CHAPTER IV
RESULTS AND DISCUSSION

4.1 Determination of Cloud Point

The cloud points of $NP(EO)_8$, $NP(EO)_9$, and $NP(EO)_{10}$ in the concentration range of 0.01 vol%-1.0vol% are shown in Table 4.1. The cloud point decreases slightly as the concentration increases. At low concentrations, the cloud point could not be detected. The cloud point is also found to increase with the number of ethylene oxide in the surfactant molecule, a well known correlation (Michael and Irene,1993). This is because the increase in the number of ethylene oxide increases the surfactant solubility.

Table 4.1 Cloud points of surfactants used.

Concentration vol%*	Cloud point of nonionic surfactants (^oC)		
	$NP(EO)_8$	$NP(EO)_9$	$NP(EO)_{10}$
0.01	not found	not found	not found
0.1	29	60	65
0.5	23	53	65
1.0	22	52	60

*1.0 vol% = 10 mL of surfactant/1 L of solution (See Appendix E for equivalent concentrations in wt% and M)

From the technical data published by Rhone-Poulenc, the cloud points of 1 wt% solutions of $NP(EO)_8$, $NP(EO)_9$, and $NP(EO)_{10}$ are given at 22-28^oC, 52-53^{o}C, and 60-65^{o}C respectively. Since the densities of the three surfactants are 1.05 wt% for NP(EO)$_8$ and 1.06 wt% for NP(EO)$_9$ and NP(EO)$_{10}$ respectively, which are close to 1, it can be said that the cloud points obtained in this work are in the same range as the ones quoted by the manufacturer.

4.2 Foaming Tests by the Ross-Miles Method

4.2.1 Effect of Temperature on Foamability and Foam Stability

4.2.1.1 Effect on Foamability. The effect of temperature on foamability of NP(EO)$_8$, NP(EO)$_9$, and NP(EO)$_{10}$ is shown in Figures 4.1-4.9. The foam height at 0 minute represents the foamability of the solution. At the low concentration of 0.01%vol. at which the cloud point could not be detected, the foam height is almost constant at the low level of 4-6 cm. throughout the whole temperature range. However, at the concentrations of 0.1 and 1.0 vol%, the foam height is independent of temperature only below the cloud point. Above the cloud point, the foam height decreases dramatically. The same effects are observed for all the three types of nonionic surfactants studied. The same qualitative results were also obtained by earlier workers (Crook et al., 1964). The results show that cloud point plays a decisive role in the foamability of nonionic surfactants. At the cloud point, the nonionic surfactant is believed to separate into a micellar-rich and micellar-poor phase. The micellar-rich phase then acts as an antifoam causing a dramatic decrease in foamability above the cloud point (Bonfillon et al., 1997).

4.2.1.2 Effect on Foam Stability. The effects of temperature on foam stability of NP(EO)$_8$, NP(EO)$_9$, and NP(EO)$_{10}$ are shown in Figures 4.10-4.12 where the stability index was plotted against temperature. The stability index is defined as the foam height at 5 minutes divided by the foam

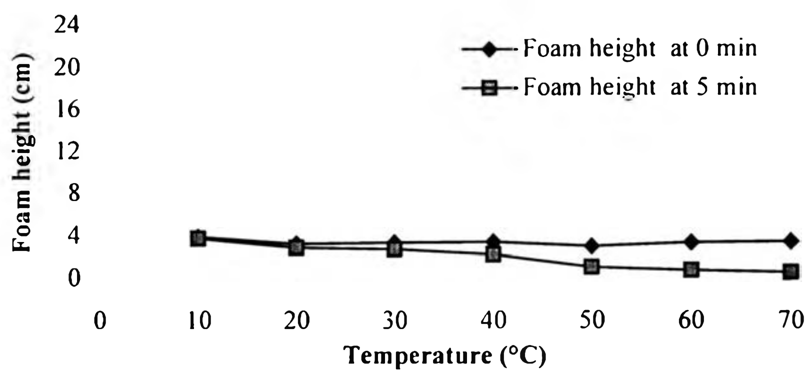

Figure 4.1 Effect of Temperature on Foamability and Foam Stability of 0.01 vol% $NP(EO)_8$ (Ross-Miles Method).

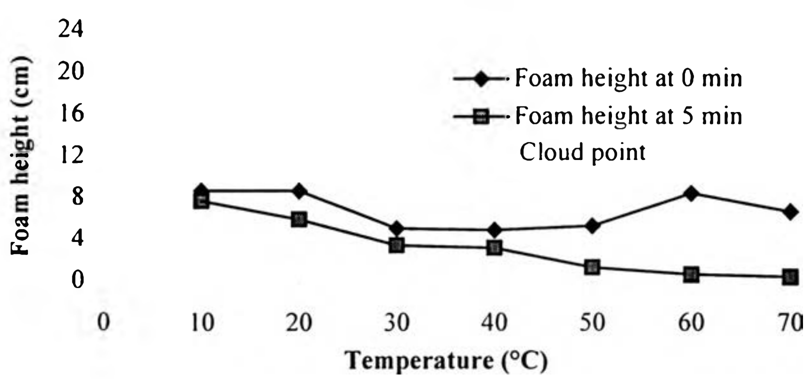

Figure 4.2 Effect of Temperature on Foamability and Foam Stability of 0.1 vol% $NP(EO)_8$ (Ross-Miles Method).

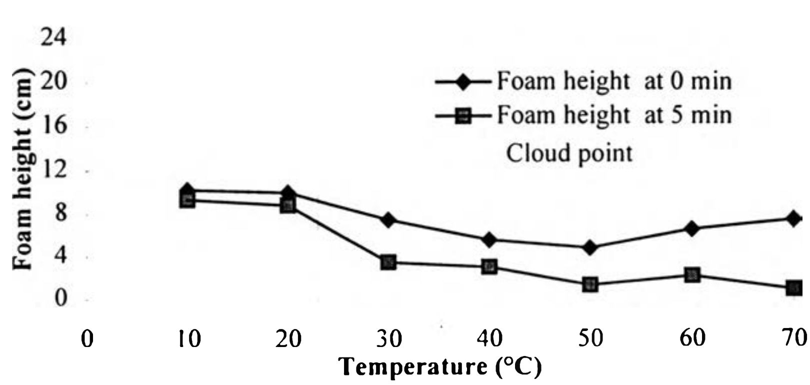

Figure 4.3 Effect of Temperature on Foamability and Foam Stability of 1.0 vol% $NP(EO)_8$ (Ross-Miles Method).

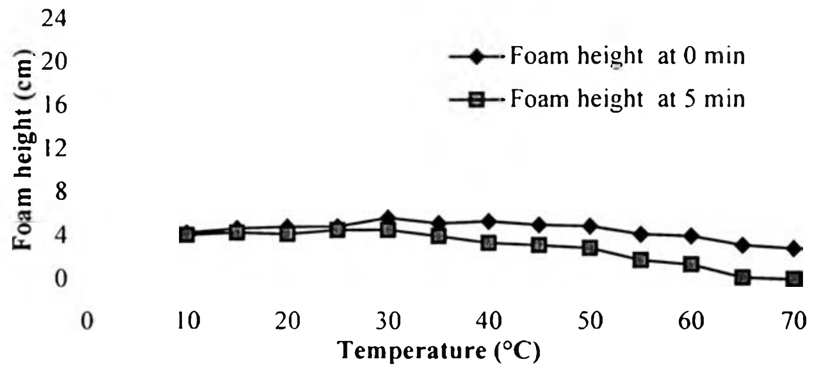

Figure 4.4 Effect of Temperature on Foamability and Foam Stability of 0.01 vol% $NP(EO)_9$ (Ross-Miles Method).

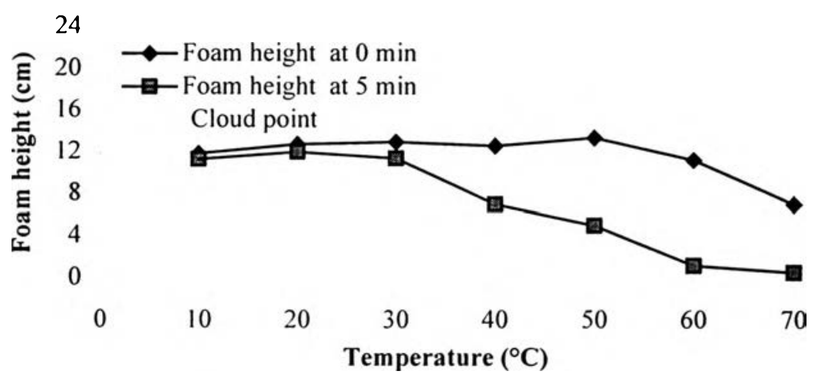

Figure 4.5 Effect of Temperature on Foamability and Foam Stability of 0.1 vol% $NP(EO)_9$ (Ross-Miles Method).

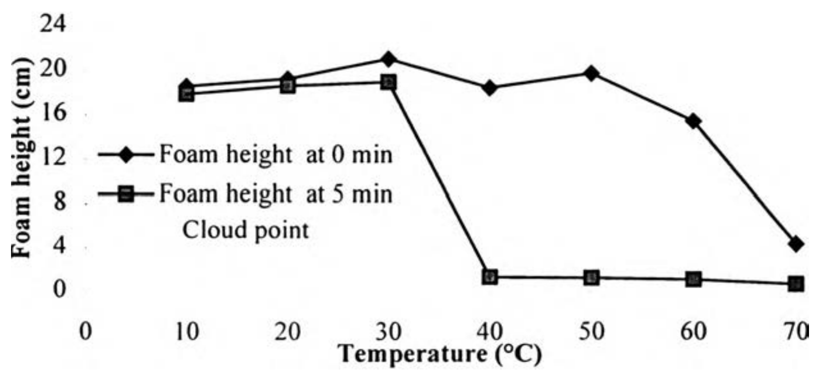

Figure 4.6 Effect of Temperature on Foamability and Foam Stability of 1.0 vol% $NP(EO)_9$ (Ross-Miles Method).

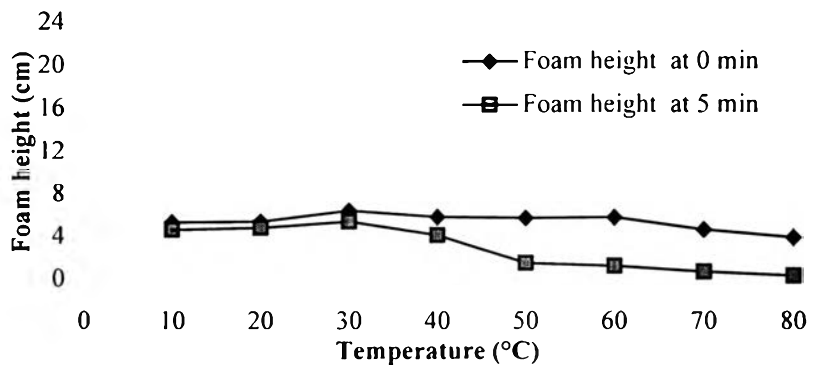

Figure 4.7 Effect of Temperature on Foamability and Foam Stability of 0.01 vol% $NP(EO)_{10}$ (Ross-Miles Method).

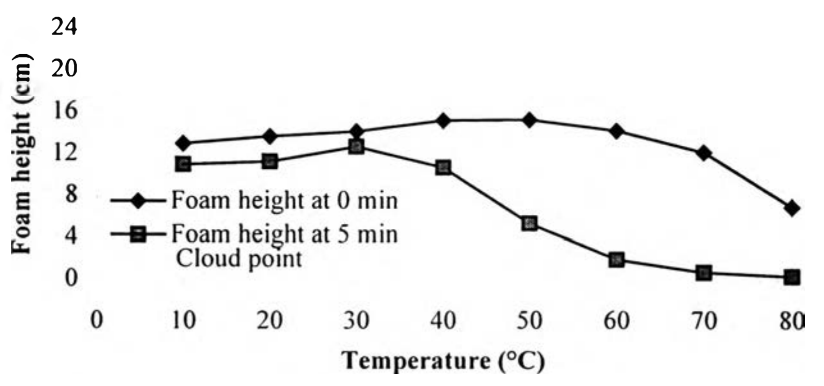

Figure 4.8 Effect of Temperature on Foamability and Foam Stability of 0.1 vol% $NP(EO)_{10}$ (Ross-Miles Method).

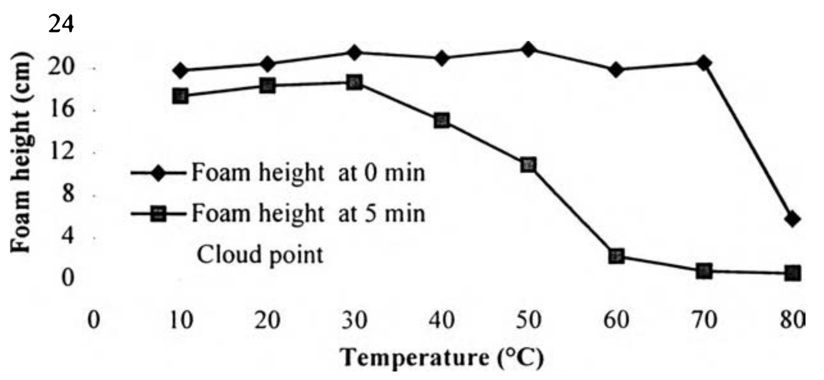

Figure 4.9 Effect of Temperature on Foamability and Foam Stability of 1.0 vol% $NP(EO)_{10}$ (Ross-Miles Method).

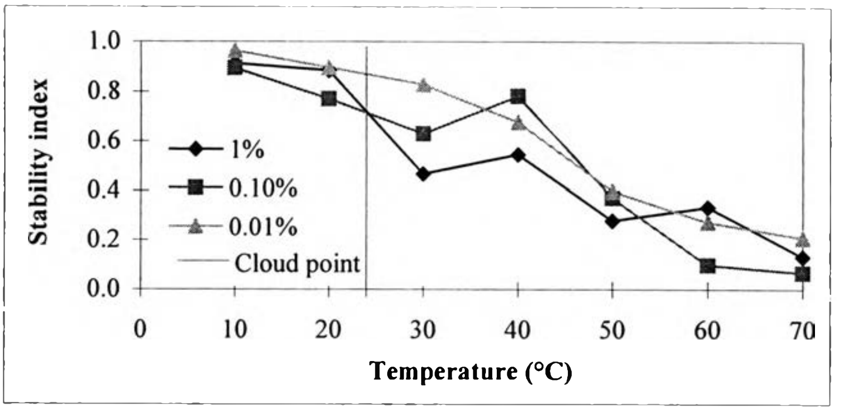

Figure 4.10 Effect of Temperature on Foam stability of $NP(EO)_8$ (Ross-Miles Method).

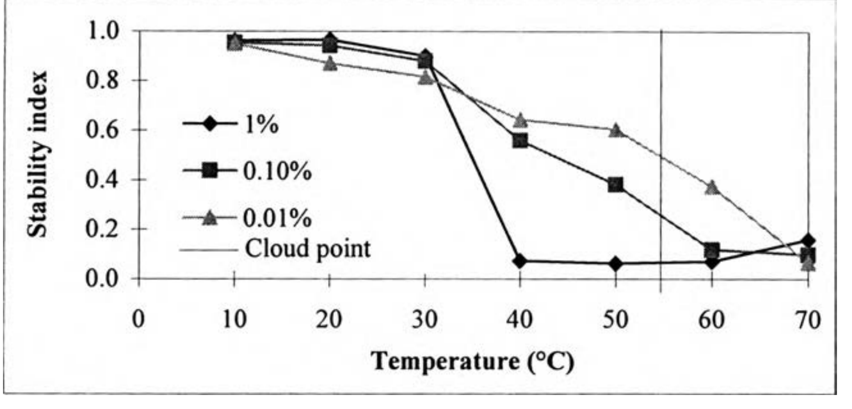

Figure 4.11 Effect of Temperature on Foam stability of $NP(EO)_9$ (Ross-Miles Method).

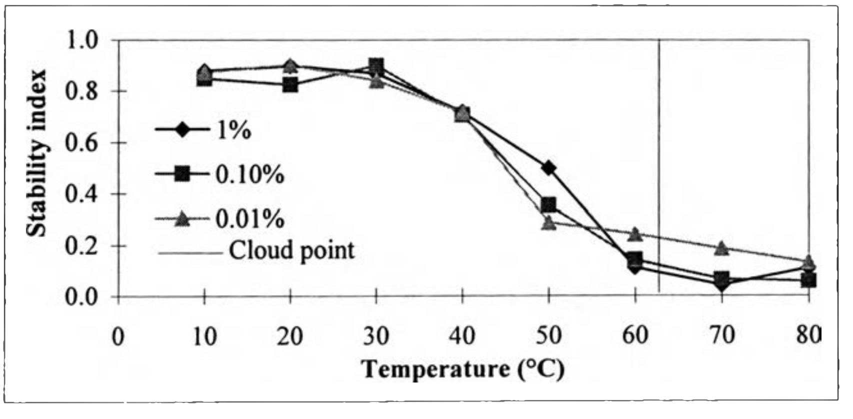

Figure 4.12 Effect of Temperature on Foam stability of $NP(EO)_{10}$ (Ross-Miles Method).

height at 0 minute. It can be seen that the stability index is generally high at low temperatures. As the temperature is increased, the stability index starts to decline at above 30°C from above 0.8 to below 0.2 over a temperature range. The same trend is found with all the three surfactants with no particular relation to the cloud point. The results show that temperature has an overiding effect on foam stability.

4.2.2 Effect of Concentration on Foamability

The effect of surfactant concentration on foamability of $NP(EO)_8$, $NP(EO)_9$, and $NP(EO)_{10}$ is shown in Figures 4.13-4.15 respectively. It can be seen that, below the cloud point, the foam height at 0 min was higher at higher surfactant concentration. However, above the cloud point, the foam height of solutions at high concentration decreases sharply to the same level as the foam height at low concentration.

4.2.3 Effect of Surfactant Structure on Foamability

The effect of surfactant structure on foamability is shown in Figure 4.16-4.18. Since foamability decreases sharply above cloud point, the foam heights at temperature below the cloud points are compared. It can be seen that the foam height of $NP(EO)_{10}$ is greatest followed by $NP(EO)_9$and $NP(EO)_8$ respectively. Although the comparison is made on an equal volume concentration basis, but since the three surfactants have almost identical specific density and $NP(EO)_8$ has the lowest molecular weight, the observed results will still be the same if the comparison is made on an equal mole basis. It can therefore be concluded that a nonionic surfactant with higher number of ethylene oxide groups will have higher foamability. Other workers had also obtained similar results (Shinoda et al., 1959).

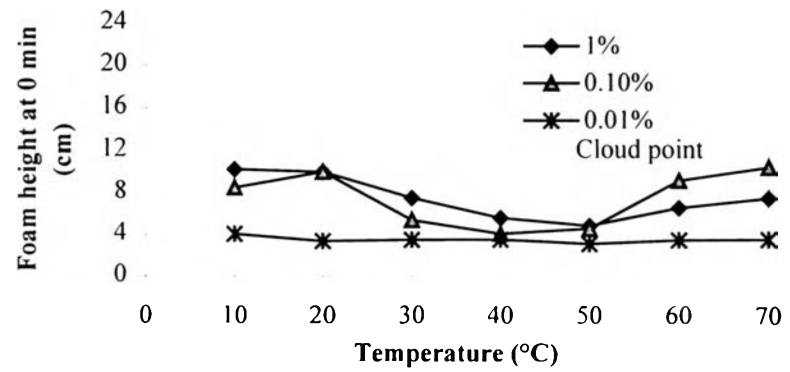

Figure 4.13 Effect of Temperature on Foamability of $NP(EO)_8$ at Different Concentrations (Ross-Miles Method).

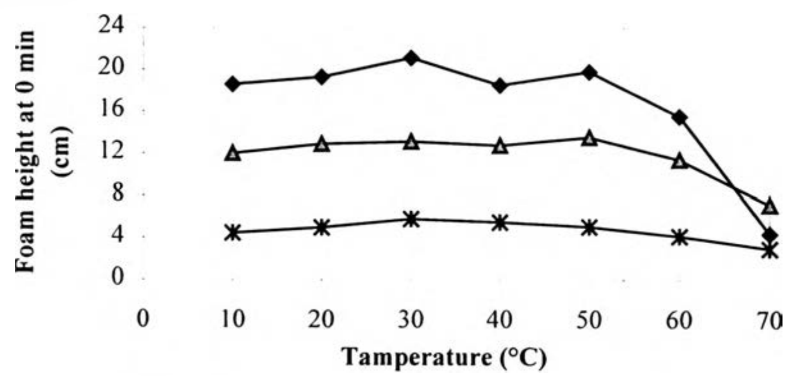

Figure 4.14 Effect of Temperature on Foamability of $NP(EO)_9$ at Different Concentrations (Ross-Miles Method).

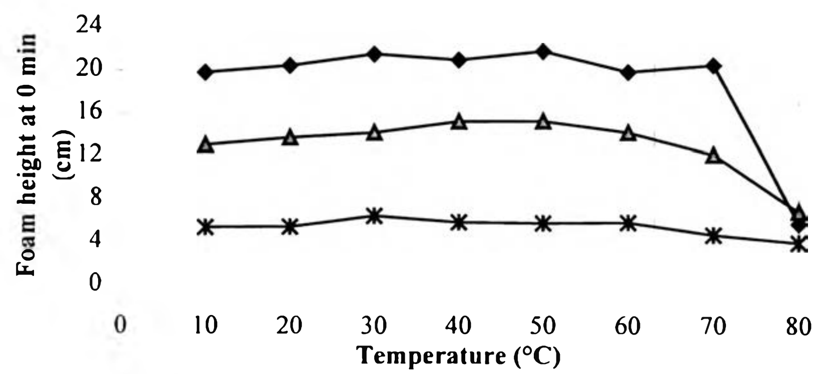

Figure 4.15 Effect of Temperature on Foamability of $NP(EO)_{10}$ at Different Concentrations (Ross-Miles Method).

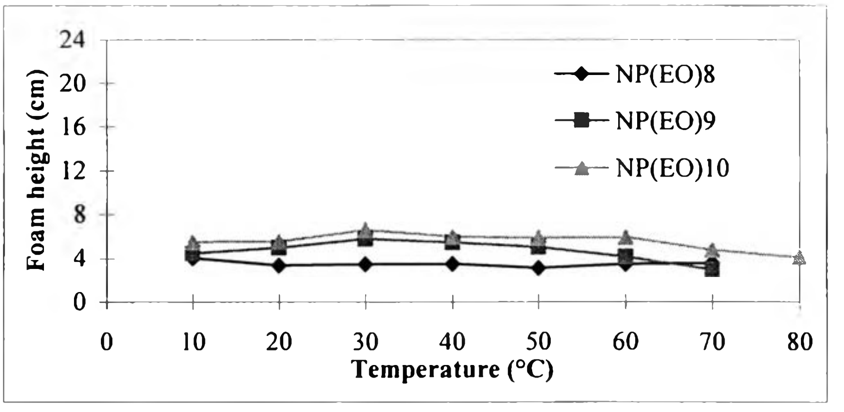

Figure 4.16 Effect of Surfactant Structure on Foamability of 0.01vol% Solution (Ross-Miles Method).

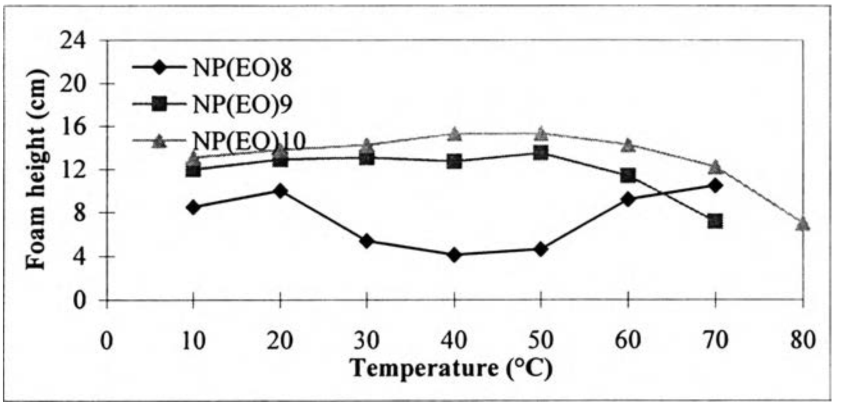

Figure 4.17 Effect of Surfactant Structure on Foamability of 0.1 vol% Solution (Ross-Miles Method).

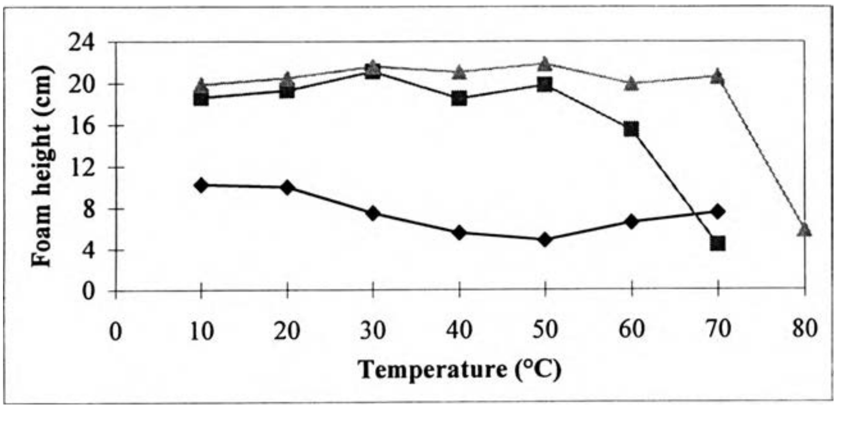

Figure 4.18 Effect of Surfactant Structure on Foamability of 1 vol% Solution (Ross-Miles Method).

4.3 Foaming Tests by the Spray Method

4.3.1 The Effect of Spraying Time

In the Spray method, the solution was drawn from underneath the column and was spray from the top of the column onto the solution. Foam was generated through the spraying mechanism and the fall of spraying liquid on top of the solution in the column. In each experiment, the foam height was read at a 1 minute interval for up to 60 minutes. The spray was then stopped and the foam height was recorded at 5 minute intervals for 30 minutes to study the foam stability. In the Spray method, the amount of foam is found to be time dependent. In this work, it is found that foaming increases rapidly in the initial state of spraying but reaches a stable state after 30 minutes. It is thought that at first, the foam height increases as more solution is sprayed into the column. At the same time, the foam already formed are collapsing. It then reaches a steady state point where the rate of foam generation equal the rate of foam collapsing. In this experiment, at temperature below the cloud point, the steady state is reached after spraying for about 30 minutes, but above the cloud point the foam height decreases after about 30 minutes and trends to reach the steady state eventually.

Measurement of foam life-time

In this experiment, when the spray is turned off, the foams are found to persist for some time before collapsing rapidly to almost zero height within 30 minutes. To measure the stability of the foam, foam height was taken every 5 minutes for 30 minutes and the life time of the foam (To) is defined as the time at the point where the greatest slope of each line intersects with the X-axis (Time-axis).(See Appendix F)

4.3.2 Effect of Temperature on Foamability and Foam Stability

4.3.2.1 Effect on Foamability. Figure 4.19-4.22 and Figure 4.23-4.26 show the foamability by the Spray method of $NP(EO)_9$ and $NP(EO)_{10}$ at 0.01vol%, 0.1vol%, 0.5vol%, and 1.0vol% respectively. It can be seen that at low surfactant concentration of 0.01% where the cloud point could not be detected (Figure 4.19 and 4.23), the foam height increases with an increase in spray time for the first 30 minutes, after this time, the foam height remains constant. This trend occurs over the whole temperature range of 30-70°C. The final foam height after 60 minutes is found to decrease as the temperature increases.

At a higher concentration of 0.1vol% where a cloud point could be detected (Figure 4.20 and 4.24), the above trend is also followed by experiments carried out below the cloud point. However, as the temperature approaches the cloud point, the foam decreases in height after 30 minutes before reaching a steady state. It is postulated that, at around the cloud point, the micellar-rich phase starts to form and it causes the collapse of foams when it is sprayed onto the solution in the column leading to the lowering of foam height after 30 minutes. The same effects are observed with higher surfactant concentrations of 0.5% and 1.0%vol (Figure 4.21-4.22 and 4.25-4.26).

4.3.2.2 Effect on Foam Stability. Figures 4.27-4.30 and 4.31-4.34 show the decay of foam after the spray was turned off. It can be seen that at low concentration of 0.01% where a cloud point could not be detected (Figure 4.27 and 4.31), there is a gradual decrease of foam height at all temperatures. At higher concentrations where cloud points exist (Figure 4.28-4.30 and 4.32-4.34), it is found that, at temperature below cloud point, the foams tend to persist for a while (about 5-10 minutes) before collapsing rapidly to zero. However, at temperatures above the cloud point, the foams are found to collapse rapidly to zero as soon as the spray is turned off. This is consistent

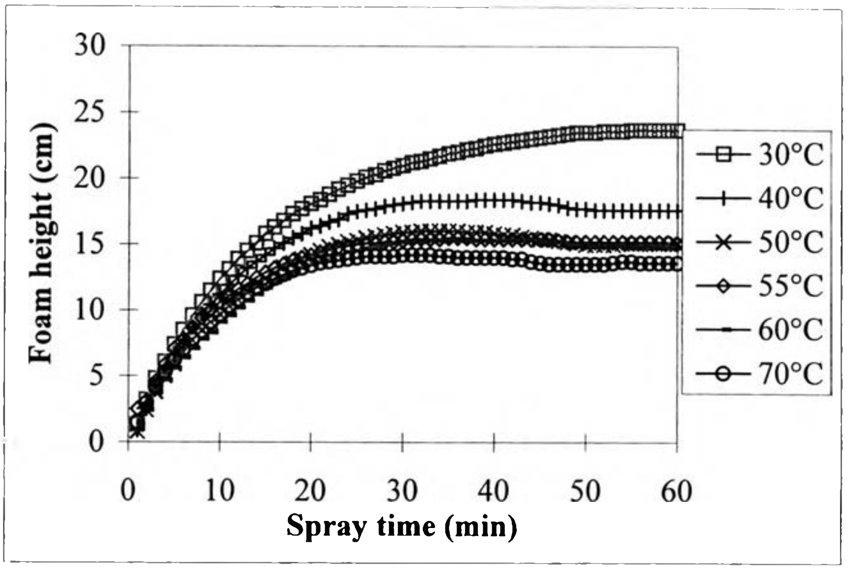

Figure 4.19 Effect of Temperature on Foamability of 0.01 vol% $NP(EO)_9$ (Spray Method).

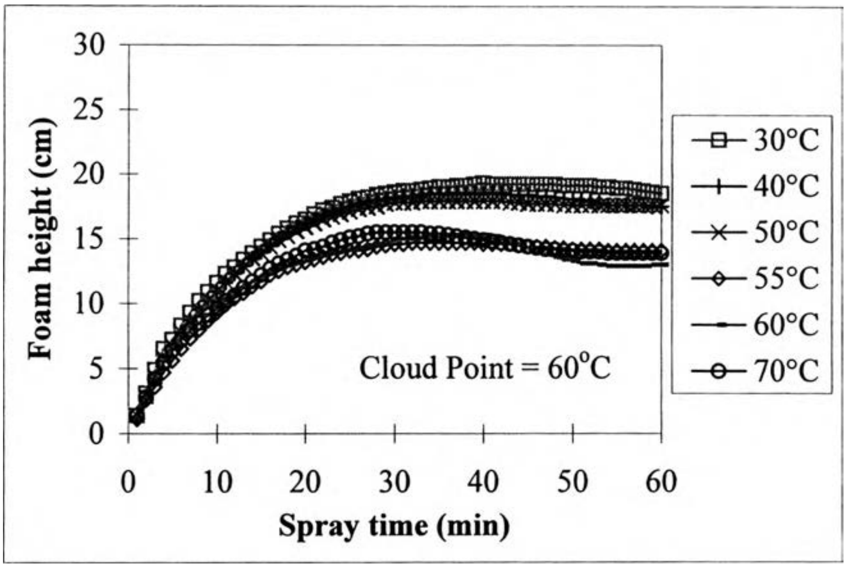

Figure 4.20 Effect of Temperature on Foamability of 0.1 vol% $NP(EO)_9$ (Spray Method).

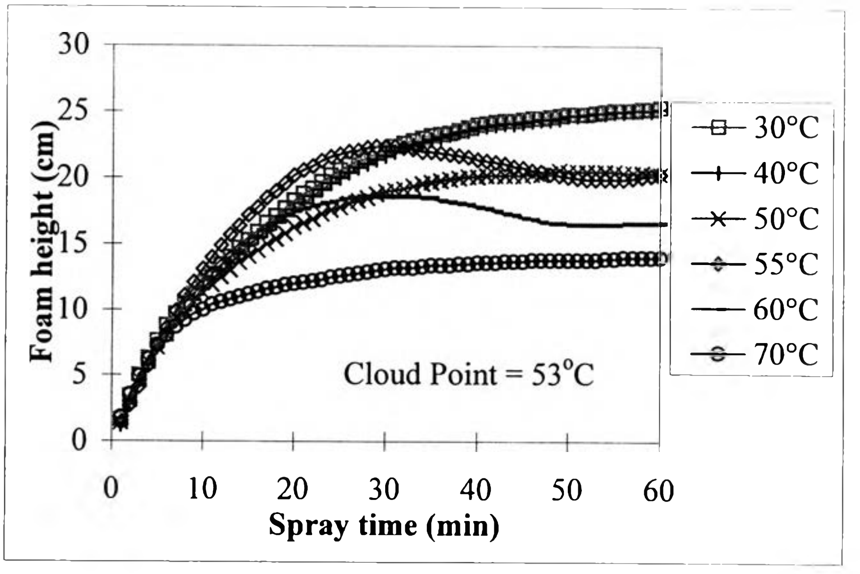

Figure 4.21 Effect of Temperature on Foamability of 0.5 vol% $NP(EO)_9$ (Spray Method).

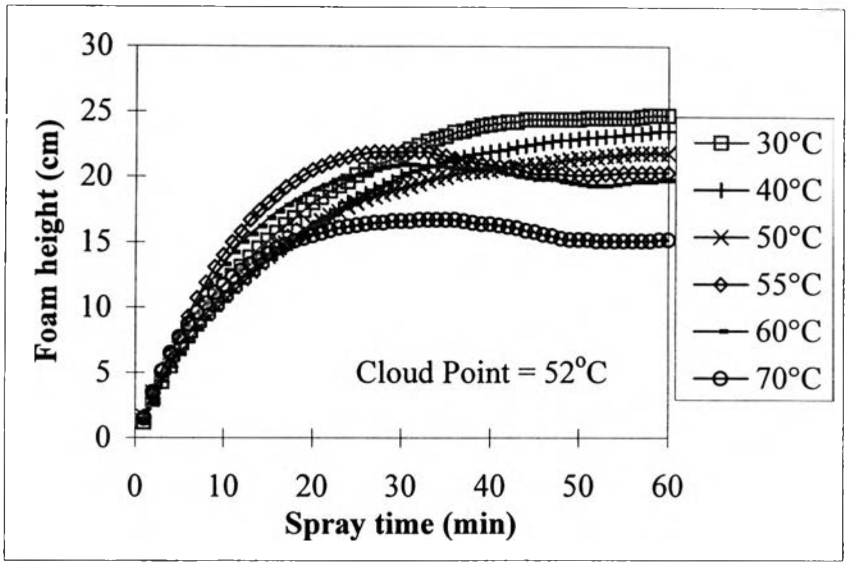

Figure 4.22 Effect of Temperature on Foamability of 1.0 vol% $NP(EO)_9$ (Spray Method).

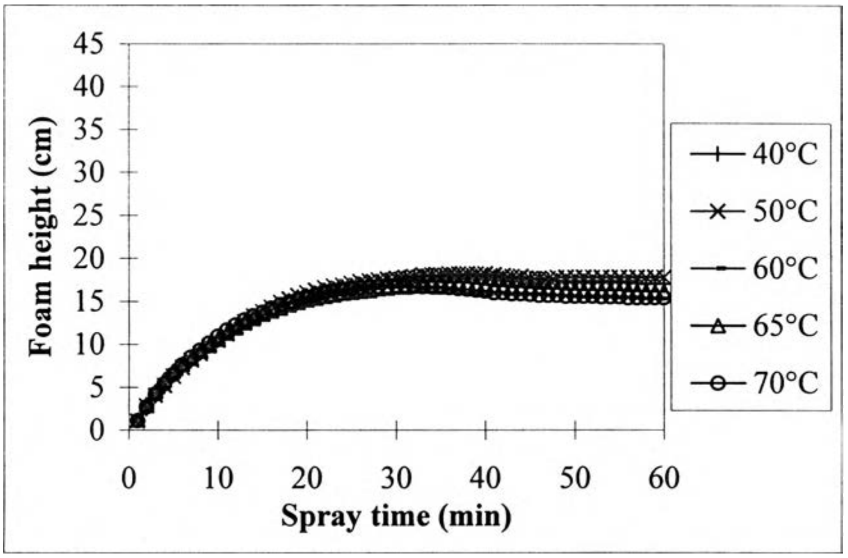

Figure 4.23 Effect of Temperature on Foamability of 0.01 vol% $NP(EO)_{10}$ (Spray Method).

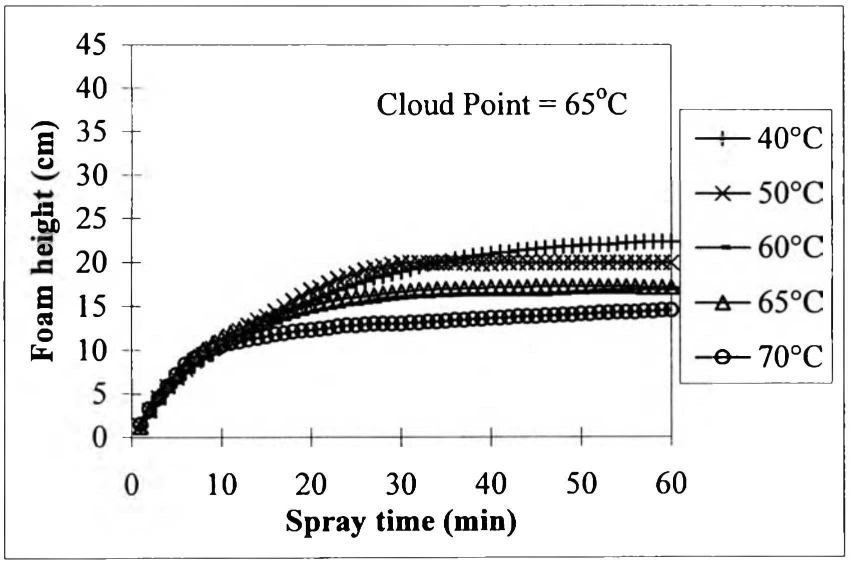

Figure 4.24 Effect of Temperature on Foamability of 0.1 vol% $NP(EO)_{10}$ (Spray Method).

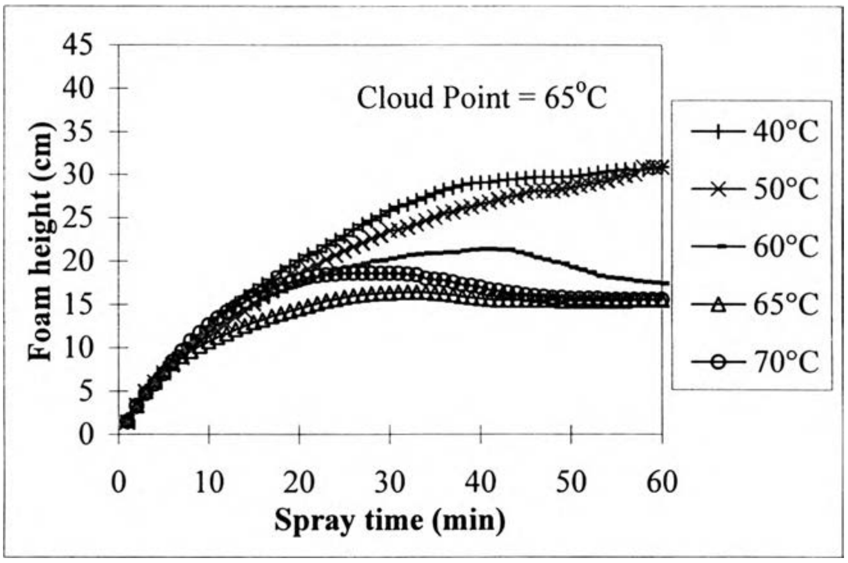

Figure 4.25 Effect of Temperature on Foamability of 0.5 vol% $NP(EO)_{10}$ (Spray Method).

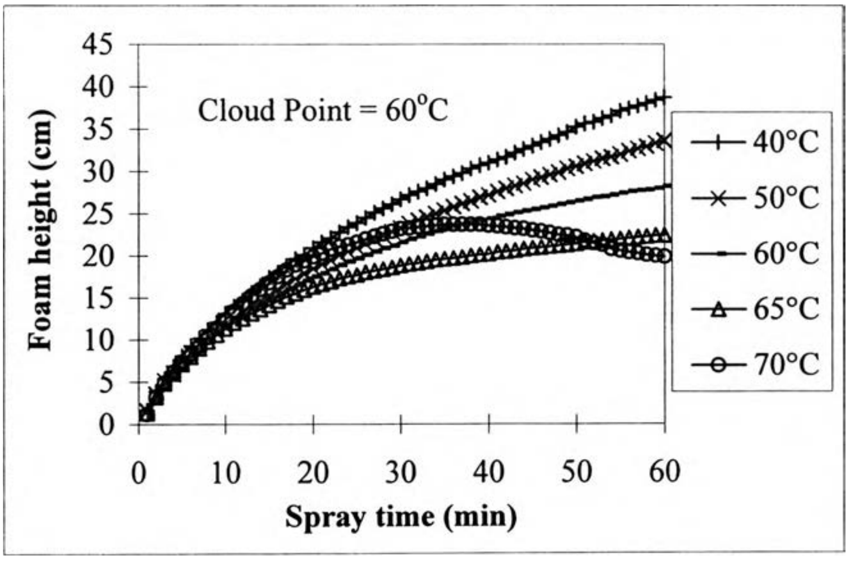

Figure 4.26 Effect of Temperature on Foamability of 1.0 vol% $NP(EO)_{10}$ (Spray Method).

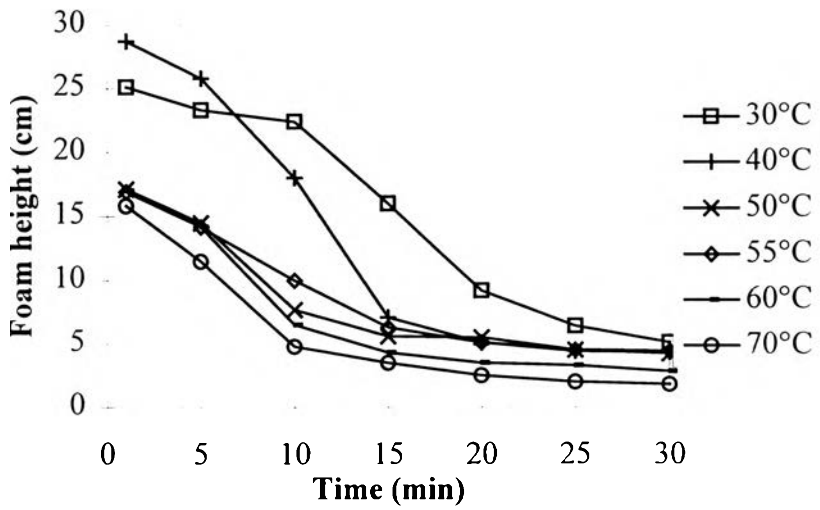

Figure4.27 Effect of Temperature on Foam Stability of 0.01 vol% $NP(EO)_9$ (Spray Method).

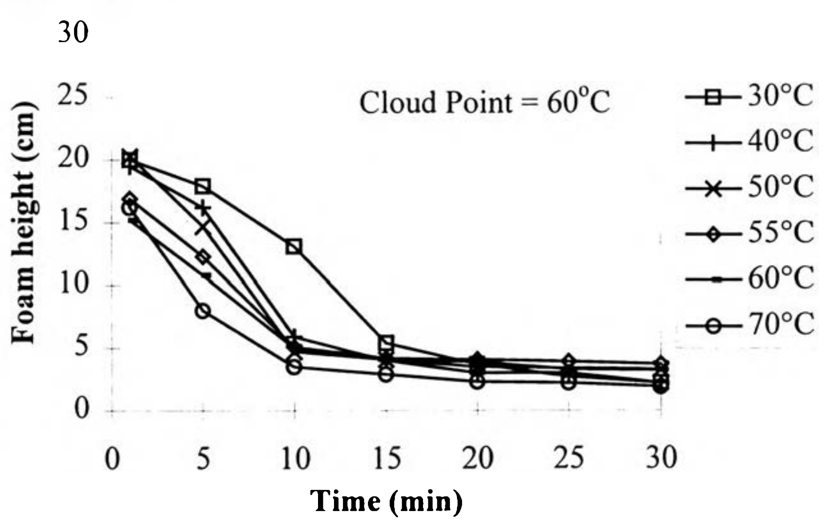

Figure 4.28 Effect of Temperature on Foam Stability of 0.1 vol% $NP(EO)_9$ (Spray Method).

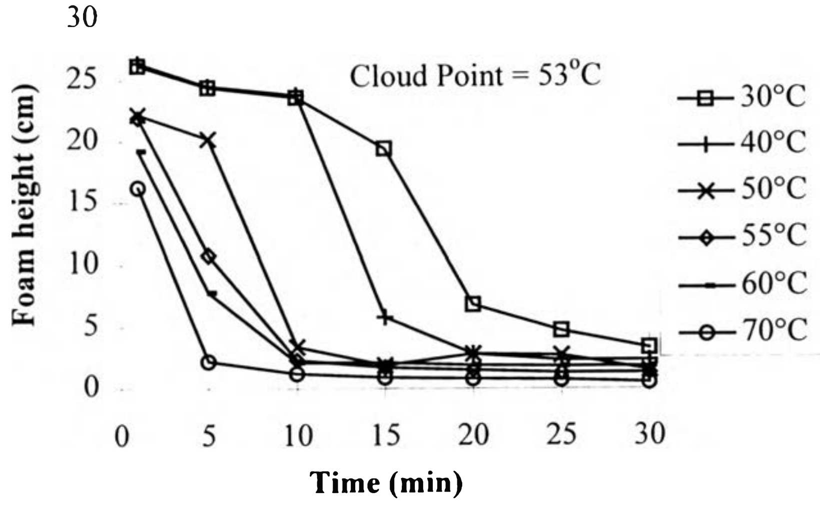

Figure 4.29 Effect of Temperature on Foam Stability of 0.5 vol% $NP(EO)_9$ (Spray Method).

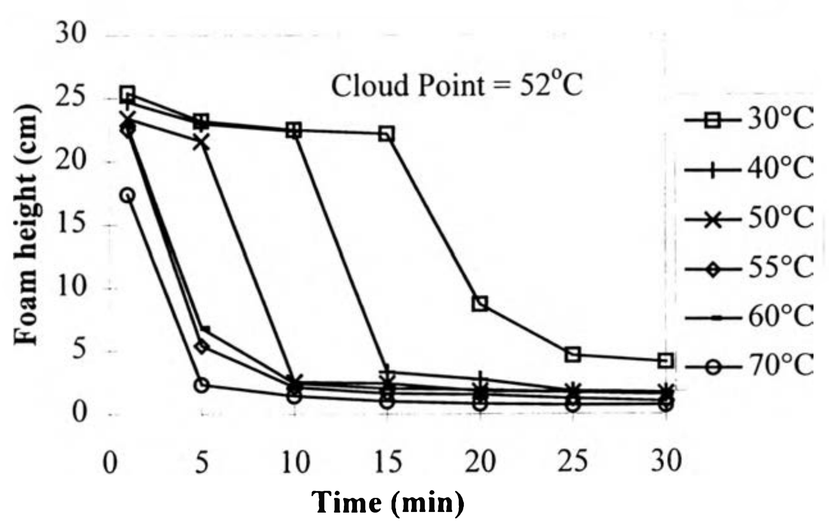

Figure 4.30 Effect of Temperature on Foam Stability of 1.0 vol% $NP(EO)_9$ (Spray Method).

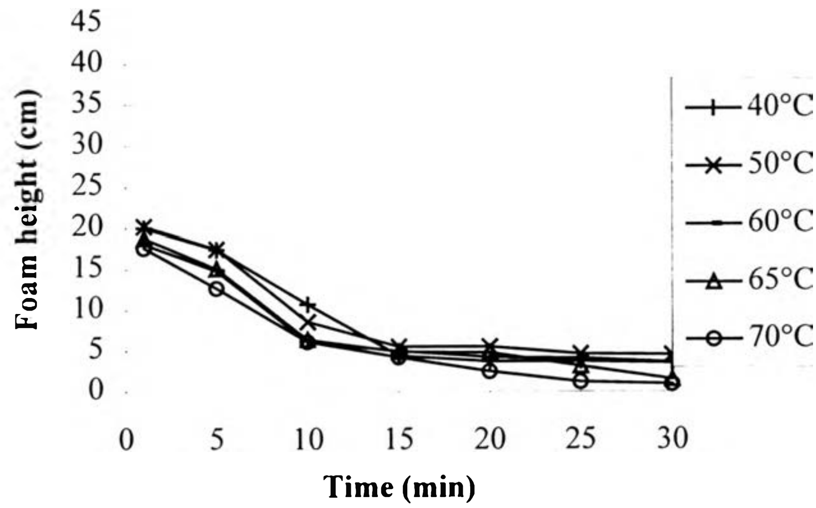

Figure 4.31 Effect of Temperature on Foam stability of 0.01 vol%NP$(EO)_{10}$ (Spray Method).

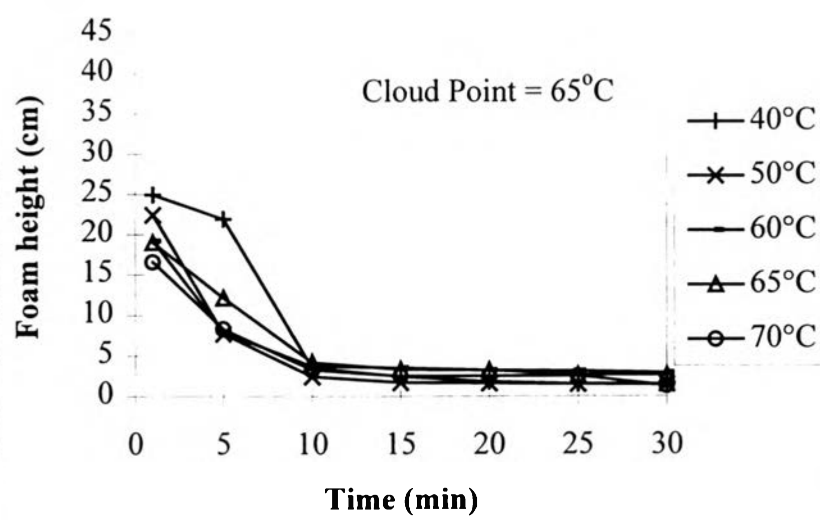

Figure 4.32Effect of Temperature on Foam stability of 0.1 vol% NP$(EO)_{10}$ (Spray Method).

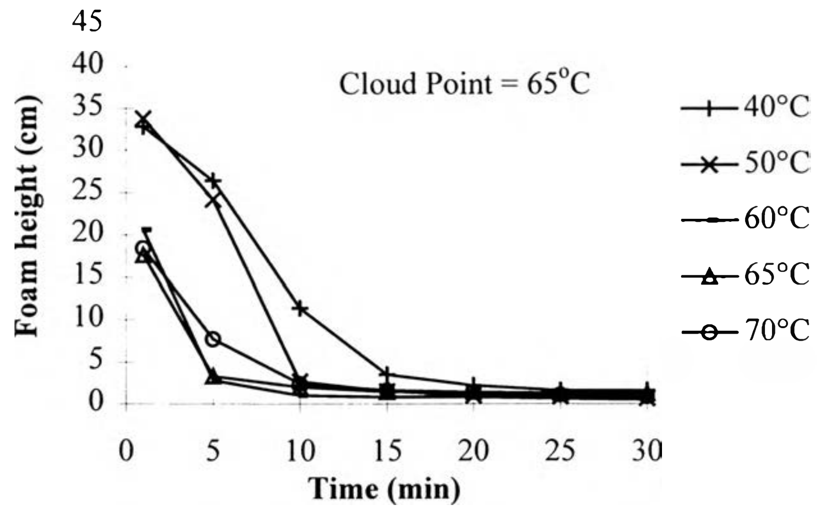

Figure 4.33 Effect of Temperature on Foam stability of 0.5 vol% $NP(EO)_{10}$ (Spray Method).

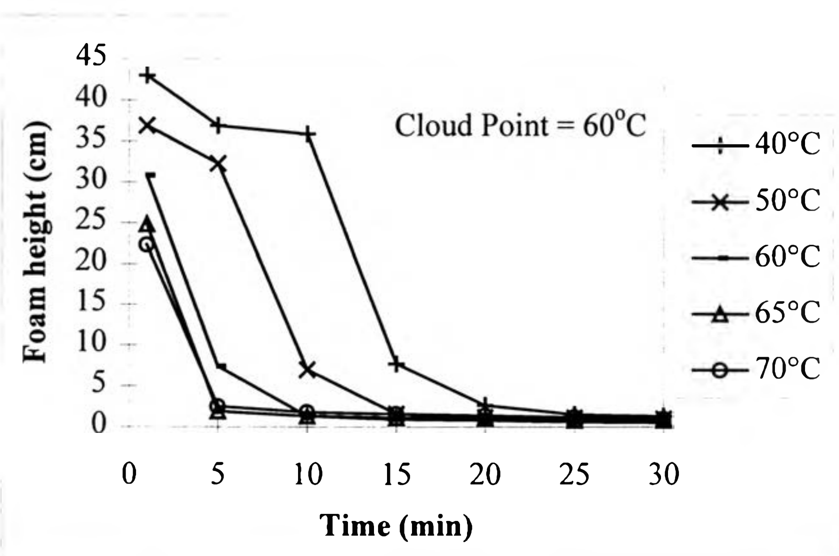

Figure 4.34 Effect of Temperature on Foam stability of 1.0 vol% $NP(EO)_{10}$ (Spray Method).

with proposition that the coacervate phase formed at the cloud-point has an antifoam effect and it causes the rapid collapse of foams.

4.3.3 Effect of Surfactant Concentration on Foamability and Foam Stability

4.3.3.1 Effect on Foamability. Figures 4.35 and 4.36 show the effect of surfactant concentration on the foamability of $NP(EO)_9$ and $NP(EO)_{10}$ respectively. It can be seen that in case of $NP(EO)_9$, the foam height after 60 minutes of spraying time at each temperature stays relatively constant throughout the whole concentration range. The effect of concentration is however more pronounced in the case of $NP(EO)_{10}$ where the foam height increases with an increase in concentration.

4.3.3.2 Effect on Foam Stability. Figure 4.37 and 4.38 show the effect of the surfactant concentration on the foam stability of $NP(EO)_9$ and $NP(EO)_{10}$ respectively. It can be seen that, in both case, the life-time of foam (To) is high at the lowest concentration of 0.01%. It then decreases at a concentration of 0.1% before increasing slightly as the concentration is increased to 0.5% and 1.0% respectively. The results around the cloud point (55°C for $NP(EO)_9$ and 65°C for $NP(EO)_{10}$) are found to be rather irregular, probably due to proximity to a phase boundary where a step function change in behavior can occur over a very small range of temperatures.

The results show that surfactant concentration generally has little effect on foam stability.

4.3.4 Effect of Surfactant Structure on Foamability and Foam Stability

4.3.4.1 Effect on Foamability. When the foam height after the spraying time of 60 minutes for $NP(EO)_9$ and $NP(EO)_{10}$ are compared, it is found that, in the case of $NP(EO)_9$, the foam height is in the range of 15-25

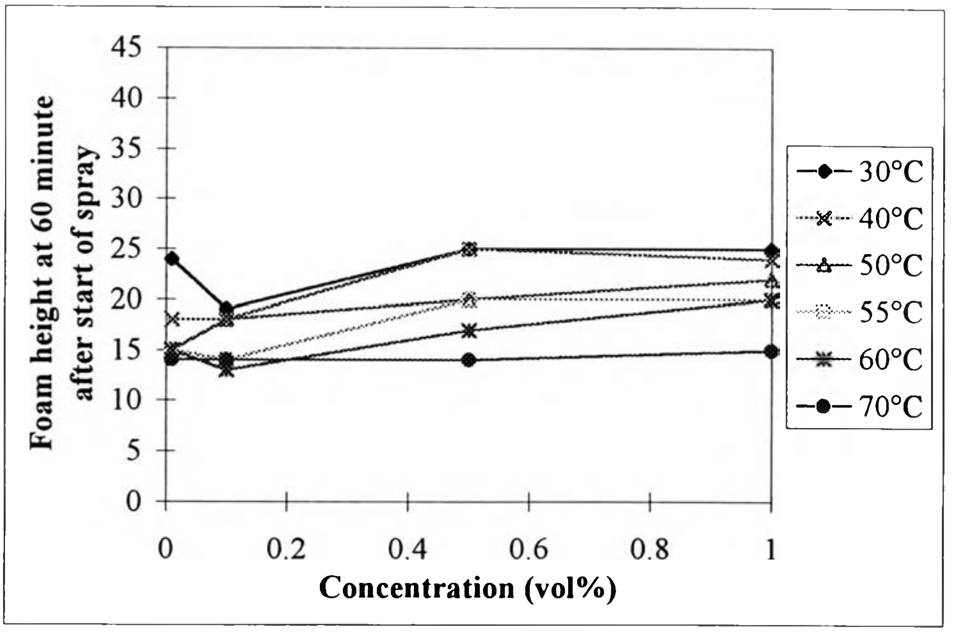

Figure 4.35 Effect of Concentration on Foamability of $NP(EO)_9$.

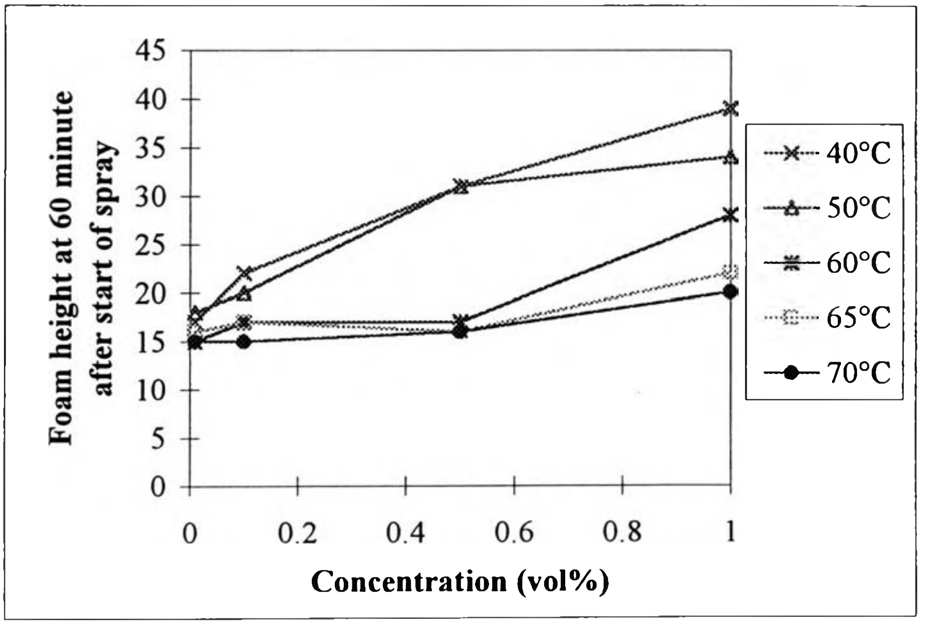

Figure 4.36 Effect of Concentration on Foamability of $NP(EO)_{10}$.

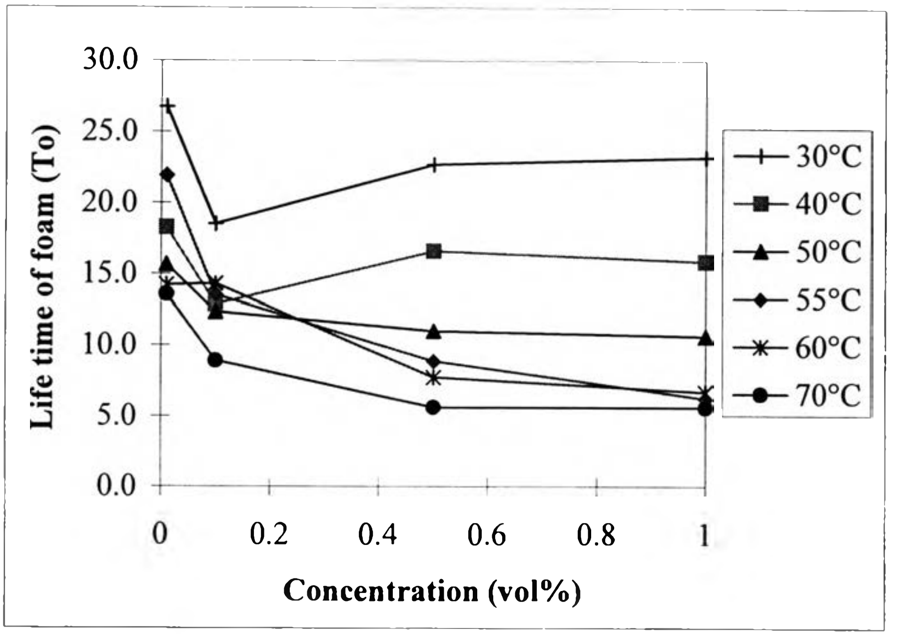

Figure 4.37 Effect of Concentration on Foam Stability of $NP(EO)_9$.

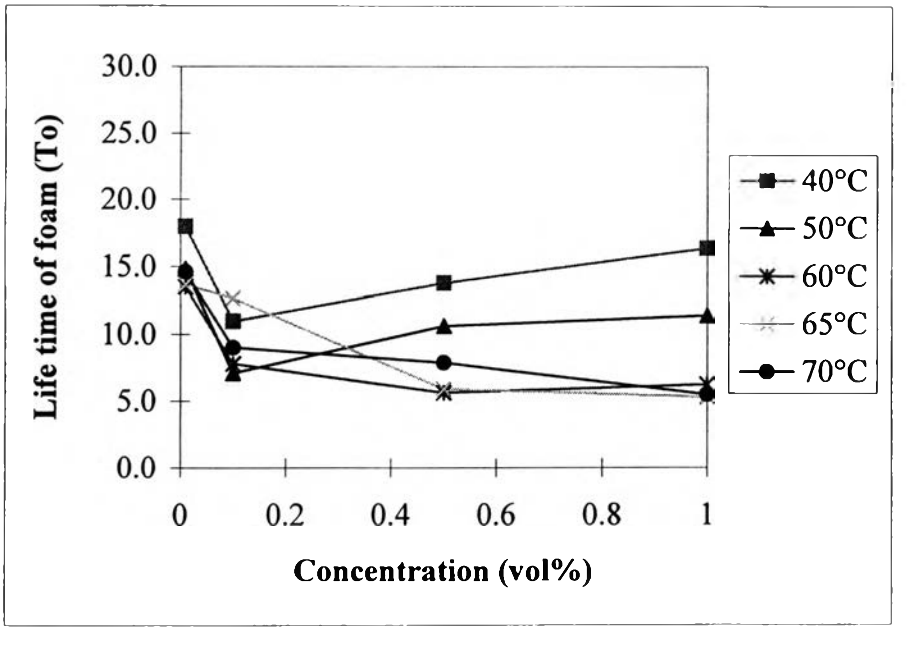

Figure 4.38 Effect of Concentration on Foam Stability of $NP(EO)_{10}$.

cm while $NP(EO)_{10}$ produces foam height in the range of 15-40 cm. $NP(EO)_{10}$ therefore seems to have more foamability than $NP(EO)_9$ especially at higher concentration.

4.3.4.2 Effect on Foam Stability. By comparing the life-time (To) of foam of $NP(EO)_9$ and $NP(EO)_{10}$ in Figure 4.37 and 4.38, it can be seen clearly that the life-time of foam of $NP(EO)_9$ is generally higher especially at lower concentrations.

4.4 Comparison of the Ross-Miles and Spray Methods

In general, the results obtain from the Ross-Miles method are similar to those from the Spray method. The nonionic surfactants show marked transition in their foaming behavior around the cloud point. In the Ross-Miles method, both foamability and foam stability are found to be relatively stable below the cloud point but both decrease sharply around the cloud point and stay at the low level thereafter. In the Spray method at around the cloud point, the foam height decreases after spraying for 30 minutes indicating that the rate of foam destruction is greater than the rate of foam generation. The foam height after 1 hour of spraying time is also found to be lower above the cloud point. The measurements of foam height after the spray is turned off showed that below the cloud point, foams generally persist for some time before collapsing, but above the cloud point, foams are found to collapse rapidly as soon as the spray is turned off. Both the Ross-Miles and Spray tests therefore confirm the important role of the cloud point on the foaming of nonionic surfactants.

The effect of concentration on the foaming of surfactants is shown clearly in the Ross-Miles method where it is found that the foamability of the surfactant increases with increase in surfactant concentration. However above the cloud point, the foam height decreases sharply to almost the same level a regardless of the surfactant concentration. In the Spray method, the surfactant concentration seems to have less pronounced effect on the foamability of the surfactant and it has little effect on the foam stability.

The effect of increasing the number of ethylene oxide group in the molecule is found to increase the foamability of surfactants by both the Ross-Miles and the Spray methods.