

## CHAPTER IV

### RESULTS AND DISCUSSION

#### Copper determination using ZDBC as spectrometric reagent.

ZDBC was selected as possible spectrometric reagent for copper determination due to spectral change after complex formation of  $\text{Cu}^{2+}$  with ZDBC was clearly observed in comparison with ZDBC alone. Optimum conditions were carefully studied in order to obtain the highest sensitivity of the method. The maximum absorbance appeared at wavelength 440 nm as shown in Figure 4.1.

In general, above critical micelle concentration (CMC) the micellization of the surfactant can be formed micelles. As a result of high electrical potential of micelles, the multivalent of copper can efficiently bind or adsorb on the micelles due to electrostatic attraction.

#### 4.1 Effect of surfactants concentration

The effect of surfactant concentration on the amount of copper detected in chloroform phase by using different initial of copper standard solution 1.00, 5.00 and 10.00 ppm was shown in Figures 4.3, 4.4 and 4.5, respectively. It was found that, the reduction of  $\text{Cu}^{2+}$  ion concentration decreased to its minimum when 0.1% w/v of surfactant was added.

The sodium dodecyl benzene sulfonate (LAS) forms micelles, roughly spherical aggregates containing generally 50-100 surfactant molecules. The micelles are highly charged and the opposite charge of  $\text{Cu}^{2+}$  ion bind onto the surfactant surface of the micelles, so  $\text{Cu}^{2+}$  ion was interior in the clusters (micelles). The  $\text{Cu}^{2+}$  ion cannot transfer from the water phase to the chloroform phase.

In the case of coco aminopropylbetaines (Tegobetaine)  $\text{Cu}^{2+}$  ion bind onto the negative charges of Tegobetaine at the micelle surface. It will be clustered around  $\text{Cu}^{2+}$  ion. Therefore, the  $\text{Cu}^{2+}$  ion cannot transfer from the water phase to the chloroform phase.

The nonylphenol ethoxylate( $\text{NP}_9$ ) has polyethoxylates group. It is capable to occur hydrogen-bonding network in the water. The  $\text{Cu}^{2+}$  ion was interior in the clusters, so it cannot transfer from the water phase to the chloroform phase.

The benzethonium chloride (Hyamine 1622) can be reacted with  $\text{Cu}^{2+}$  ion, so it forms complex. The reaction also depends on the nature of the ligand that can be formed the chelate.

Hence, the optimum surfactant concentration is 0.1% w/v. This is the necessary minimum concentration to reduce transferred  $\text{Cu}^{2+}$  ion from the water phase to the chloroform phase.

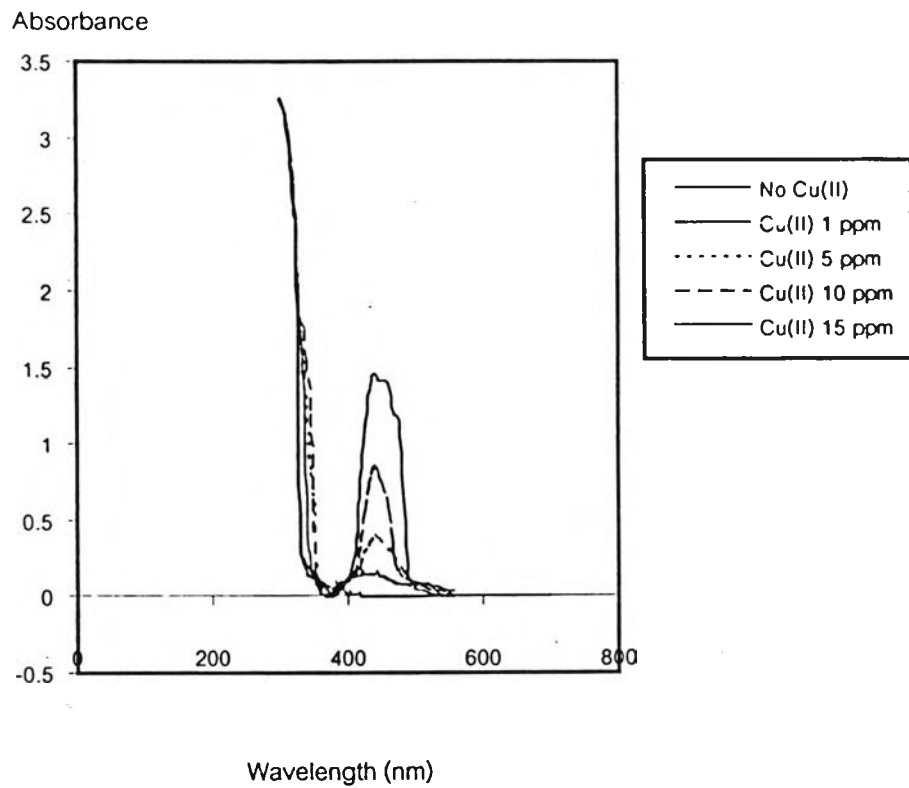


Fig 4.1 Visible absorption spectra of Cu(II)-ZDBC complex in chloroform phase at constant ZDBC concentration (0.1% w/v)

Table 4.1 Calibration data of Cu-ZDBC complex at 440 nm.

Copper concentration (ppm)	Absorbance
0.30	0.01
0.50	0.09
1.00	0.18
3.00	0.45
5.00	0.78
7.00	1.1
10.00	1.55

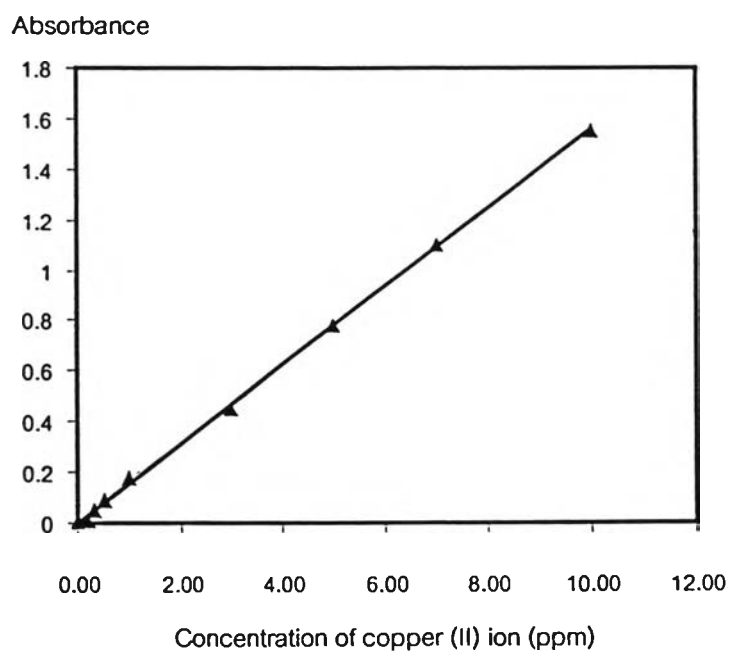


Fig4.2 Calibration curve of Cu(II)-ZDBC complex.

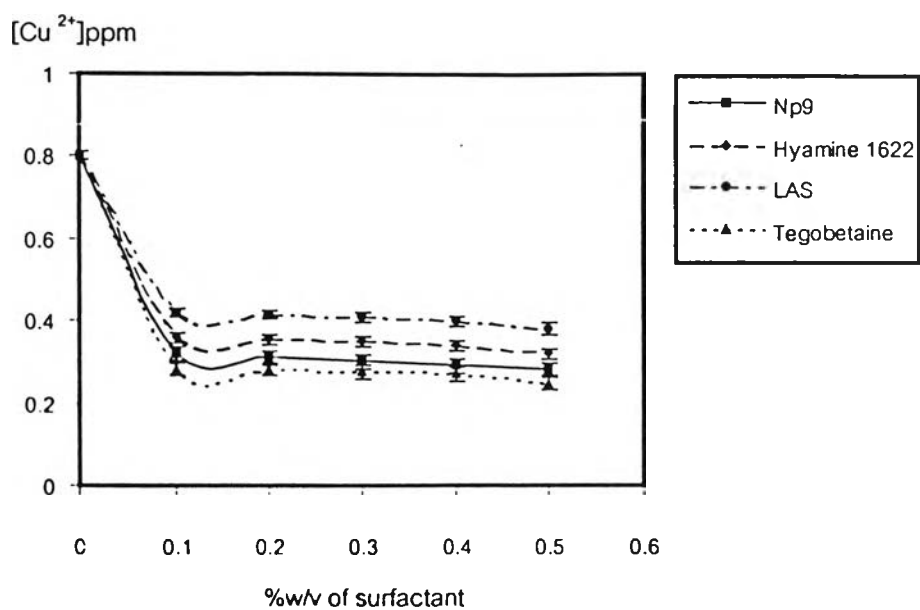


Fig 4.3 Effect of surfactant concentration on  $\text{Cu}^{2+}$  ion concentration in chloroform phase at initial concentration of 1 ppm copper nitrate standard solution.

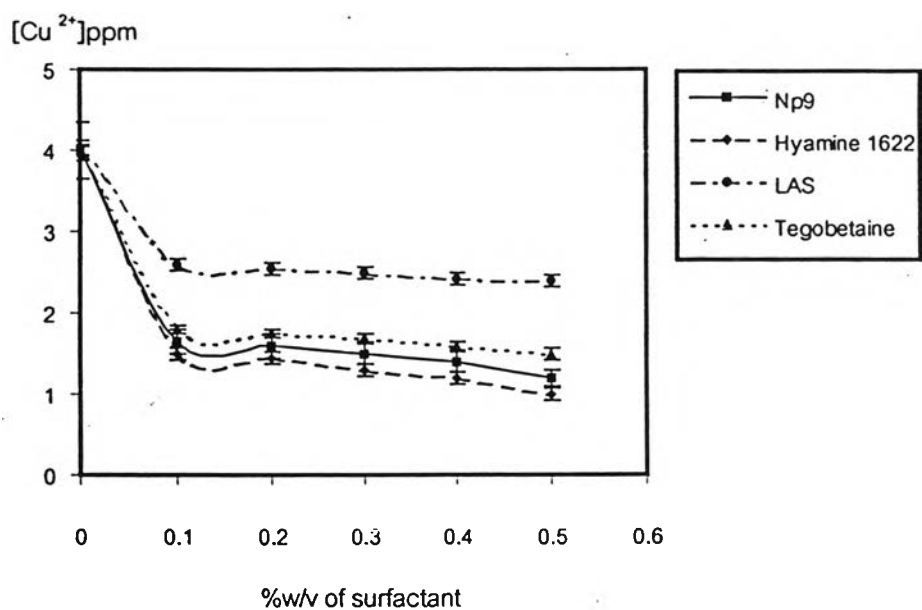


Fig 4.4 Effect of surfactant concentration on  $\text{Cu}^{2+}$  ion concentration in chloroform phase at initial concentration of 5 ppm copper nitrate standard solution.

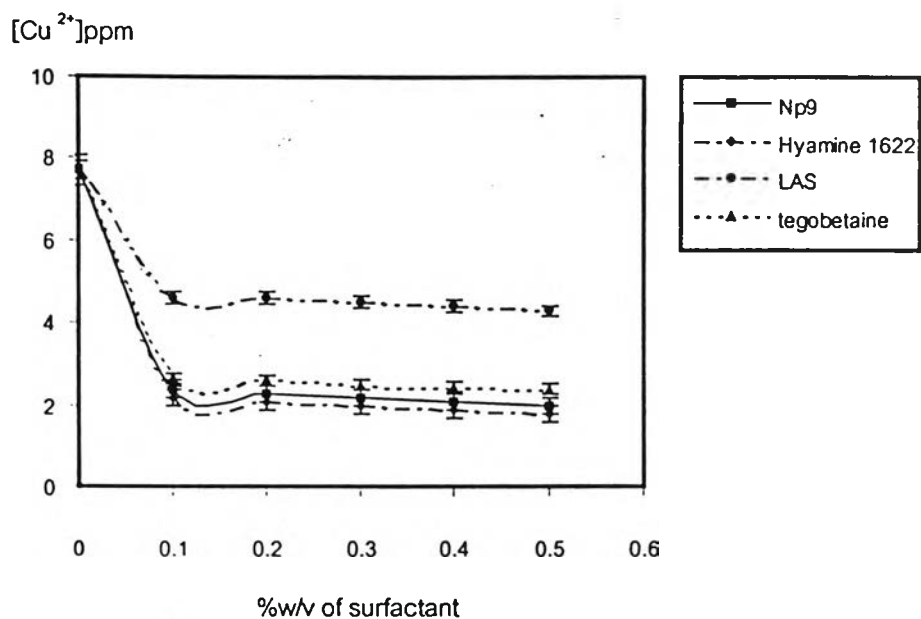


Fig 4.5 Effect of surfactant concentration on  $\text{Cu}^{2+}$  ion concentration in chloroform phase at initial concentration of 10 ppm copper nitrate standard solution.

#### 4.2 Effect of pH

The results of the effect of copper nitrate standard solution at pH 4.27 to pH 8.27 on transfer  $\text{Cu}^{2+}$  ion from the water phase to the chloroform phase are presented in Tables 4.1 to 4.3 and Figures 4.6 to 4.9 for copper standard solution 1.00, 5.00 and 10.00 ppm, respectively. In case of  $\text{NP}_9$ , the amount of  $\text{Cu}^{2+}$  ion was independent of pH which can be explained by the fact that  $\text{NP}_9$  is nonionic surfactant bearing no charge and the  $\text{Cu}^{2+}$  ion was absorbed inside the interior of the clusters(micelles).

Hyamine 1622 contains a positive charge of quaternary ammonium nitrogen, when pH of copper nitrate standard solution was increased above  $pK_a$  of Hyamine 1622 the positive charge became neutralised, thus has less capacity to absorb  $Cu^{2+}$  ion. The  $Cu^{2+}$  ion concentration in chloroform phase was increased as pH increased.

Since LAS contains a negative charge the binding of,  $Cu^{2+}$  ion was increased, therefore the transfer of  $Cu^{2+}$  ion to the chloroform phase decreased. Tegobetaine contains a quaternary nitrogen atom regardless of pH. When increase the pH of copper nitrate standard solution, the negative charge on the carboxylic acid group of Tegobetaine was also increased.  $Cu^{2+}$  ion binding increased with the negative charge of surfactant slightly at high pH 8.27.

Table 4.2 The results of the study of pH of copper standard solution at 1 ppm concentration.

pH of 1 ppm Cu(II) ion	pH of mixture 1 ppm Cu(II) ion and NP <sub>9</sub>	pH of mixture 1 ppm Cu(II) ion and Hyamine1622	pH of mixture 1 ppm Cu(II) ion and LAS	pH of mixture 1 ppm Cu(II) ion and Tegobetaine
4.27	5.84	5.88	5.39	4.85
5.27	6.05	6.05	5.75	4.97
6.27	6.60	6.67	6.25	5.05
7.27	7.27	7.58	6.80	5.10
8.27	8.10	8.14	7.81	5.45

Table 4.3 The results of the study of pH of copper standard solution at 5 ppm concentration.

pH of 5 ppm Cu(II) ion	pH of mixture 5 ppm Cu(II) ion and NP <sub>9</sub>	pH of mixture 5 ppm Cu(II) ion and Hyamine1622	pH of mixture 5 ppm Cu(II) ion and LAS	pH of mixture 5 ppm Cu(II) ion and Tegobetaine
4.27	5.83	5.80	5.40	4.84
5.27	6.07	6.08	5.72	4.96
6.27	6.58	6.67	6.28	5.07
7.27	7.27	7.55	6.78	5.10
8.27	8.13	8.17	7.81	5.48



Table 4.4 The results of the study of pH of copper standard solution at 10 ppm concentration.

pH of 10 ppm Cu(II) ion	pH of mixture 10 ppm Cu(II) ion and NP <sub>9</sub>	pH of mixture 10 ppm Cu(II) ion and Hyamine1622	pH of mixture 10 ppm Cu(II) ion and LAS	pH of mixture 10 ppm Cu(II) ion and Tegobetaine
4.27	5.82	5.85	5.38	4.82
5.27	6.03	6.08	5.75	4.95
6.27	6.62	6.62	6.27	5.08
7.27	7.29	7.55	6.82	5.10
8.27	8.12	8.14	7.85	5.45

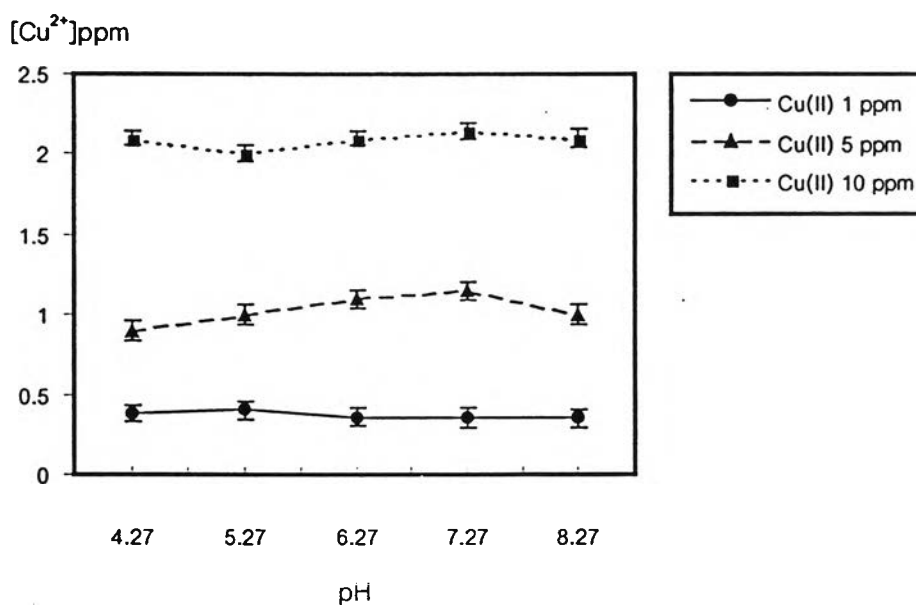


Fig 4.6 Effect of pH of copper nitrate standard solution on Cu<sup>2+</sup> ion concentration in chloroform phase at NP<sub>9</sub> 0.1%w/v.

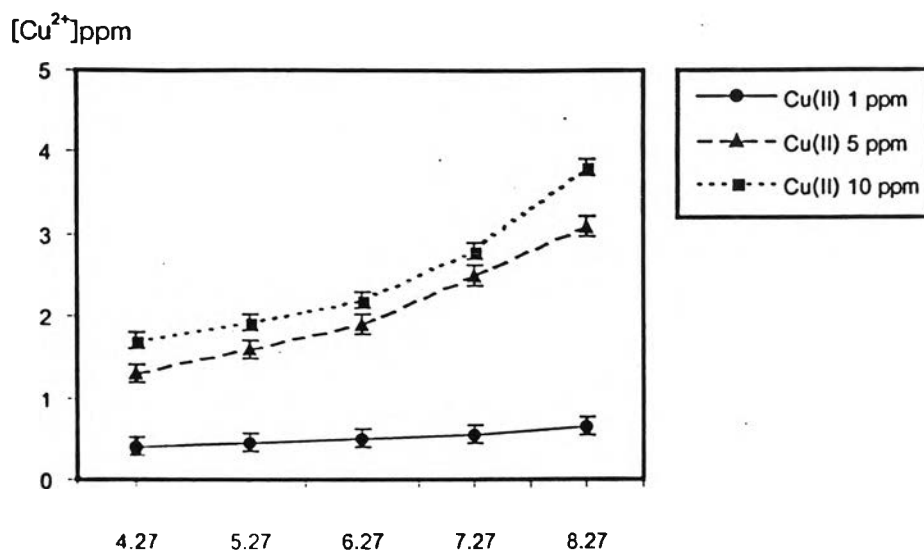


Fig 4.7 Effect of pH of copper nitrate standard solution on  $\text{Cu}^{2+}$  ion concentration in chloroform phase at Hyamine 1622 0.1%w/v.

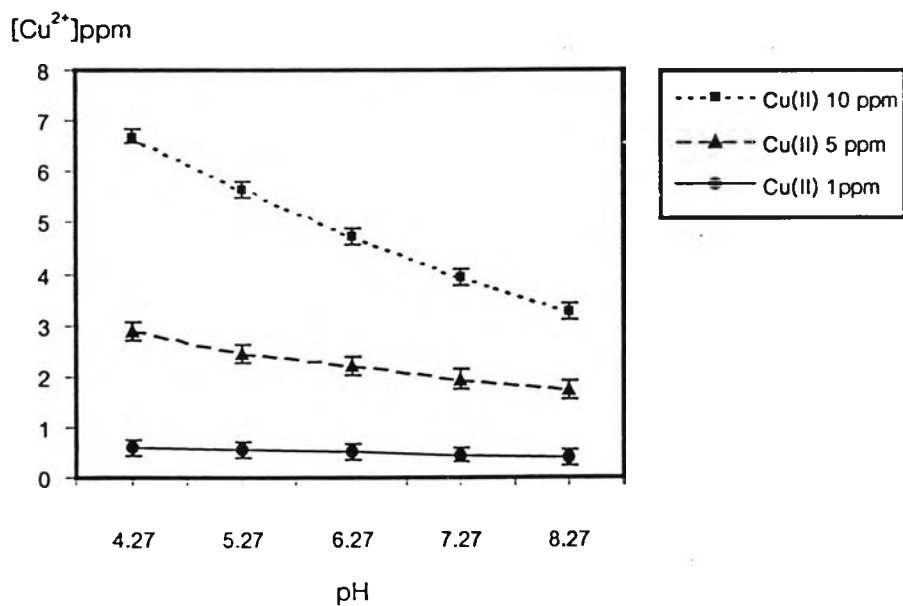


Fig 4.8 Effect of pH of copper nitrate standard solution on  $\text{Cu}^{2+}$  ion concentration in chloroform phase at LAS 0.1%w/v.

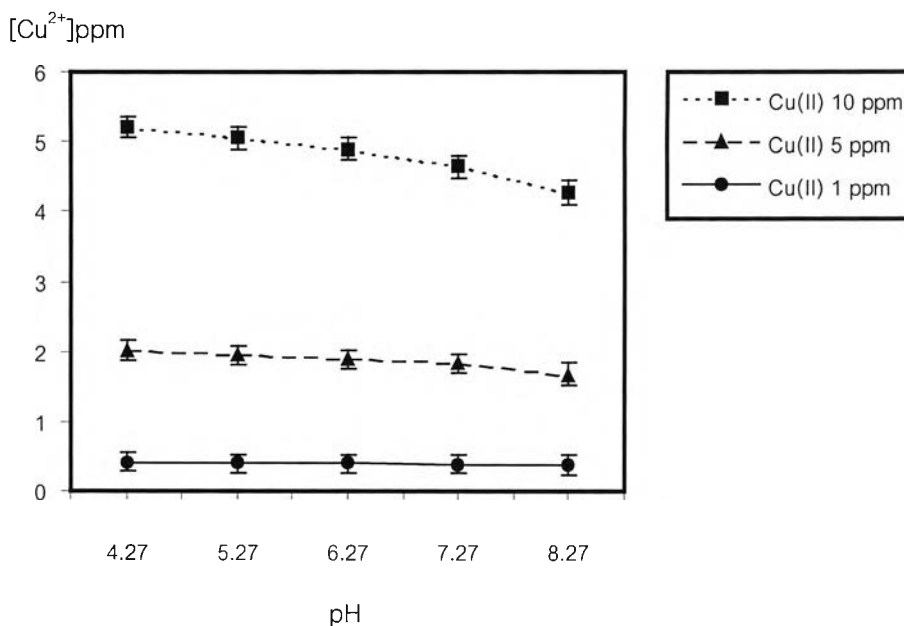


Fig 4.9 Effect of pH of copper nitrate standard solution on  $\text{Cu}^{2+}$  ion concentration in chloroform phase at Tegobetaine 0.1%w/v.

#### 4.3 Effect of temperature

Effect of temperature on transfer  $\text{Cu}^{2+}$  ion from the water phase to the chloroform phase by varying temperature in the range of 20 to 40 °C are presented in Figures 4.10 to 4.22. It was found that, when the temperature of copper nitrate standard solution was increased. The transfer of  $\text{Cu}^{2+}$  ion from water phase to the chloroform phase was also increased, especially at 40 °C. Vibration of water molecule at high temperature around surfactant led to less effective  $\text{Cu}^{2+}$  ion binding to micelles of surfactant. When the temperature was increased, the size of surfactant head was decreased due to dehydration of water. Therefore the head group of surfactant is sensitive with temperature.

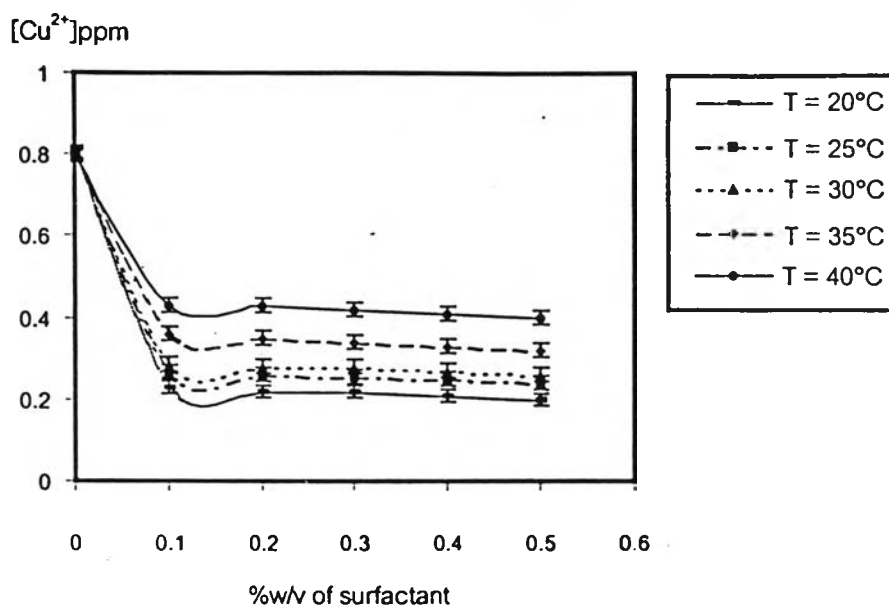


Fig 4.10 Effect of temperature on  $\text{Cu}^{2+}$  ion concentration in chloroform phase at initial concentration of 1 ppm copper nitrate standard solution and  $\text{NP}_9$  0.1%w/v.

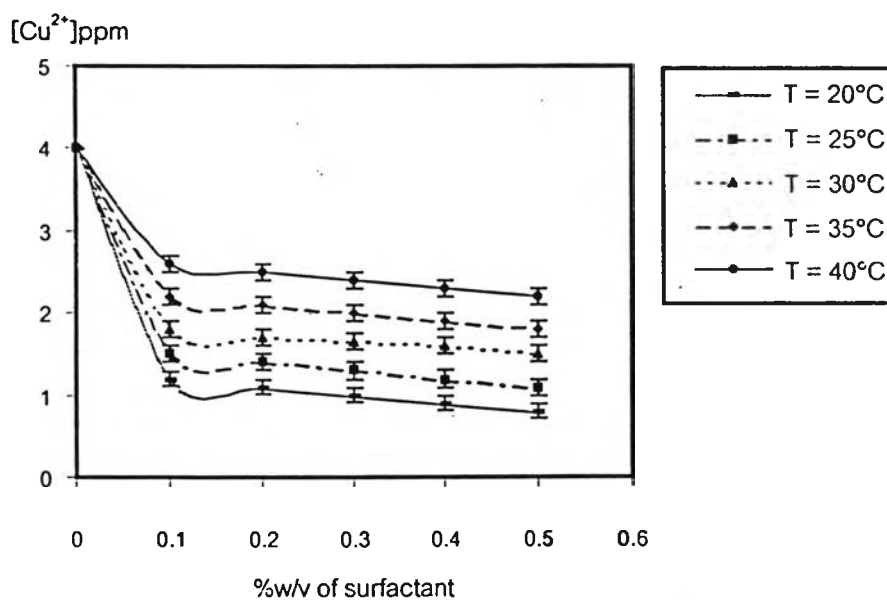


Fig 4.11 Effect of temperature on  $\text{Cu}^{2+}$  ion concentration in chloroform phase at initial concentration of 5 ppm copper nitrate standard solution and  $\text{NP}_9$  0.1%w/v.

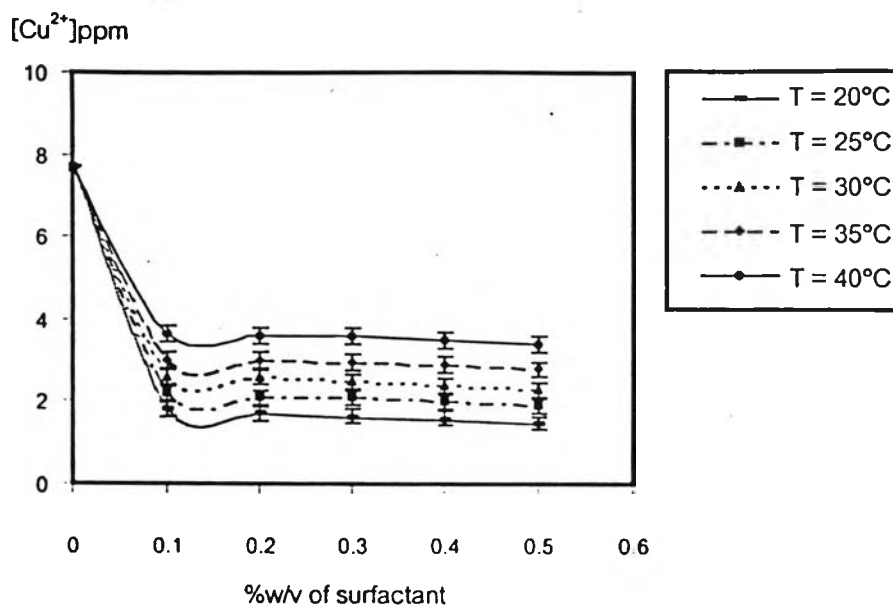


Fig 4.12 Effect of temperature on  $\text{Cu}^{2+}$  ion concentration in chloroform phase at initial concentration of 10 ppm copper nitrate standard solution and  $\text{NP}_9$  0.1%w/v.

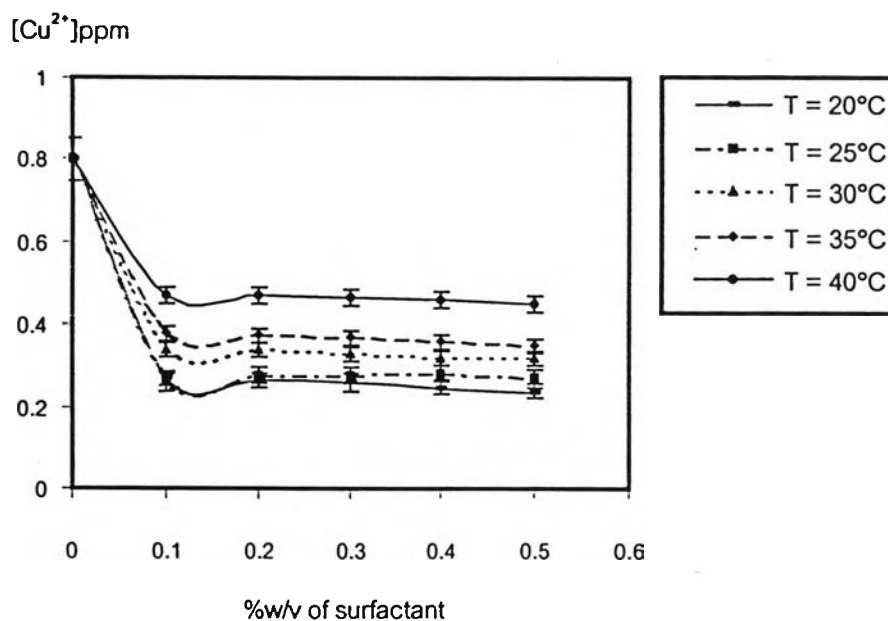


Fig 4.13 Effect of temperature on  $\text{Cu}^{2+}$  ion concentration in chloroform phase at initial concentration of 1 ppm copper nitrate standard solution and Hyamine 1622 0.1%w/v.

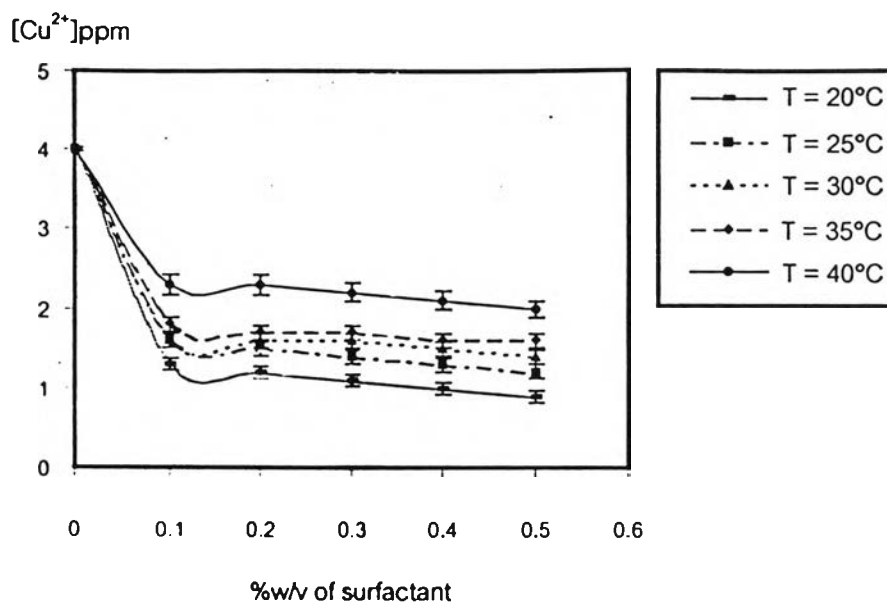


Fig 4.14 Effect of temperature on  $\text{Cu}^{2+}$  ion concentration in chloroform phase at initial concentration of 5 ppm copper nitrate standard solution and Hyamine 1622 0.1%w/v.

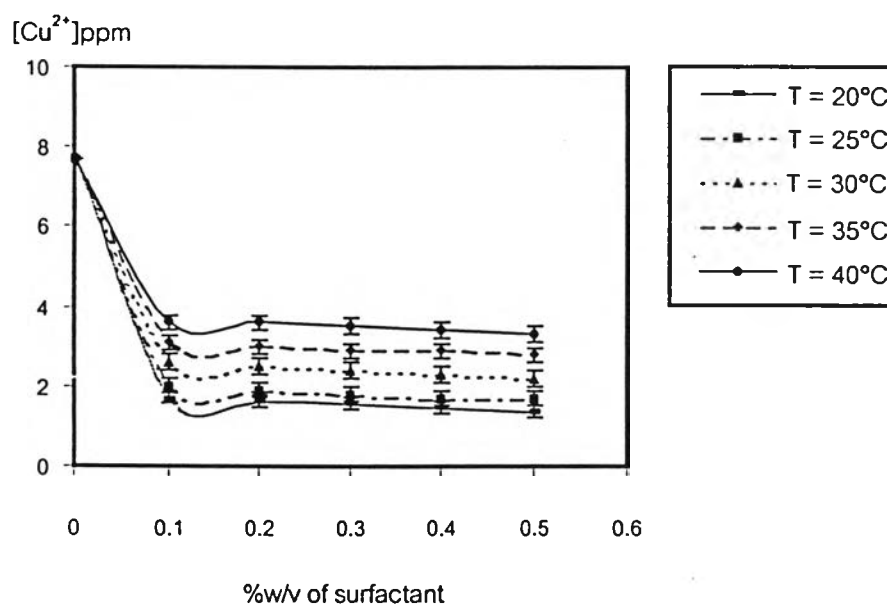


Fig 4.15 Effect of temperature on  $\text{Cu}^{2+}$  ion concentration in chloroform phase at initial concentration of 10 ppm copper nitrate standard solution and Hyamine 1622 0.1%w/v.

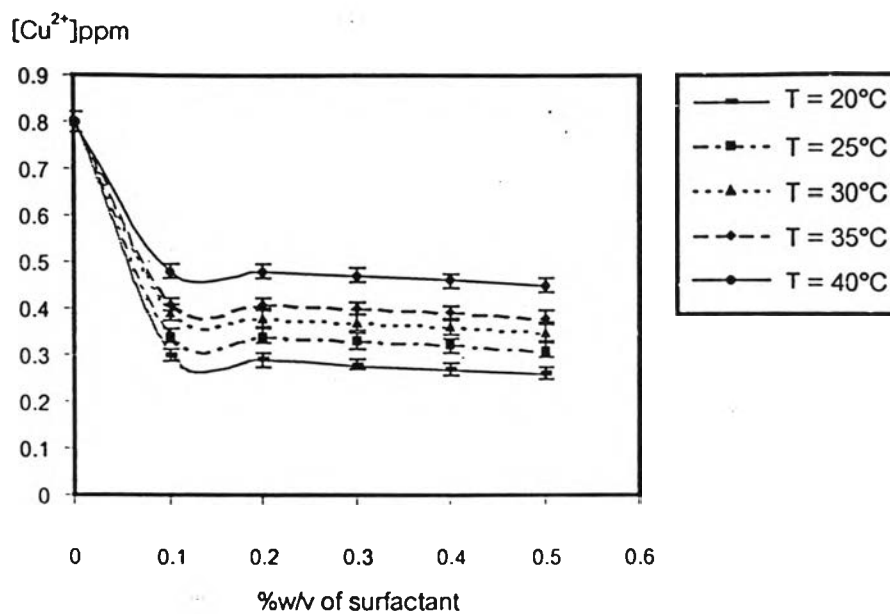


Fig 4.16 Effect of temperature on  $\text{Cu}^{2+}$  ion concentration in chloroform phase at initial concentration of 1 ppm copper nitrate standard solution and LAS 0.1%w/v.

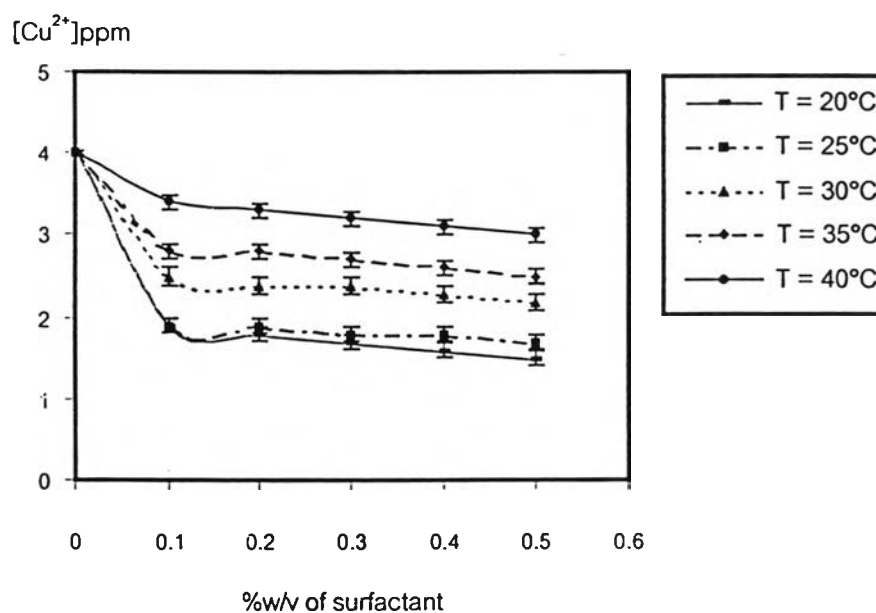


Fig 4.17 Effect of temperature on  $\text{Cu}^{2+}$  ion concentration in chloroform phase at initial concentration of 5 ppm copper nitrate standard solution and LAS 0.1%w/v.

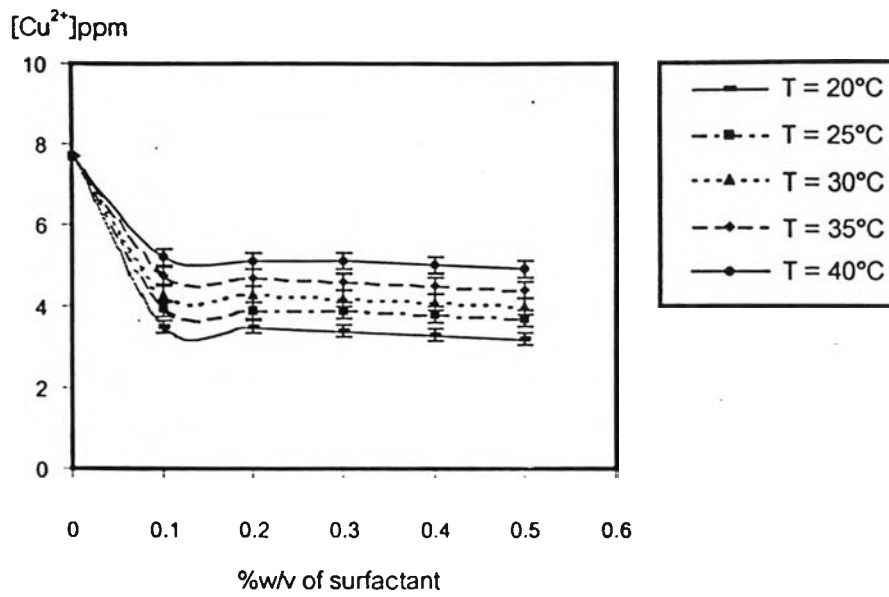


Fig 4.18 Effect of temperature on  $\text{Cu}^{2+}$  ion concentration in chloroform phase at initial concentration of 10 ppm copper nitrate standard solution and LAS 0.1%w/v.

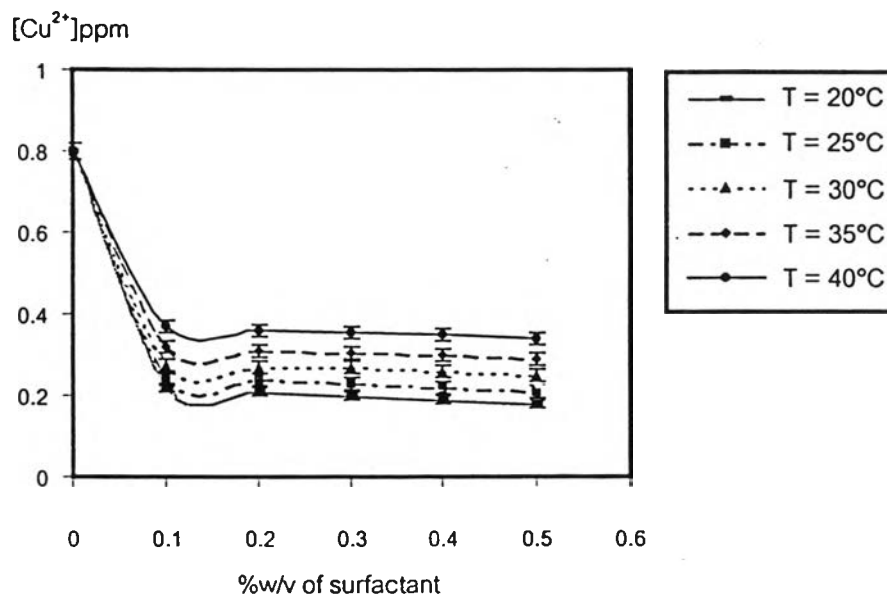


Fig 4.19 Effect of temperature on  $\text{Cu}^{2+}$  ion concentration in chloroform phase at initial concentration of 1 ppm copper nitrate standard solution and Tegobetaine 0.1%w/v.



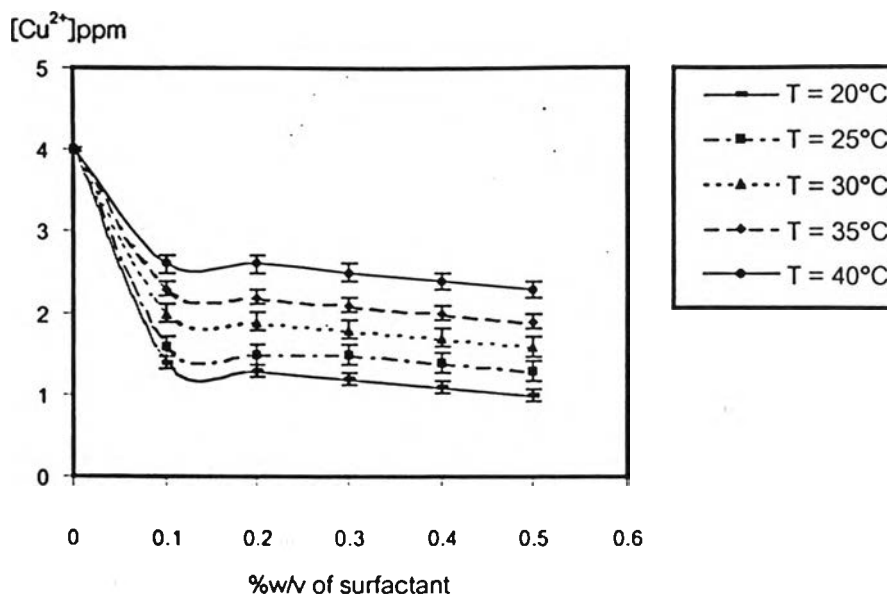


Fig 4.20 Effect of temperature on  $\text{Cu}^{2+}$  ion concentration in chloroform phase at initial concentration of 5 ppm copper nitrate standard solution and Tegobetaine 0.1%w/v.

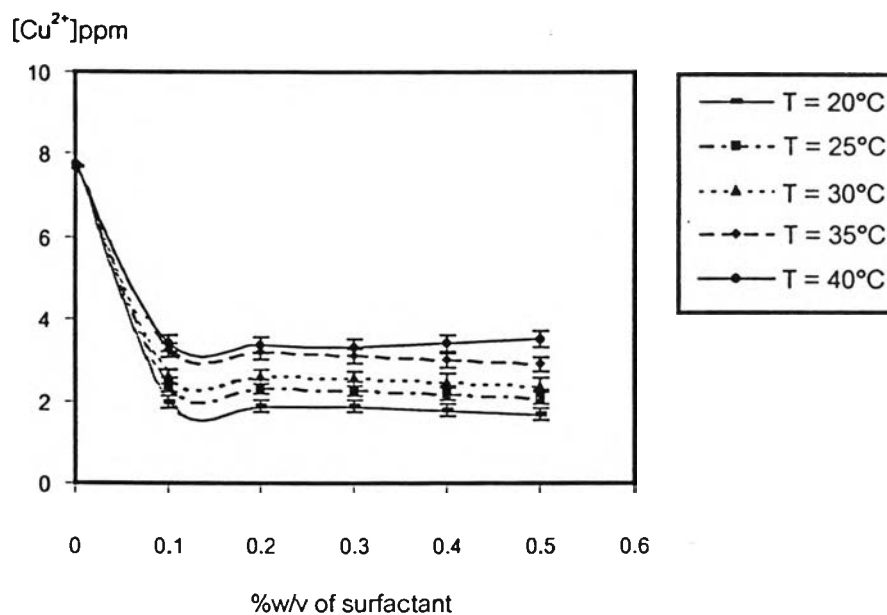
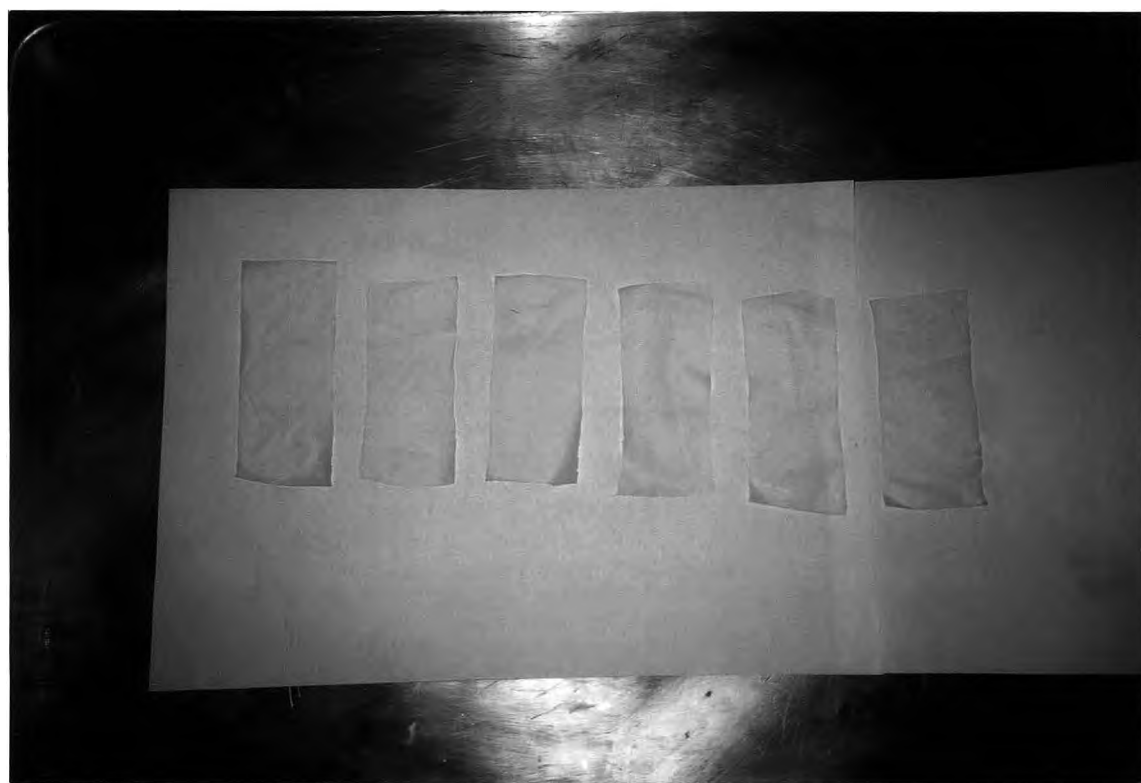


Fig 4.21 Effect of temperature on  $\text{Cu}^{2+}$  ion concentration in chloroform phase at initial concentration of 10 ppm copper nitrate standard solution and Tegobetaine 0.1%w/v.

#### 4.4 Formation of copper stain on gloves.

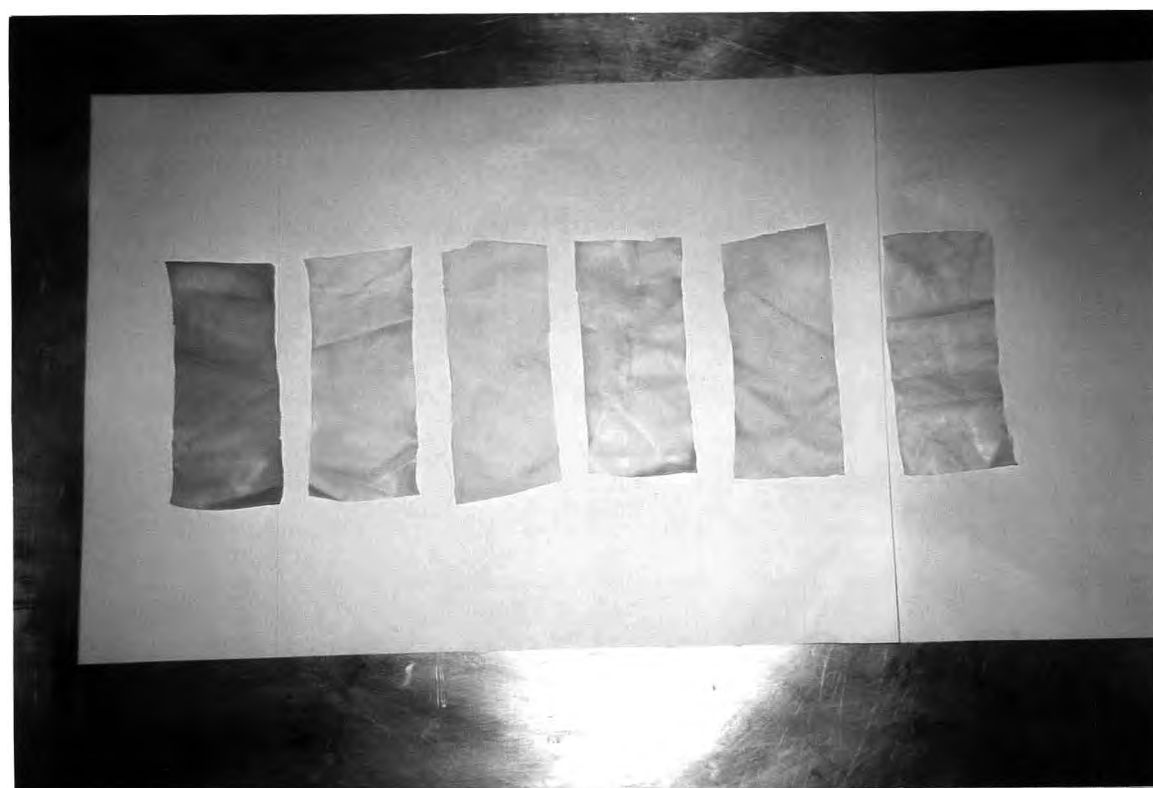
It was found that, after dipping piece A with initial concentration of 10 ppm copper nitrate standard solution for 10 min, there was dark-brown color appearing on the surface of the glove, due to  $\text{Cu}^{2+}$  ion reacts with ZDBC in the glove.

In the other case, after dipping pieces B, C, D, E and F with the mixture of initial concentration of 10 ppm copper nitrate standard solution and 0.1, 0.2, 0.3, 0.4, and 0.5 %w/v of  $\text{NP}_9$  surfactant, respectively. It was found that, the surface of the pieces B, C, D, E and F have lighter color than piece A. This result suggested that  $\text{NP}_9$  surfactant can bind to  $\text{Cu}^{2+}$  ion and thus reduce the stain formation caused by copper carbamate.



A B C D E F

Fig 4.22 The appearance of pieces A to F before dipping.



A B C D E F

Fig 2.23 The appearance of pieces A to F after dipping.