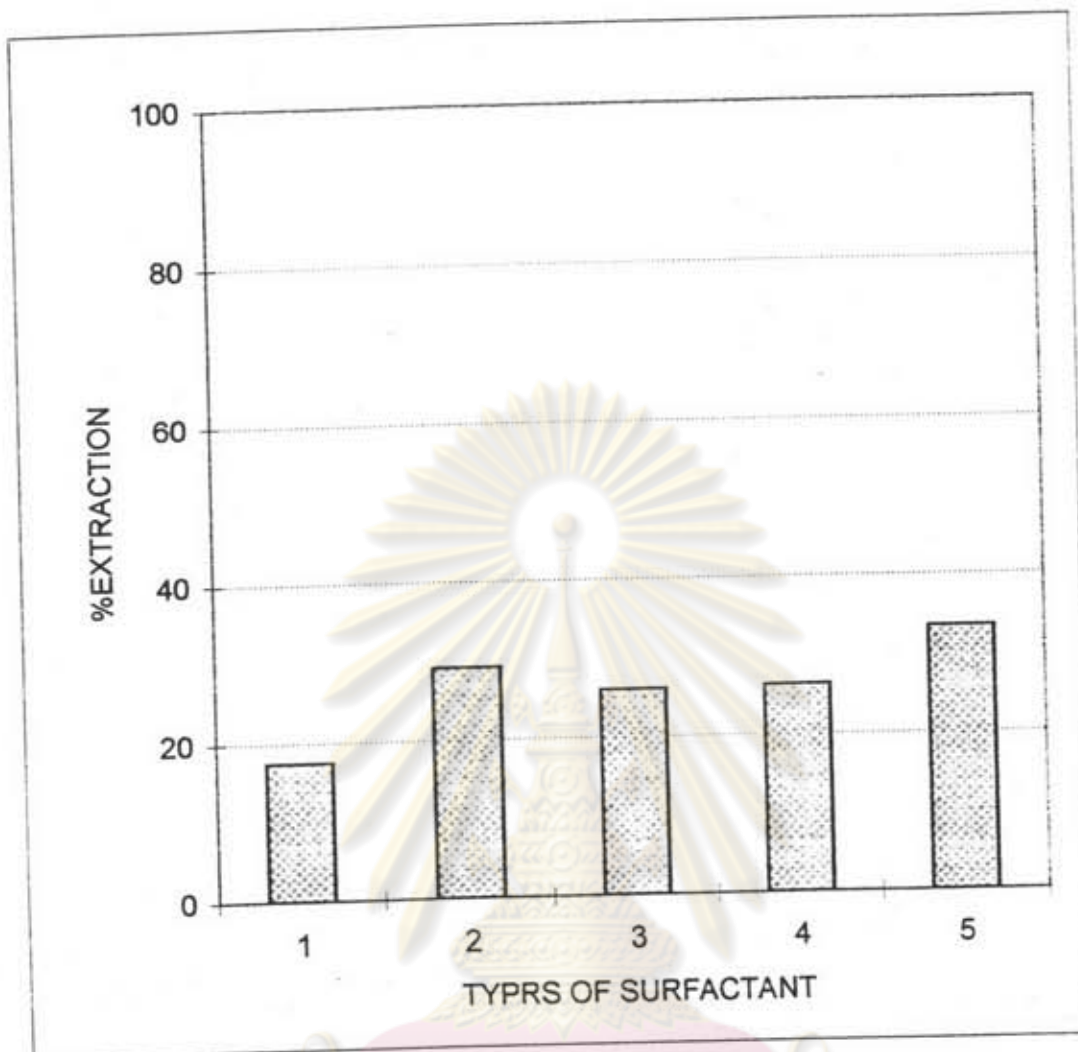


Figure 5.5 % Extraction of extracting solution consisting of various types of surfactant and ammonium persulfate.

Note :

1 = no surfactant

2 = Sodium lauryl sulfate

3 = Sodium dodecyl benzene sulfonate

4 = Sodium dioctylsulfosuccinate

5 = Disodium laurethsulfosuccinate

Experimental conditions

Extractant : 5 % wt/wt of ammonium persulfate

Initial zinc concentration : 884 ppm.

Agitator speed : 600 rpm.

Phase ratio : 1:1

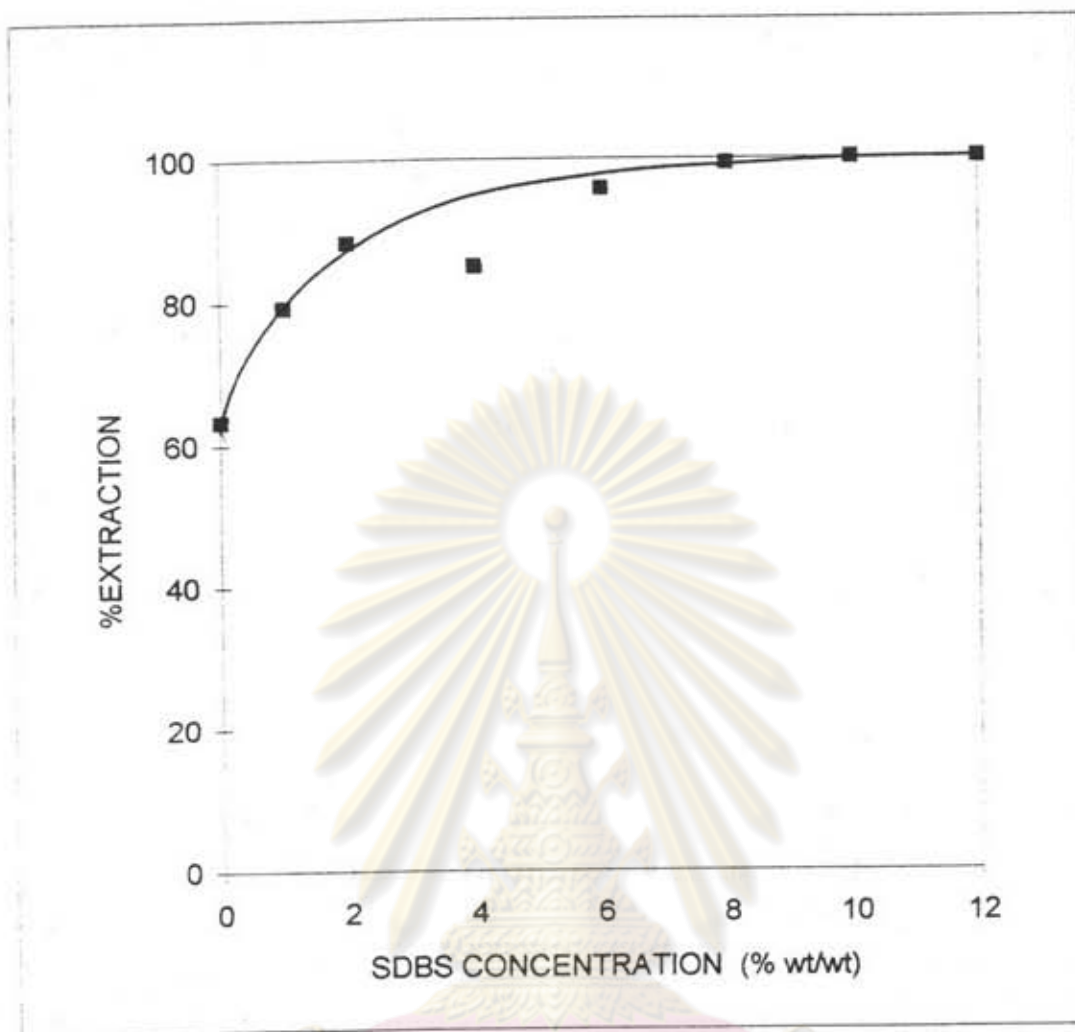


Figure 5.6 %Extraction at various SDBS concentrations, diammonium dihydrogen phosphate.

Experimental conditions

Extractant : 8 % wt/wt of diammonium dihydrogen phosphate

Initial zinc concentration : 847 ppm.

Agitator speed : 600 rpm.

Phase ratio : 1:1

Table 5.5 K value of extracting solution consisting of various types of surfactant and ammonium persulfate. The initial zinc concentration was 884 ppm.

Types of surfactant	K value
no surfactant	0.21
Sodium lauryl sulfate	0.41
Sodium dodecyl benzene sulfate	0.35
Sodium dioctylsulfosuccinate	0.36
Disodium laurethsulfosuccinate	0.50

Table 5.6 K value of extracting solution consisting of various SDBS concentrations and diammonium hydrogen phosphate. The initial zinc concentration was 847 ppm.

Concentration (% wt/wt)	K value
0	1.72
1	3.81
2	7.56
4	5.62
6	21.89
8	140.17
10	∞
12	∞

as extractant in the solution. This indicated that the surfactant was able to increase zinc extraction.

From figure 5.6 and table 5.6, an increase SDBS concentration varied from 1 to 8% wt/wt concentration increased percentage of extraction and K value. When extracting solution consisting of SDBS and diammonium hydrogen phosphate could remove all of zinc from oil phase at approximately 10 to 12% wt/wt SDBS concentration. And at 8% wt/wt SDBS concentration, almost zinc could be removed.

From above results, suitable extractant using in the extracting solution was a aqueous solution of 8% wt/wt of diammonium hydrogen phosphate and selected surfactant was SDBS.

5.2 Chemical reaction

In this system, the extractant was diammonium hydrogen phosphate and the solute was ZDDP. ZDDP had been used as antiwear and antioxidant additives in lubricating oil. It was typically prepared by reacting a dialkyl dithiophosphoric acid with a basic zinc compound. The structure of ZDDP including those of the formulae as shown in figure 5.7 were proposed by Colclough (1989).

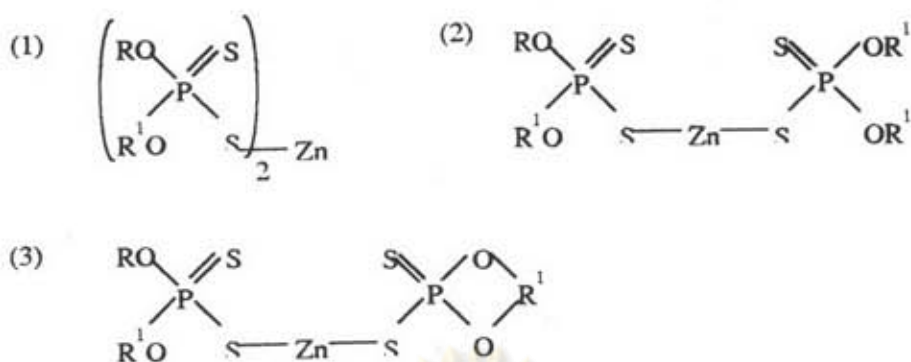
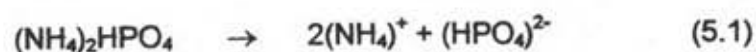


Figure 5.7 Structure of ZDDP

Where the group R might be an aliphatic hydrogen- and carbon- containing group having at least 4 carbon atoms, e.g. 4-10 carbon atom.

R¹ was a hydrogen- and carbon- containing group containing at least 12 carbon atoms and either (a), >C=N group or (b) the group $-(\text{C}_n\text{H}_{2n-p}\text{R}^2\text{P}_p\text{O})_q$, R² was an alkyl group, n was an integer range from 2 to 5, p was zero or an integer range from 1 to 5 and q was an integer range from 2 or more.

Diammonium hydrogen phosphate dissolved in water was ionized into cation (NH₄⁺) and anion (HPO₄²⁻). The ionization reaction of diammonium hydrogen phosphate could be illustrated in equation 5.1 :



In a liquid-liquid extraction process, the ZDDP which dissolved in oil was contacted with diammonium hydrogen phosphate which dissolved in extraction

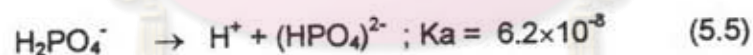
solution. Agitation would break bonds between zinc ion and ligands of ZDDP and therefore zinc ion was free in mixture of oil and extraction solution. HPO_4^{2-} had an affinity to bind zinc ion to complex forms. These complexes would gradually precipitate after settling system for a moment. For this mechanism, zinc ion was transferred from oil phase into aqueous phase. The reaction between zinc ion and hydrogen phosphate ion was proposed in two different ways that were



and/or



From ionization of phosphoric acid, steps of ionization and ionization constant of each step could be shown in following equations



From ionization constants of above equations, it was found that hydrogen phosphate ions had rarely an occasion to ionize into hydrogen ion and phosphate ion since it had very low ionization constant. So the equation 5.3 had rarely an occasion to occur. The hypothesis for the reaction between zinc ion and anion of extractant was shown in equation 5.2. The structural mechanism of the extraction reaction written from above assumption was shown in figure 5.8.

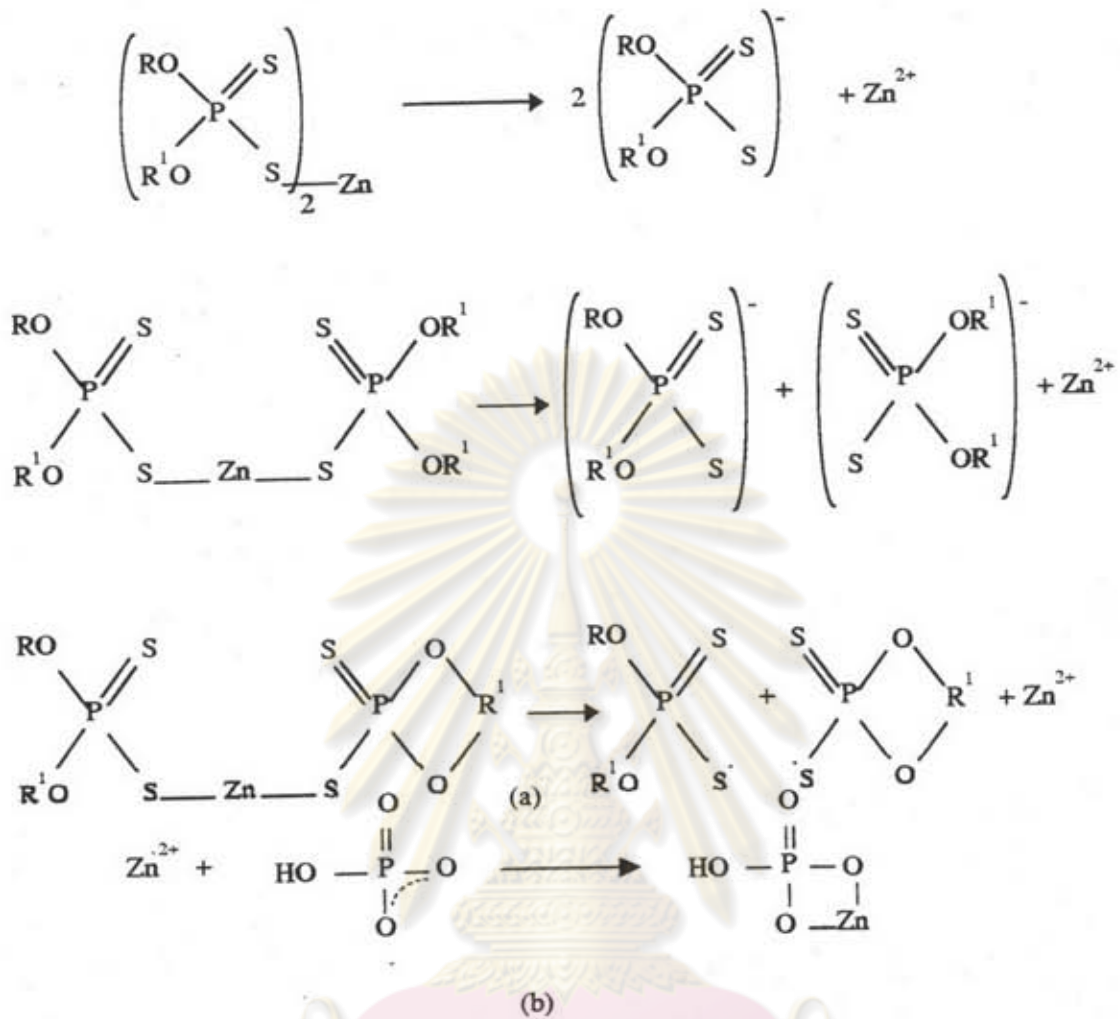


Figure 5.8 Structural mechanism of the extraction reaction.

(a) ionization reaction of ZDDP,

(b) reaction between zinc ion and hydrogen phosphate ion.

5.3 Effect of agitator speed

In batch process, figure 5.9 was a plot between agitator speed varied from 400 to 800 rpm and percentage of extraction. It seemed that all agitator speeds gave relatively constant percentage of extraction being in the range of 58 to 68% extraction. In the liquid-liquid extraction process, mass transfer depended upon the interfacial area. Agitation had been expected to break large drops into small one which might increase interfacial area and thus the mass transfer was increased. Obviously, experimental results were not corresponding to this principle. But it could be explained by the extraction with chemical reaction. Since mass transfer of this system arose from chemical reaction between zinc ion and hydrogen phosphate ion which the rate of reaction was important above the effect of interfacial area, it was found that the rate of a liquid-liquid extraction was entirely controlled by the kinetics of the reaction, then it should be independent on the interfacial area and hence of the degree of agitation. But rate of reaction occurred more quickly by degree of agitation. In addition, agitator speeds at holding constant contact time varied from 400 to 800 rpm was sufficient to make well-mixed system, then the reaction could occur completely. It indicated that agitator speed at 600 rpm which was used in various conditions of all the experiments was enough for the reaction occurred completely.

In continuous process, the experimental results were similar to those in the batch process as shown in figure 5.10. The percentage of extraction was around 20 to 30%. It was found that low agitator speed was preferred to operate the agitated extraction column because of practical operation especially in the system which

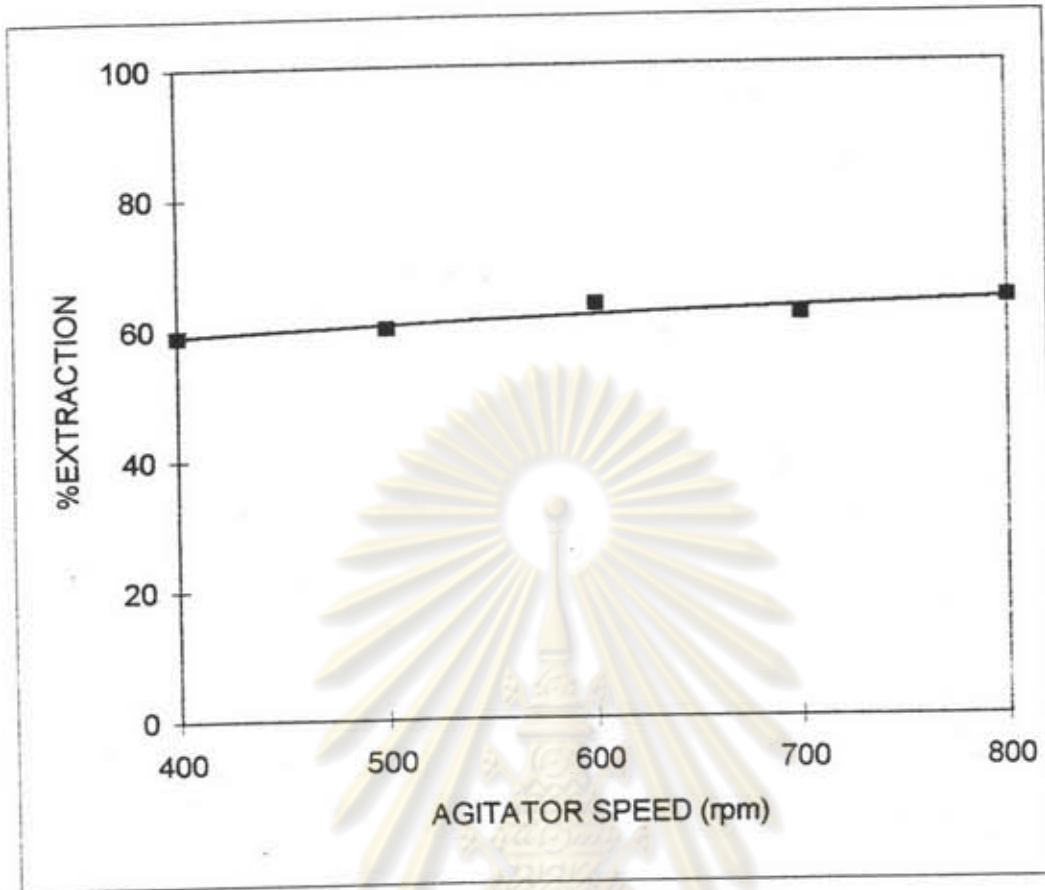


Figure 5.9 %Extraction at various agitator speeds in batch process.

Experimental conditions

Extractant : 8% wt/wt of diammonium hydrogen phosphate

Initial zinc concentration : 873 ppm

Phase ratio : 1:1

ศูนย์วิทยาศาสตร์
จุฬาลงกรณ์มหาวิทยาลัย

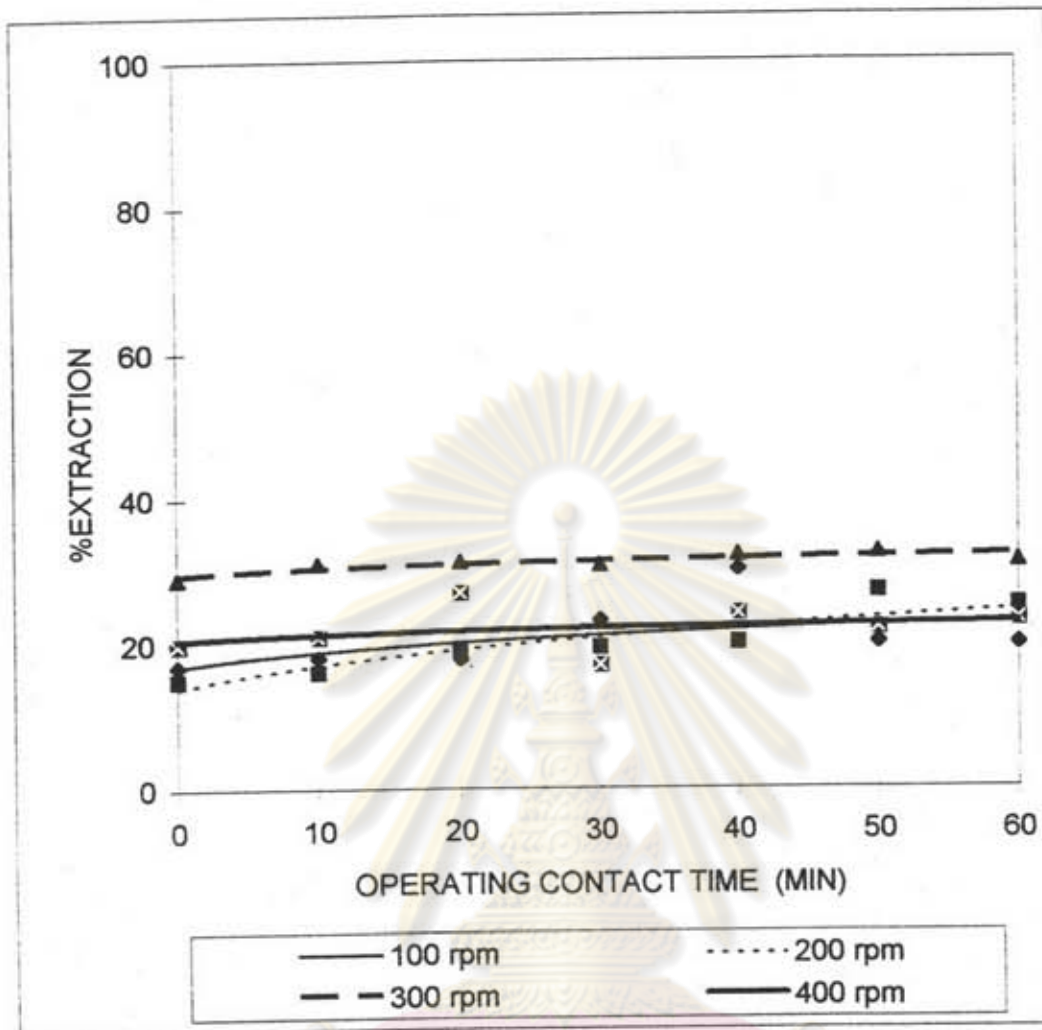


Figure 5.10 %Extraction at various agitator speeds in continuous process.

Experimental conditions

Extractant : 8% wt/wt of diammonium hydrogen phosphate

Initial zinc concentration : 842 ppm.

Phase ratio : 1:1

Table 5.7 K value at various agitator speeds in batch process.
The initial zinc concentration was 873 ppm.

Agitator speed (rpm)	K value
400	1.44
500	1.50
600	1.73
700	1.60
800	1.76

Table 5.8 K value at various agitator speeds in continuous process
The initial zinc concentration was 842 ppm.

Agitator speeds (rpm)	K value
100	0.26
200	0.25
300	0.45
400	0.28

จุฬาลงกรณ์มหาวิทยาลัย

emulsion occurred. At higher agitator speed, continuous process could not be operated because of error condition that was oil feed could not flow up in column and the aqueous solution could not flow down to the bottom end of the column. This condition was occurred from improper characteristic of agitator .

Table 5.7 and 5.8 indicated that K value related to variation of agitator speed and gave corresponding result to the graph of percentage of extraction in both of batch process and continuous process.

5.4 Effect of SDBS concentration

From figure 5.11, in batch process, percentage of extraction of the process without surfactant process was about 50 to 60%. After the addition of surfactant as a promoter of the extraction, percentage of extraction increased to 80% at 1% wt/wt SDBS concentration and to 99% at 8% wt/wt SDBS concentration.

Effect of SDBS concentration in this experiment, the surfactant was used as promoter of the extraction of zinc complex ions from lubricating oil. When surfactant was dissolved in water at the concentration above the critical micelle concentration, CMC value, their molecules would aggregate into cluster called micelle. The outer portion and the inner portion of micelle showed ionic and nonionic charges, respectively. The micellization of anionic surfactant gives profit for the extraction as the micelle having negative charge of hydrophilic portions which directed to the aqueous solution, could capture positive charge of zinc ion. After oil phase and aqueous phase were mixed, then zinc ion broken from zinc complex ion by agitating

force was interacted at the surface of micelle and transferred to aqueous solution. At below critical micelle concentration, surfactant molecule could interact with cationic ions but this ability to capture was lower than that at above critical micelle concentration because micelles had been higher charge density than surfactant molecules and therefore had higher ability to capture cationic metals. When micelles bound zinc ion was transferred from oil phase to aqueous phase, hydrogen phosphate ion dissolved in aqueous solution could be interacted to zinc ion, due to higher affinity to bound cation. So zinc ion was removed from oil phase to another phase. Increasing surfactant concentration increased amount of micelles, then improved ability to bind cation.

The other important property that effect on this system was solubilization. This property occurred when surfactant formed micelle, promoted the percentage of extraction. When oil was contacted with micellar solution, it would apparently dissolve into the interior of a micelle which had hydrophobic portions. ZDDP dissolved in oil could be transferred into the core of a micelle by this way. This phenomenon led zinc to the third phase occurred at the interface of two liquid phase. So zinc content in oil phase was reduced.

When using higher concentration of surfactant, it tended to get higher amount of micelles. If a large amount of micelles present in the system, more zinc ion was bound to micelles, it preferred high percentage of extraction. But when concentration of surfactant increased, it would increase emulsion formation that retarded the coalescence of drops, results in slow phase separation. This effect had been most considered especially operating in the column.

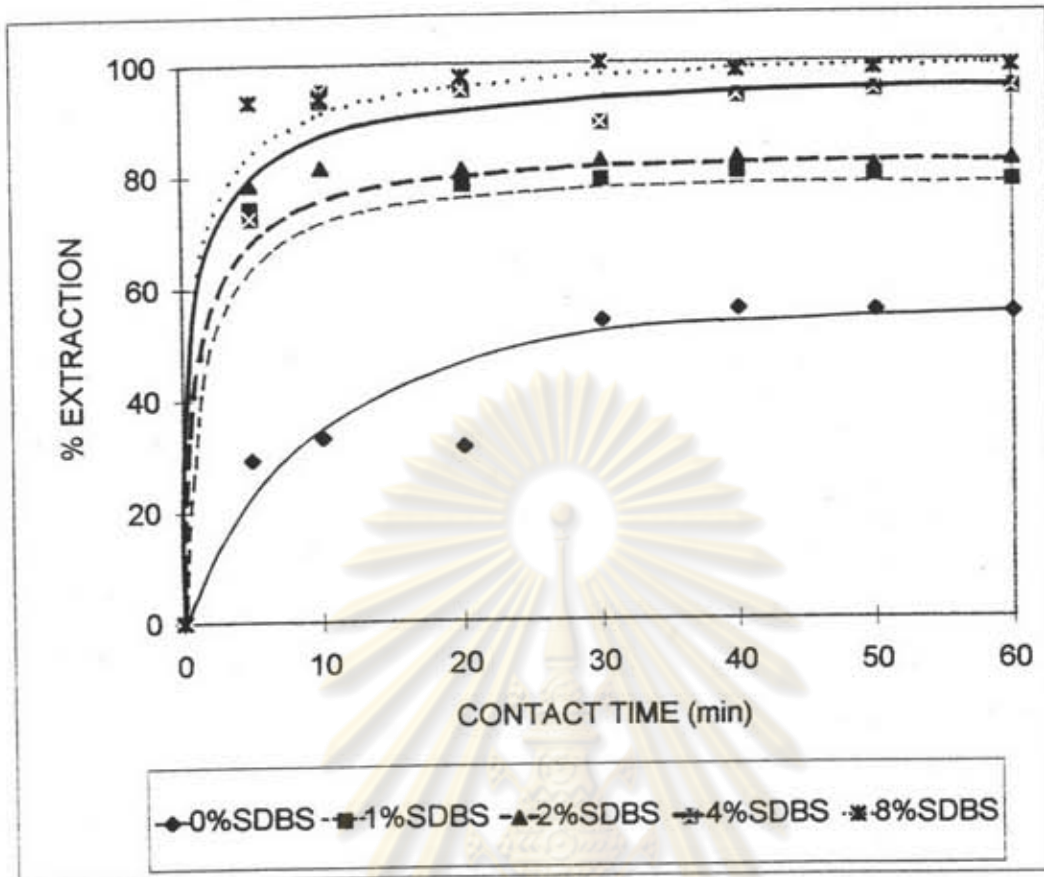


Figure 5.11 %Extraction at various SDBS concentrations in batch process.

Experimental conditions

Extractant : 8% wt/wt of diammonium hydrogen phosphate

Surfactant : SDBS

Initial zinc concentration : 845 ppm.

Agitator speed : 100 rpm

Phase ratio : 1:1

จุฬาลงกรณ์มหาวิทยาลัย

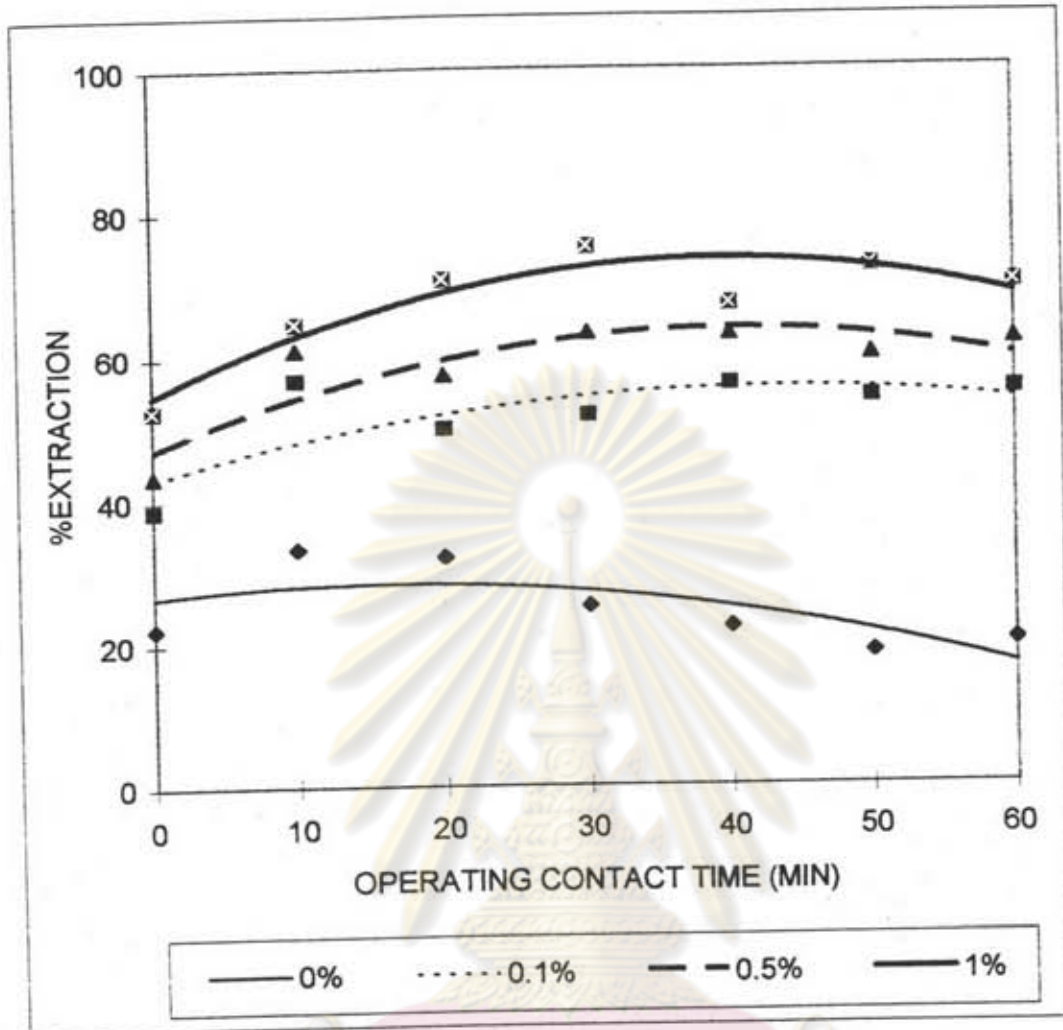


Figure 5.12 %Extraction at various SDBS concentrations in continuous process.

Experimental conditions

Extractant : 8% wt/wt of diammonium hydrogen phosphate

Surfactant : SDBS

Initial zinc concentration : 802 ppm.

Agitator speed : 100 rpm.

Phase ratio : 1:1

Table 5.9 K value at various SDBS concentrations in batch process.
The initial zinc concentration was 845 ppm.

SDBS concentration (% wt/wt)	K value
0	1.21
1	3.61
2	4.63
4	19.65
8	96.64

Table 5.10 K value at various SDBS concentrations in continuous process
The initial zinc concentration was 802 ppm.

SDBS concentration (% wt/wt)	K value
0	0.33
0.1	1.07
0.5	1.41
1	2.08

จุฬาลงกรณ์มหาวิทยาลัย

In continuous process, the results gave agreement with batch process as shown in figure 5.12. In addition, we found that using a large amount of surfactant made problems to operate the extraction column. Since viscosity was increased due to emulsion property. It might oppose the flow of the oil from the bottom end to the top end and the flow of the aqueous solution from the top end to the bottom end. For this reason, low concentration was preferred to use in the system.

K value in table 5.9 and 5.10 indicated that K value increased with concentration of SDBS in both batch and continuous process. These results had alignment with the graph of percentage of extraction.

5.5 Effect of phase ratio

The word, phase ratio, was defined as the ratio of volume fraction of extracting solution to that of oil feed for batch processes and defined as volumetric flow rate of extracting solution to that of oil feed for continuous processes. The effect of phase ratio in batch and continuous process were shown in figure 5.13 and 5.14. Percentage of extraction were plotted with volume portion of the oil feed. The line of graph indicates that when volume of oil increased, percentage of extraction had a tendency to decrease. These could be described by the extraction with chemical reaction and the micellar properties. Since volume portion of extraction fixed at 1 portion, when volume portion of oil was increased, that meant amount of ZDDP increased in the system. Due to this system controlled by chemical reaction and capacity of micelle to capture zinc ion at the surface and in its core, which were limited, so there were partial portion of zinc ions which were not

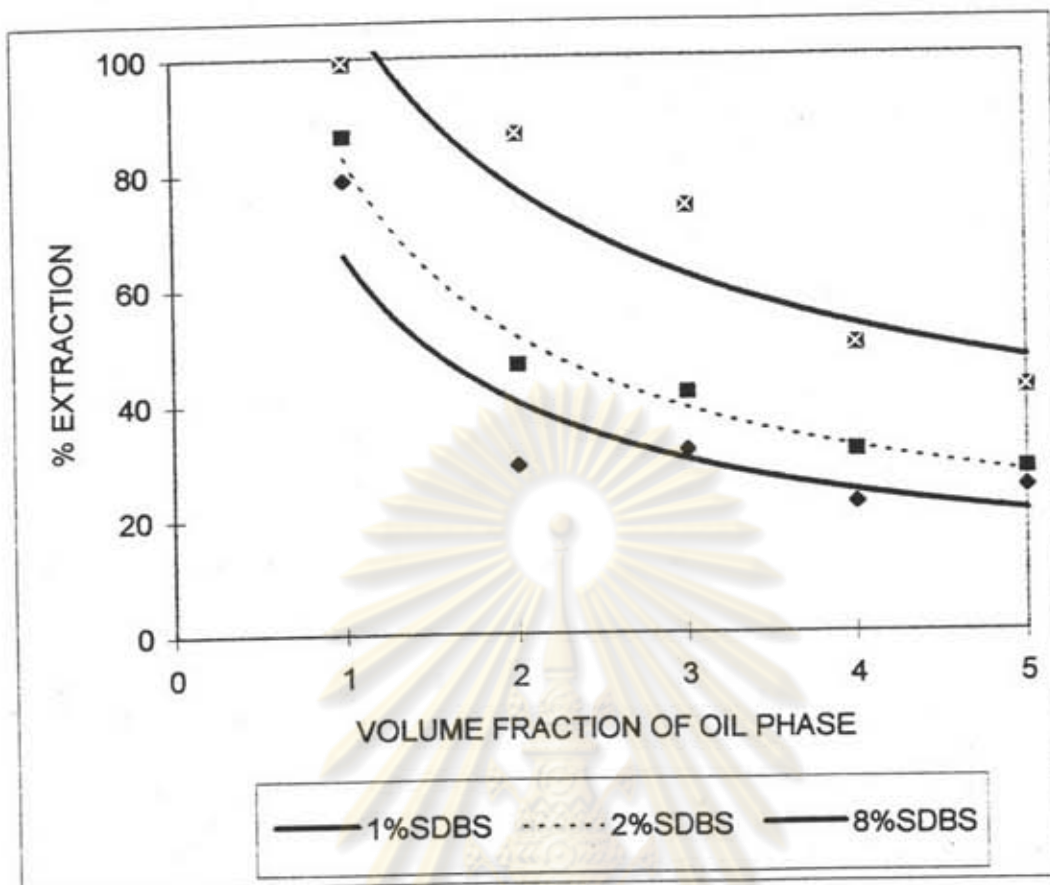


Figure 5.13 %Extraction at various phase ratios in batch process

Note

Volume fraction of extracting solution was fixed at 1.

Experimental conditions

Extractant : 8% wt/wt of diammonium hydrogen phosphate

Surfactant : 1% SDBS

Initial zinc concentration : 845 ppm

Agitator speed : 100 rpm

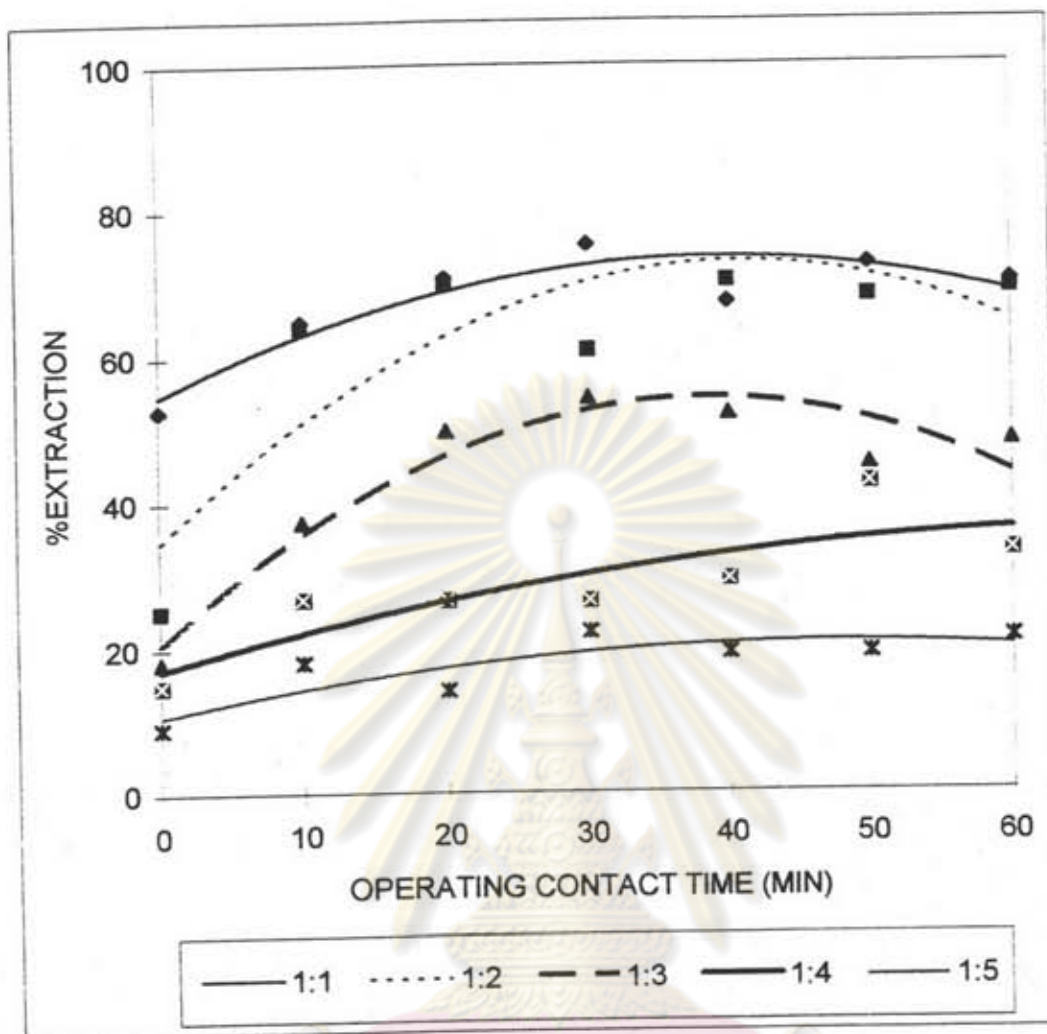


Figure 5.14 %Extraction at various phase ratios in continuous process.

Experimental conditions

Extractant : 8% wt/wt of diammonium hydrogen phosphate

Surfactant : 1% SDBS

Initial zinc concentration : 890 ppm.

Agitator speed : 100 rpm.

Table 5.11 K value at various phase ratios (extracting solution volume : oil volume) in batch process.

The initial zinc concentration was 845 ppm.

Phase ratio	K value at various SDBS concentration (%)			
	1%	2%	4%	8%
1:1	3.73	6.35	27.26	133.25
1:2	0.41	0.87	1.48	6.56
1:3	0.46	0.71	0.94	2.85
1:4	0.29	0.46	0.26	1.00
1:5	0.33	0.39	0.13	0.73

Table 5.12 K value at various phase ratios (extracting solution flow rate : oil flow rate) in continuous process.

The initial zinc concentration was 890 ppm.

Phase ratios	K value
1:1	2.08
1:2	1.56
1:3	0.77
1:4	0.40
1:5	0.21

captured and still remained in the system. In addition, at high concentration of SDBS, percentage of extraction was higher than that of low SDBS concentration. It was properly connected with the increasing quantity of micelle were increased. Similar results could be seen in table 5.11 and 5.12 which showed relationship between various ratios and K value.

5.6 Effect of initial zinc concentration

The effects of the initial zinc concentration as constant SDBS concentration was shown in figure 5.15, 5.16, 5.17 and table 5.13, 5.14. At low zinc concentration about 100 ppm, the percentage of extraction was almost 100%. As initial zinc concentration increased, the percentage of extraction had a tendency to decrease. This could be explained by relating to the micellar properties of surfactant. When a small amount of zinc it could be completely capture by micelle, so zinc content did not remain in oil phase. While quantity of zinc content in oil were larger than capacity of extracting solution to, there were a large amount of zinc remained in oil phase. In figure 5.16, final zinc concentration and initial zinc concentration were plotted, this graph indicated that all zinc content could be removed from lubricating oil when initial zinc concentration was in the range of 100 to 200 ppm when using 1% SDBS. Increasing the initial zinc concentration caused an increase in the final zinc concentration. In addition, increasing SDBS concentration was able to improve percentage of extraction. At 8% SDBS, zinc was not remained in the oil when initial zinc concentration was about 100 to 800 ppm.

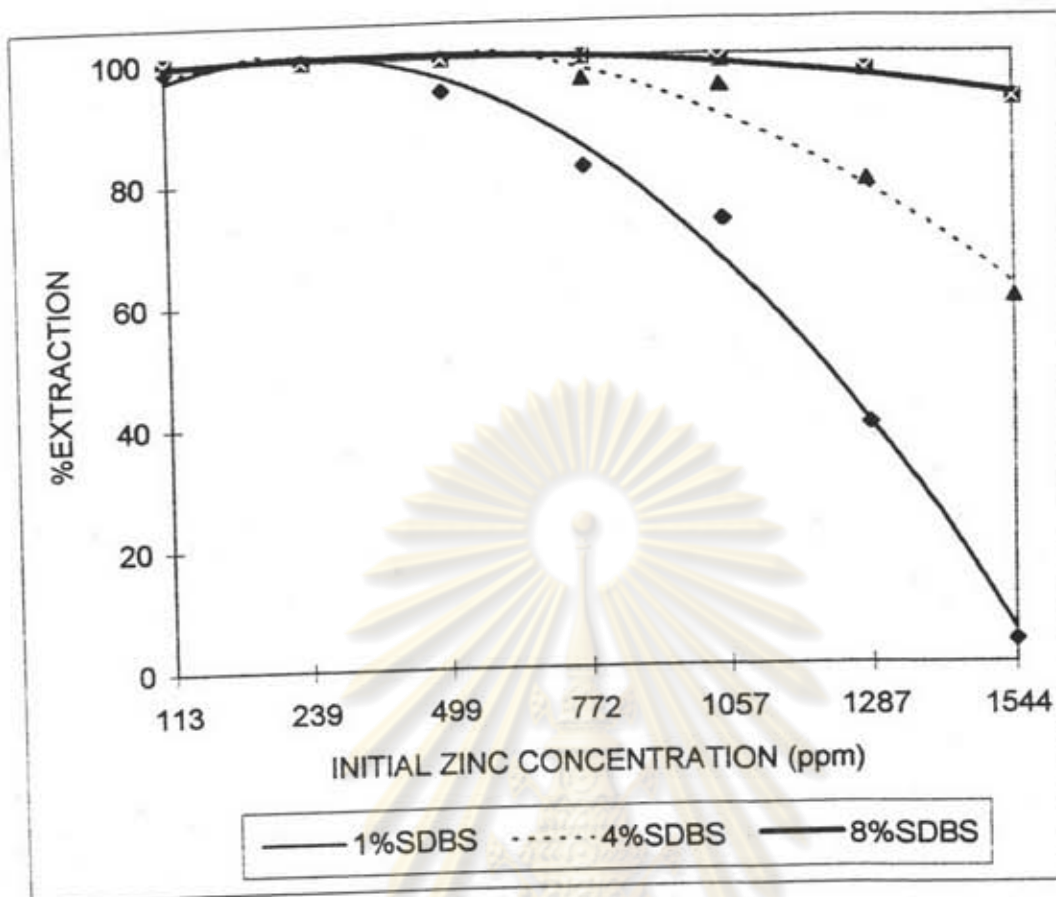


Figure 5.15 %Extraction at various initial zinc concentrations in batch process.

Experimental conditions

Extractant : 8% wt/wt of diammonium hydrogen phosphate

Surfactant : 1% SDBS

Agitator speed : 100 rpm

Phase ratio : 1:1

จุฬาลงกรณ์มหาวิทยาลัย

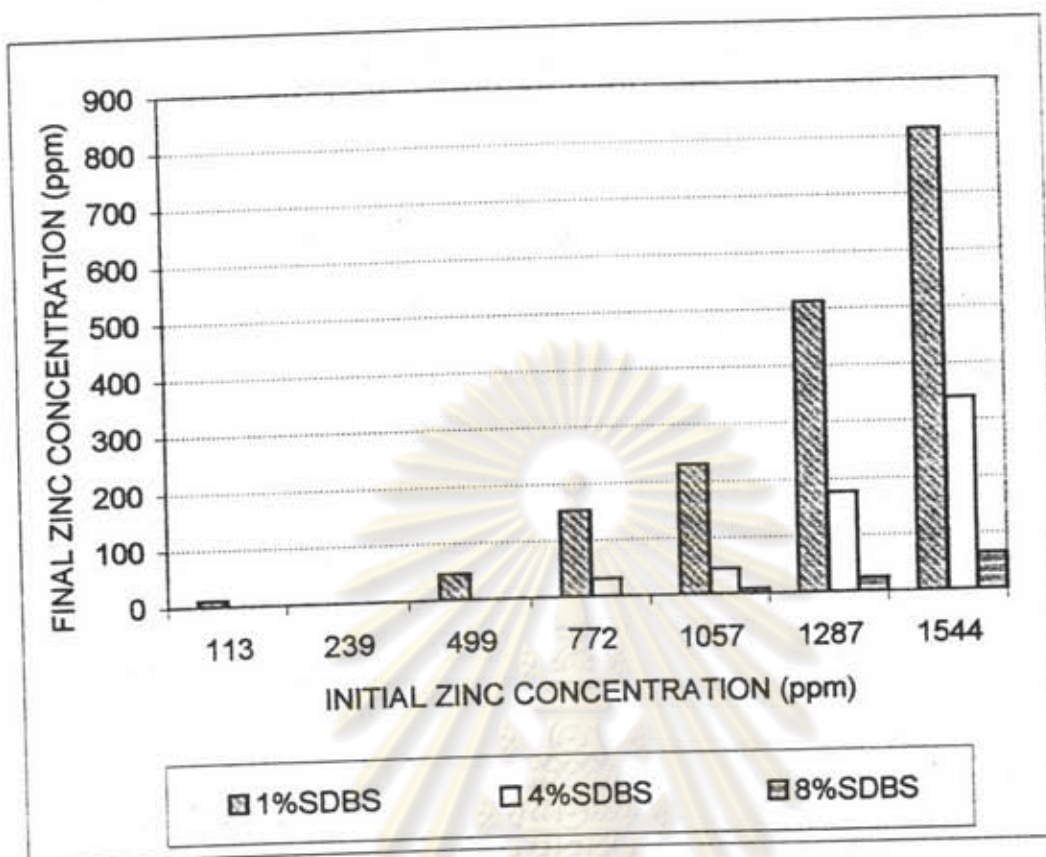


Figure 5.16 Relationship between initial zinc concentration at various initial zinc concentration.

Experimental conditions

Extractant : 8% wt/wt of diammonium hydrogen phosphate

Surfactant : 1% SDBS

Agitator speed : 100 rpm

Phase ratio : 1:1

จุฬาลงกรณ์มหาวิทยาลัย
คณะวิทยาศาสตร์

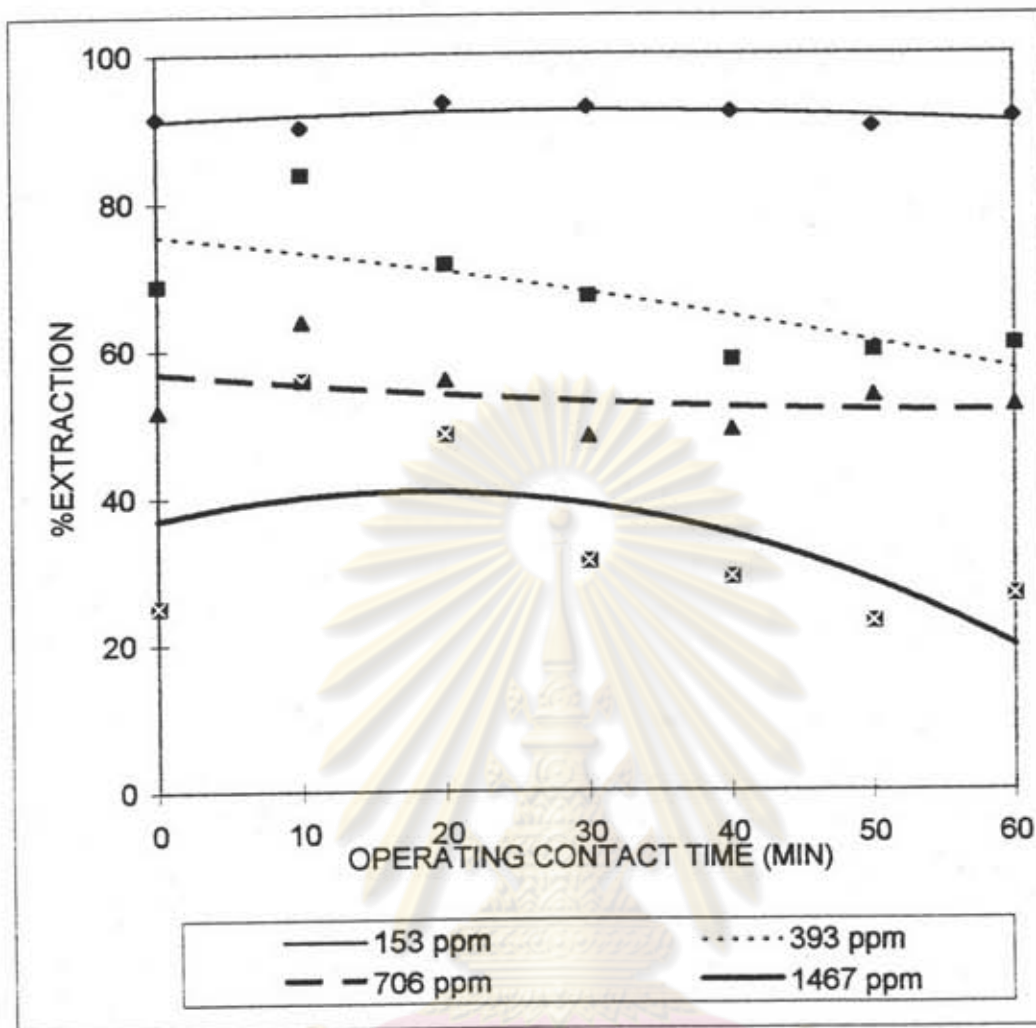


Figure 5.17 %Extraction at various initial zinc concentrations in continuous process.

Experimental conditions

Extractant : 8% wt/wt of diammonium hydrogen phosphate

Surfactant : 1% SDBS

Agitator speed : 100 rpm.

Phase ratio : 1:1

Table 5.13 K value at various initial zinc concentration in batch process.

Initial zinc concentration (ppm)	K value at various SDBS concentration (%)			
	1%	2%	4%	8%
113	83.50	∞	∞	∞
239	∞	92.89	∞	∞
499	17.78	11.43	∞	∞
772	4.56	3.59	26.26	∞
1057	2.69	3.20	18.20	104.63
1287	0.65	1.92	3.80	34.21
1544	0.04	0.85	1.49	12.41

Table 5.14 K value at various initial zinc concentrations in continuous process

Initial zinc concentration (ppm)	K value
153	11.03
393	2.04
706	1.15
1467	0.52