CHAPTER IV
RESULTS AND DISCUSSION

4.1 Cloud Point Determination

4.1.1 Nonionic Surfactants

The cloud points of $NP(EO)_8$, $NP(EO)_9$, and $NP(EO)_{10}$ in the concentration range of 0.001-0.02 M are shown in Table 4.1. The cloud point decreases slightly as the concentration increases, and also found to increase with the number of ethylene oxide in the surfactant molecules. This is because the increase in the number of ethylene oxide increases the surfactant solubility (Michael and Irene, 1993).

Table 4.1 Cloud points of the nonionic surfactants used.

Concentration (M)	Cloud point of nonionic surfactants (° C)		
	$NP(EO)_8$	$NP(EO)_9$	$NP(EO)_{10}$
0.001	29	56	65
0.002	28	56	65
0.01	27	55	64
0.02	27	54	63

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°C, 52-53°C, and 60-65°C respectively. Since the concentration of 1 wt% solution is in between 0.01 M and 0.02 M (See Appendix B for equivalent concentration in wt% and M), and the cloud point of those two concentrations are almost the same, it can be said that the cloud points obtained in this work are in the same range as the ones quoted by the manufacturer.

4.1.2 Mixed Nonionic/Anionic Surfactants

In this experiment, the mole ratios of NP(EO)$_8$/SDS and NP (EO)$_9$/SDS were varied from 0.999/0.001, 0.998/0.002, 0.997/0.003, 0.996/0.004 to 0.995/0.005 and the total concentration was fixed at 0.01 M.

Figure 4.1 shows the cloud point of solutions containing different ratios of NP(EO)$_8$/SDS and NP(EO)$_9$/SDS. It can be seen that the cloud point increases markedly upon addition of minute amounts (about 10^{-5} M) of SDS. At such small concentrations (far below the CMC of SDS) the SDS molecules exist either as monomers or as mixed micelles with the nonionic surfactants. As the SDS molecules are added to the system, they go into the nonionic micelles and create charges on the surface of the micelle. These added surface charges increase the repulsion between micelles and make it harder for them to cross the potential barrier for coalescence and correspondingly the cloud point is raised (Valaulikar and Manohar, 1985; Marszall, 1988).

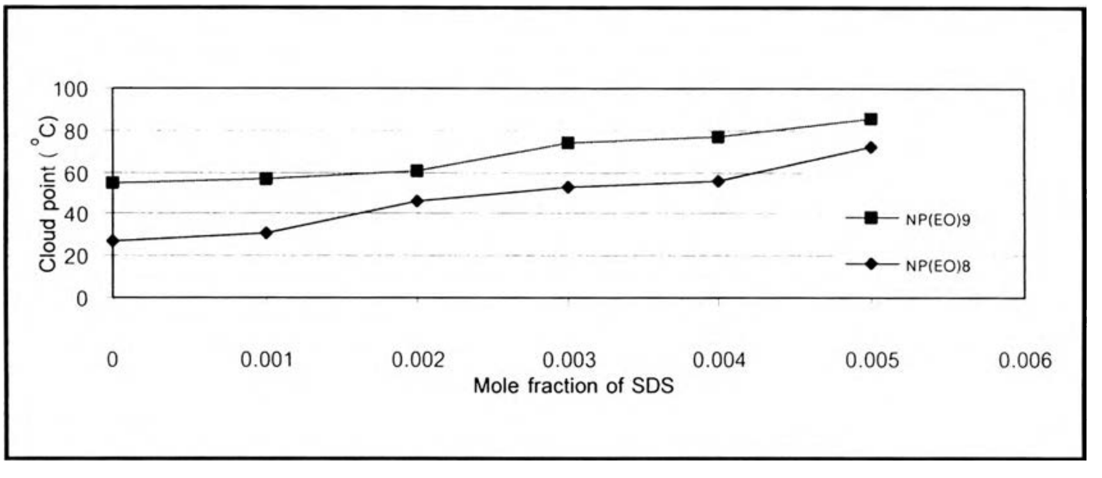

Figure 4.1 Cloud point of 0.01 M NP(EO)$_8$/SDS, NP(EO)$_9$/SDS mixtures at varying mole ratio.

4.1.3 Effect of Surfactant Structure on Cloud Point Temperature

In this experiment, the mole ratio of $NP(EO)_8$/SDS, $NP(EO)_9$ /SDS, and $NP(EO)_{10}$/SDS were fixed at 0.9/0.1 and the total concentration was 0.01 M. The NaCl concentration in the mixture was varied to cover the regions above and below the cloud point temperature quoted by the manufacturer.

The results in Figure 4.2 show that the cloud point of the mixtures decreases dramatically and then gradually decrease with the increase in NaCl. There is however a sharp decrease of cloud point as soon as a small amount of NaCl is added. Addition of NaCl to these mixed systems reduced the cloud point considerably. This observation seems logical because addition of salt results in the swamping of micellar charge resulting in the screening of intermicellar repulsions (Marszall, 1988; Vora *et al.*, 1999).

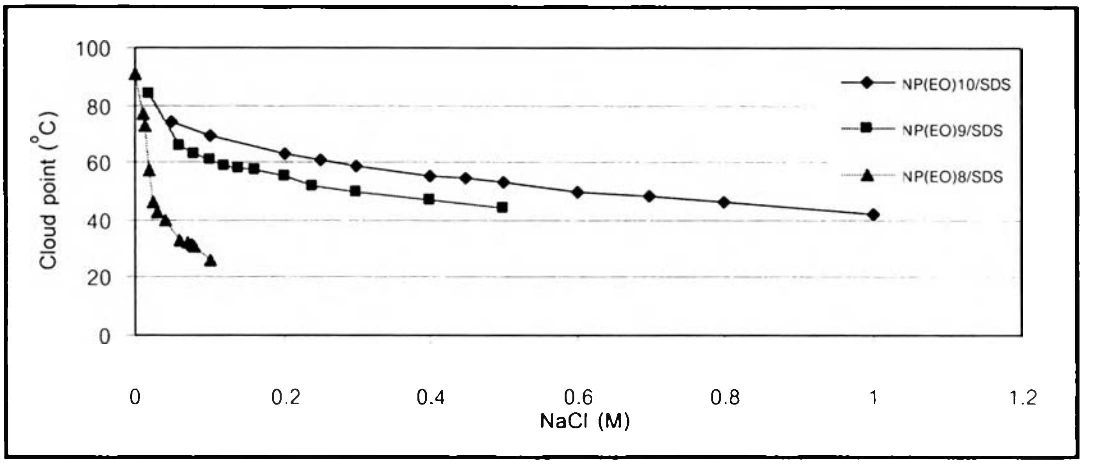

Figure 4.2 Cloud point of 0.01 M $NP(EO)_8$/SDS, $NP(EO)_9$/SDS, and NP $(EO)_{10}$ /SDS mixtures at the ratio 0.9/0.1.

4.1.4 Effect of Mole Ratio on Cloud Point Temperature

In this experiment, the mole ratio of $NP(EO)_8/SDS$ was varied from 1.0/0.0, 0.8/0.2, 0.7/0.3 to 0.6/0.4. The total concentration was fixed at 0.01 M and the NaCl concentration in the mixture was varied to cover the regions above and below the cloud point temperature quoted by manufacturer.

Figure 4.3 shows the effect of mole ratio of nonionic/anionic on the cloud point of the mixtures. As the mole ratio of $NP(EO)_8/SDS$ decreases, the amount of NaCl needed to reduce the cloud point to the same temperature also increases. The mixture with higher ratio of SDS showed higher cloud point. Thus, the NaCl added to suppress the cloud point is greater as compared to those with lower ionic content.

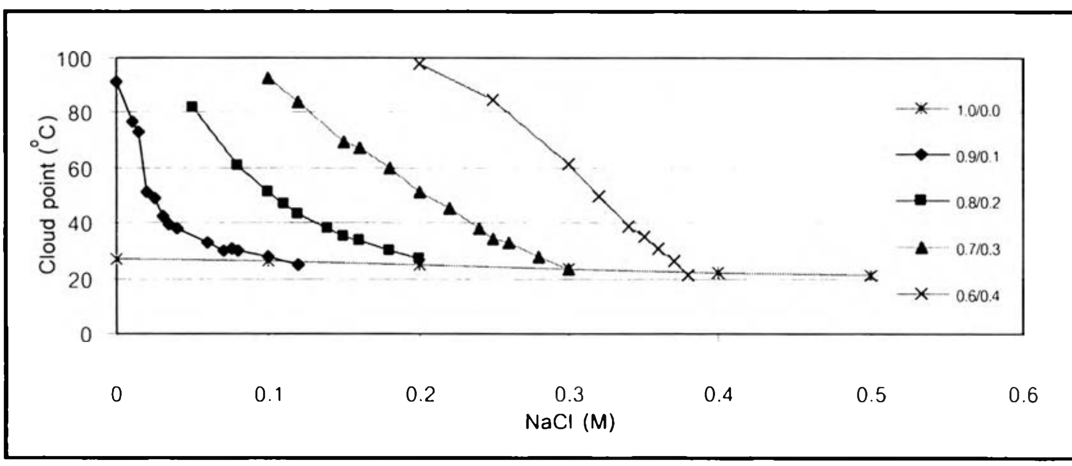

Figure 4.3 Cloud point of 0.01 M $NP(EO)_8/SDS$ mixtures at varying mole ratio.

4.2 Foaming of Anionic, Nonionic, and Their Mixtures

All the foaming tests were done by the Ross-Miles method (ASTM D1173-53) and shake test method. Both methods are widely used and suitable for the study of moderate foaming solutions. Shake test method is an example of the dynamic method while the Ross-Miles foam test is semistatic method (Schick and Schmolka, 1987).

4.2.1 Foaming of Anionic Surfactants

Ross-Miles Method

Figure 4.4 shows the foamability of SDS in the concentration range of 0.002 M to 0.02 M with the Ross-Miles method. The concentration range covers roughly below and above the CMC of SDS at 0.008 M. It can be seen that the foam height increased with an increase in concentration and reached the maximum of 226 mm in the neighborhood of CMC. The foam height remained constant regardless of concentration above the CMC. There was only a slight decrease in foam height throughout the whole concentration range showing that the foam stability was high.

Figure 4.5 shows the foamability and foam stability of SDS concentration 0.01 M. In this system the temperature was varied in order to study the effect of temperature on the foaming above the CMC of SDS. It can be seen that foamability and foam stability were high and started to decrease over 40°C. This is due to the decomposition of SDS at high temperature (Cohen *et al.*, 1993).

Shake Test Method

Figure 4.6 shows the foamability and foam stability of SDS solutions by the shake test method. Similar results were obtained as in the case of the Ross-Miles method, i.e. the foamability increased with concentration up to 100 mm in the neighborhood of CMC and remained constant after the CMC. The foam stability of SDS was also high before declining slightly beyond the CMC.

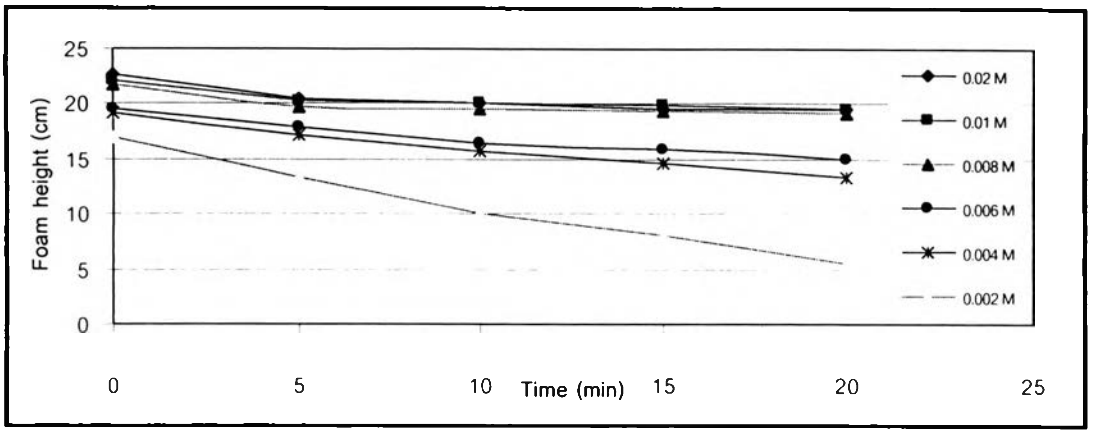

Figure 4.4 Relationship between foam height of SDS and time at varying SDS concentrations by the Ross-Miles method, temperature = 30°C.

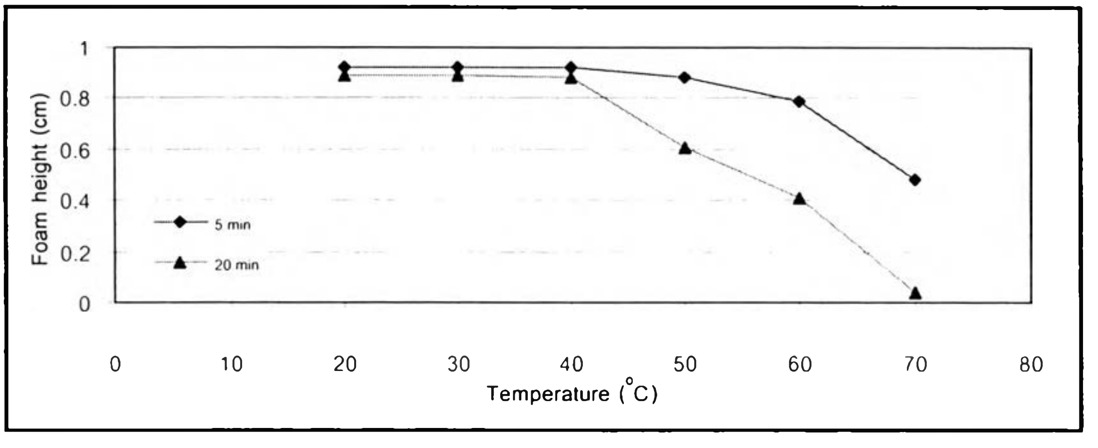

Figure 4.5 Relationship between foam height of 0.01 M SDS and temperature at t=0 min, 5 min, and 20 min by the Ross-Miles method.

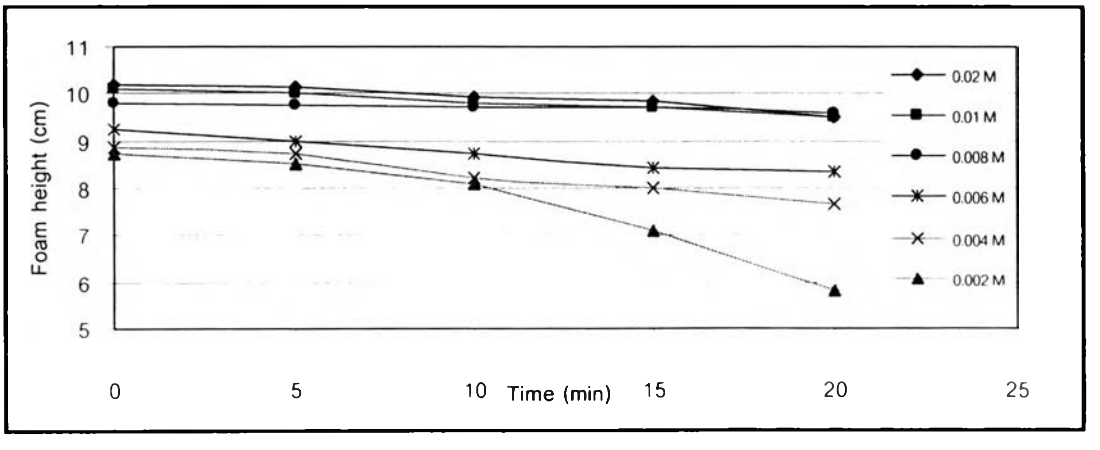

Figure 4.6 Relationship between foam height of SDS and time at varying SDS concentrations by the shake test method, temperature = 30°C.

4.2.2 Foaming of Nonionic Surfactants

4.2.2.1 Effect of Surfactant Structure on Foamability

Ross-Miles Method

Figure 4.7 shows the foamability of 0.01 M $NP(EO)_8$, $NP(EO)_9$ and $NP(EO)_{10}$ at varying temperature. Below the cloud point, the foam height is independent of temperature. Above the cloud point, the foam height decreases dramatically. The same effects were observed for all the three types of nonionic surfactants studied. Similar qualitative results have been obtained by earlier workers (Watanavitukul, 1998; Chaisalee, 1999). The results show that the cloud point plays an important 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). Since foamability decreases drastically above cloud point, the foam heights at temperature below the cloud points are compared. It was found that the foam height of $NP(EO)_{10}$ is greatest followed by $NP(EO)_9$ and $NP(EO)_8$ respectively. It can therefore be concluded that a nonionic surfactant with higher number of ethylene oxide groups will have higher foamability. Similar results were also obtained by earlier workers (Shinoda *et al.*, 1961).

Shake Test Method

Figure 4.8 shows the effect of surfactant structure on the foamability of $NP(EO)_8$, $NP(EO)_9$, and $NP(EO)_{10}$ by shake test method. Similar results were obtained as in the case of the Ross-Miles tests, i.e. NP $(EO)_{10}$ and $NP(EO)_9$ have more foamability than $NP(EO)_8$, and $NP(EO)_{10}$ produces the highest foamability.

4.2.2.2 Effect of Temperature on Foam Stability

Figures 4.9 – 4.11 shows the foam stability of 0.01 M $NP(EO)_8$, $NP(EO)_9$, and $NP(EO)_{10}$ respectively. It can be seen that the foam stability is generally high at low temperature. As the temperature is increased, the foam stability starts to decline at above 30°C. The same trend is found with all the three surfactants with no particular relation to the cloud point. In this case, the foam stability only depends on the temperature.

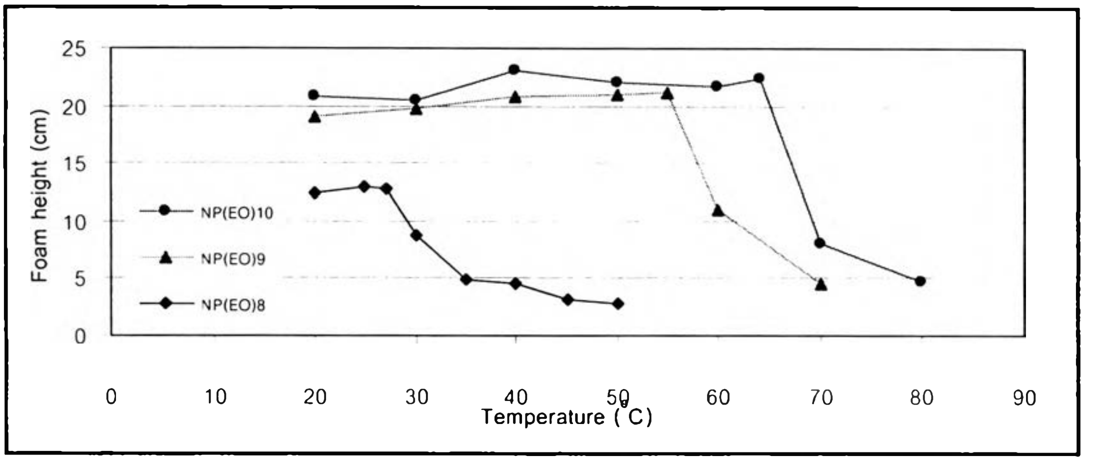

Figure 4.7 Relationship between foam height of 0.01 M nonionic surfactants and temperature by the Ross-Miles method.

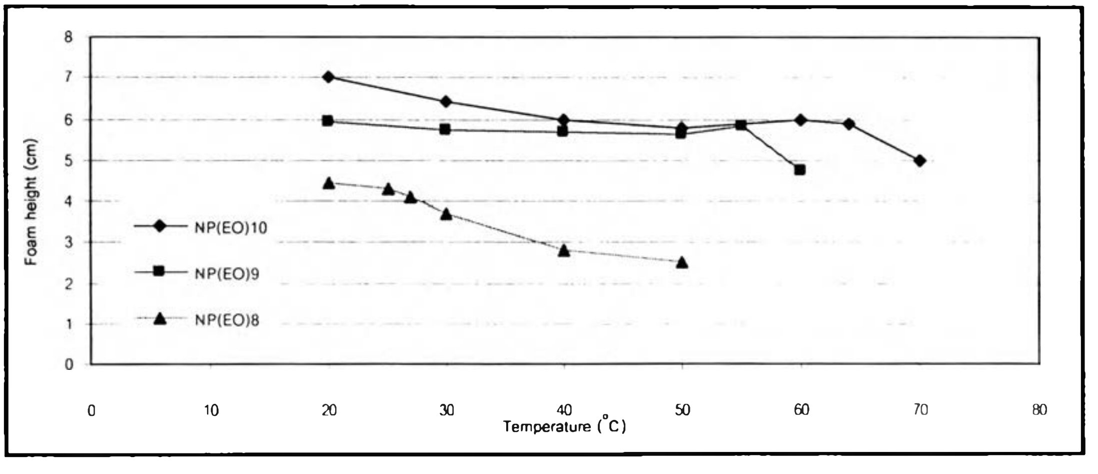

Figure 4.8 Relationship between foam height of 0.01 M nonionic surfactants and temperature by the shake test method.

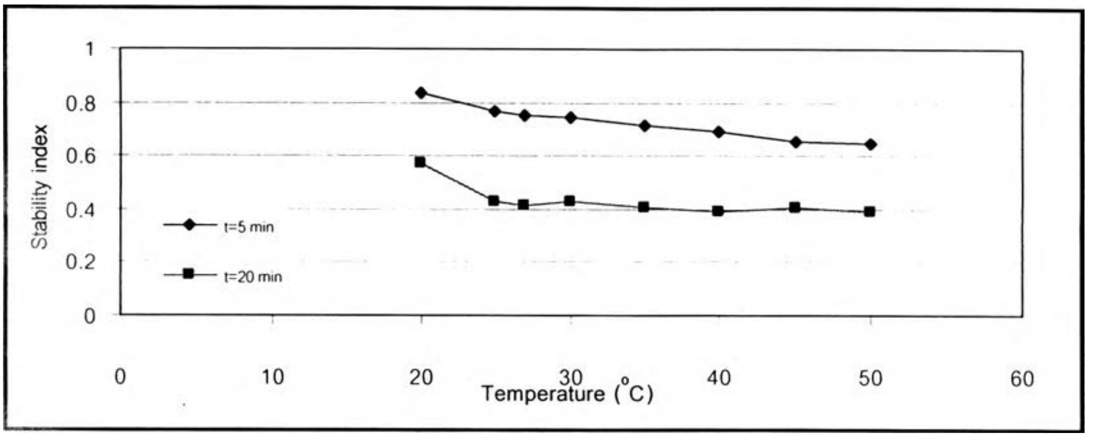

Figure 4.9 Relationship between foam height of 0.01 M $NP(EO)_8$ and temperature at different time periods by the Ross-Miles method.

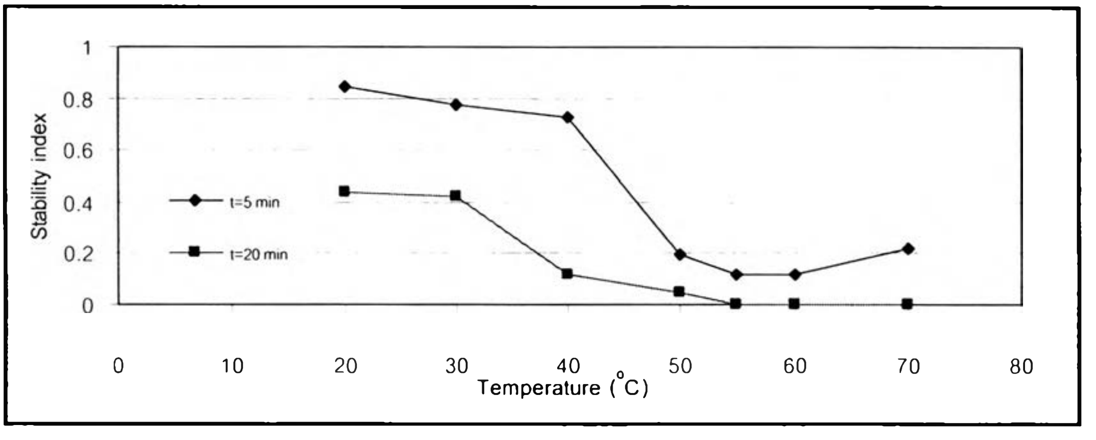

Figure 4.10 Relationship between foam height of 0.01 M $NP(EO)_9$ and temperature at different time periods by the Ross-Miles method.

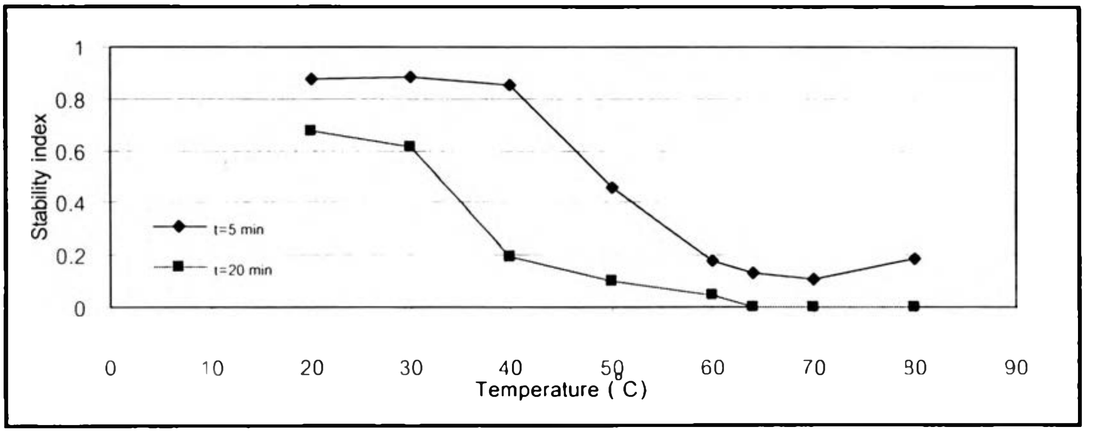

Figure 4.11 Relationship between foam height of 0.01 M $NP(EO)_{10}$ and temperature at different time periods by the Ross-Miles method.

4.2.3 Foaming of Nonionic/Anionic Systems

Ross-Miles Method

In this experiment, the mole ratios of $NP(EO)_8$/SDS, $NP(EO)_9$/ SDS, and $NP(EO)_{10}$/SDS were varied from 0.0/10., 0.2/0.8, 0.5/0.5, 0.8/0.2 to 1.0/0.0. The total concentration was 0.01 M and the temperature was fixed at 30°C.

Figures 4.12 - 4.13 show the foamability and foam stability of solutions containing different ratios of $NP(EO)_8$/SDS, $NP(EO)_9$/SDS, and NP $(EO)_{10}$ /SDS. It can be seen that in all cases there is a slight decrease in foam height with an increase in molar ratio of nonionic surfactants. It is significant to note that there was no phase separation in this system. The slight decrease in foam height is presumably due to the drainage rate or surface rheological effects.

Shake Test Method

Figures 4.14 - 4.15 show the foamability and foam stability of solutions containing different ratios of $NP(EO)_8$/SDS, $NP(EO)_9$/SDS, and NP $(EO)_{10}$ with the total concentration fixed at 0.01 M.

In the shake test method, it can be clearly seen that the foamability and foam stability was decreased with an increase in mole ratio of nonionic surfactants. In all cases where the cloud point could not be detected, there is a gradual decrease of foam height at all temperatures.

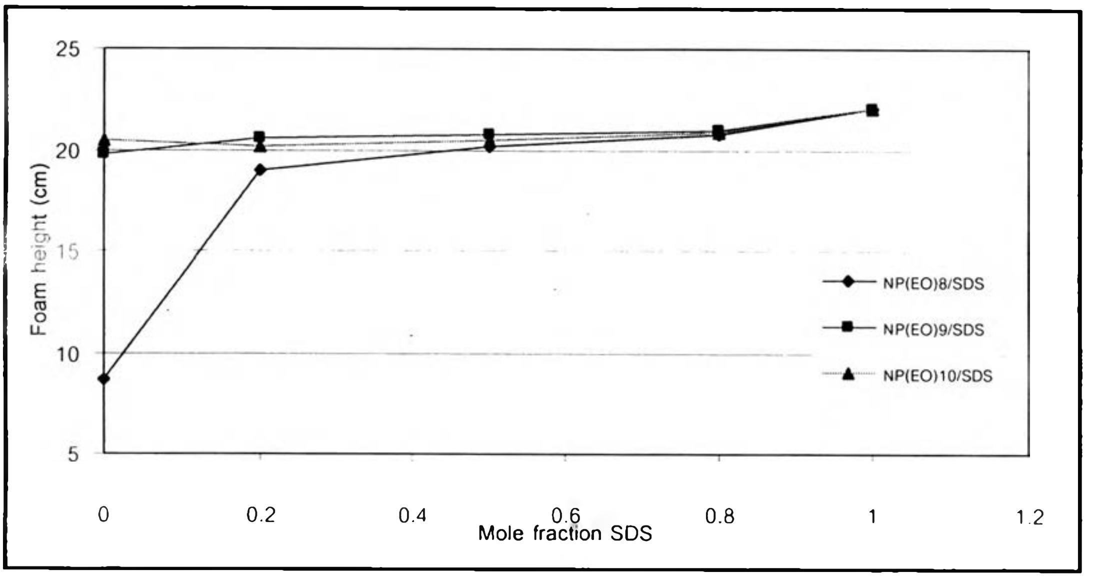

Figure 4.12 Relationship between foam height and 0.01 M $NP(EO)_8/SDS$, NP $(EO)_9/SDS$, and $NP(EO)_{10}/SDS$ at varying mole ratio by the Ross-Miles method, temperature = 30°C.

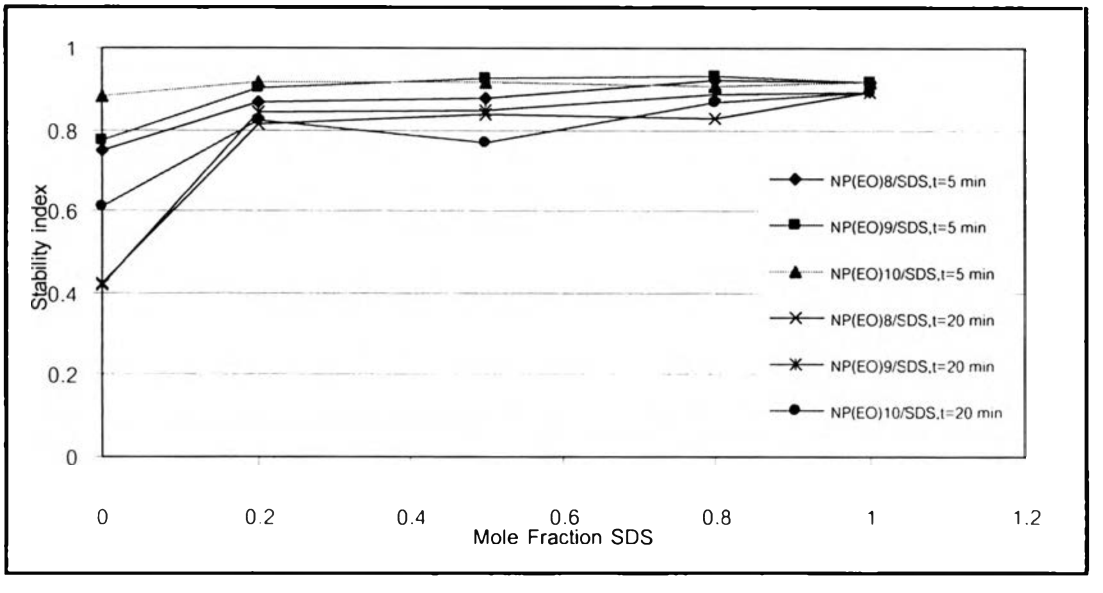

Figure 4.13 Relationship between stability index of 0.01 M $NP(EO)_8/SDS$, $NP(EO)_9/SDS$, and $NP(EO)_{10}/SDS$ at varying mole ratio by the Ross-Miles method, temperature = 30°C.

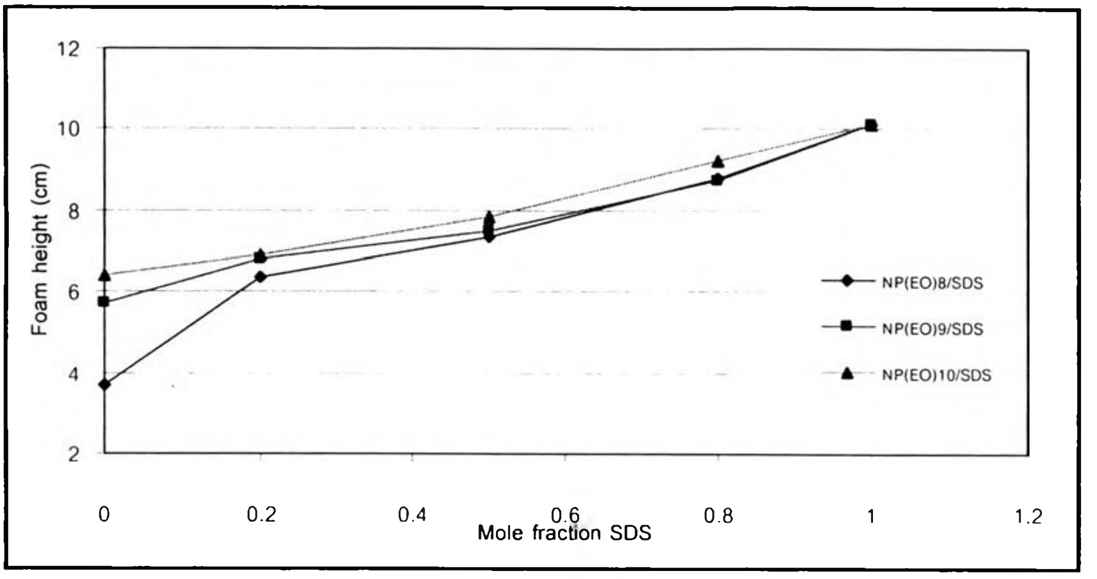

Figure 4.14 Relationship between foam height and 0.01 M $NP(EO)_8/SDS$, NP $(EO)_9/SDS$, and $NP(EO)_{10}/SDS$ at varying mole ratio by the shake test method, temperature = 30°C.

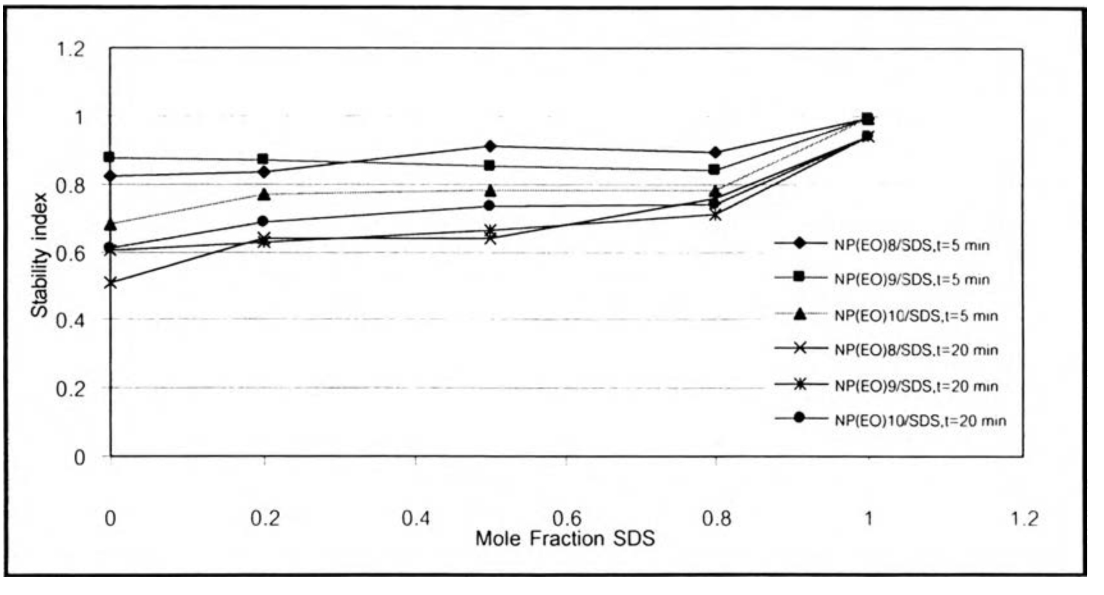

Figure 4.15 Relationship between stability index and 0.01 M $NP(EO)_8/SDS$, $NP(EO)_9/SDS$, and $NP(EO)_{10}/SDS$ at varying mole ratio by the shake test method, temperature = 30°C.

4.3 Effect of Cloud Point Temperature on Foaming of NonionicAnionic Surfactant Systems

4.3.1 Systems with no Electrolyte Added

In this work, the mole ratio of $NP(EO)_8/SDS$ was varied from 1.000/0.000, 0.999/0.001, to 0.998/0.002 with the total concentration fixed at 0.01 M.

Figures 4.16 and 4.18 show the foamability of solutions containing different ratios of $NP(EO)_8/SDS$ and $NP(EO)_9/SDS$ in the absence of electrolyte. It can be seen that, below the cloud point, there is no significant change in foamability upon addition of very small amounts of SDS (about 10^{-5} M). However, above the cloud point, a substantial decrease in the foam height occurs.

Figures 4.17 and 4.19 compare the foam stability at 5 min and 20 min respectively. It can be seen that when there was small amount of SDS in the system, the foam stability increased indicating that the stability of nonionic foams depended mainly not only on the liquid drainage characteristics but also on the addition of a small amount of anionic surfactant.

4.3.2 Systems with Electrolyte Added

In this experiment, the total concentration was fixed at 0.01 M and the mole ratio of $NP(EO)_8/SDS$, $NP(EO)_9/SDS$, and $NP(EO)_{10}/SDS$ was fixed at 0.9/0.1. The temperature was varied to cover the regions below and above the cloud point of the mixture as shown in Figures 4.1 and 4.2. The NaCl concentration in the mixture at each ratio was fixed at specific cloud point temperature.

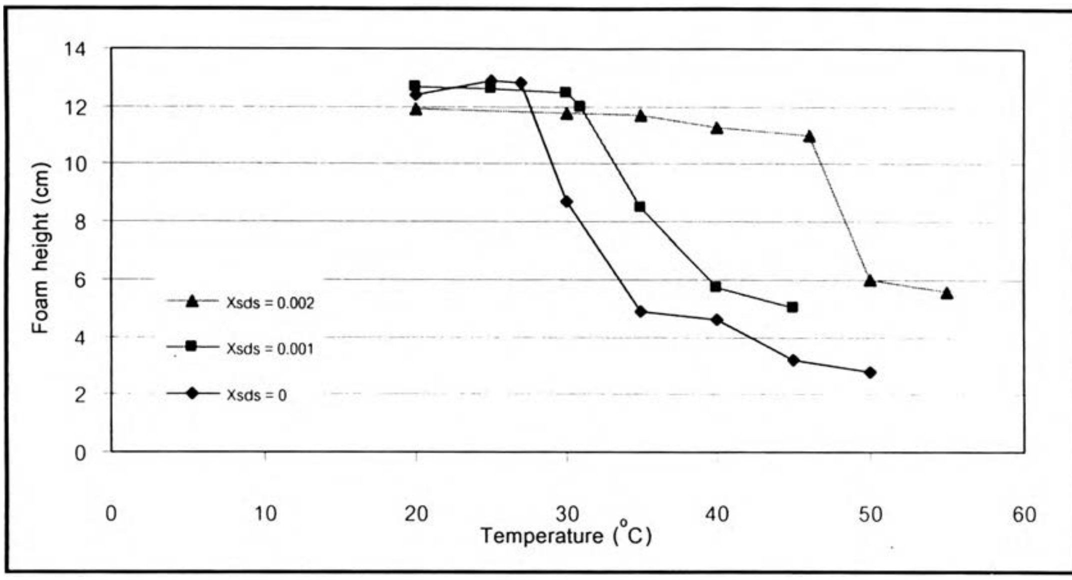

Figure 4.16 Relationship between foam height of 0.01 M NP(EO)$_8$/SDS at varying mole ratio and temperature by the Ross-Miles method.

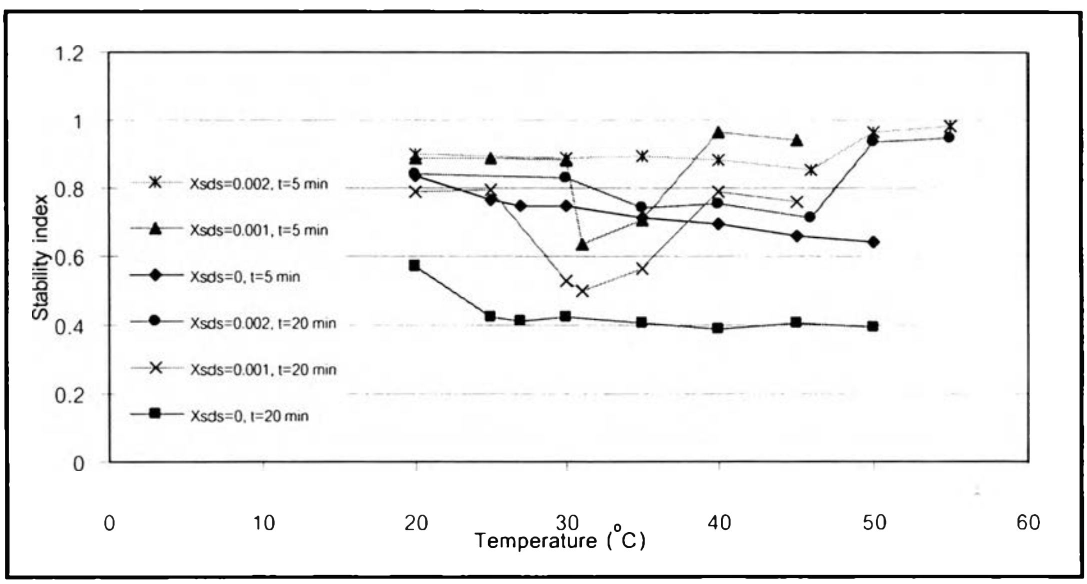

Figure 4.17 Relationship between stability index of 0.01 M NP(EO)$_8$/SDS at varying mole ratio and temperature by the Ross-Miles method.

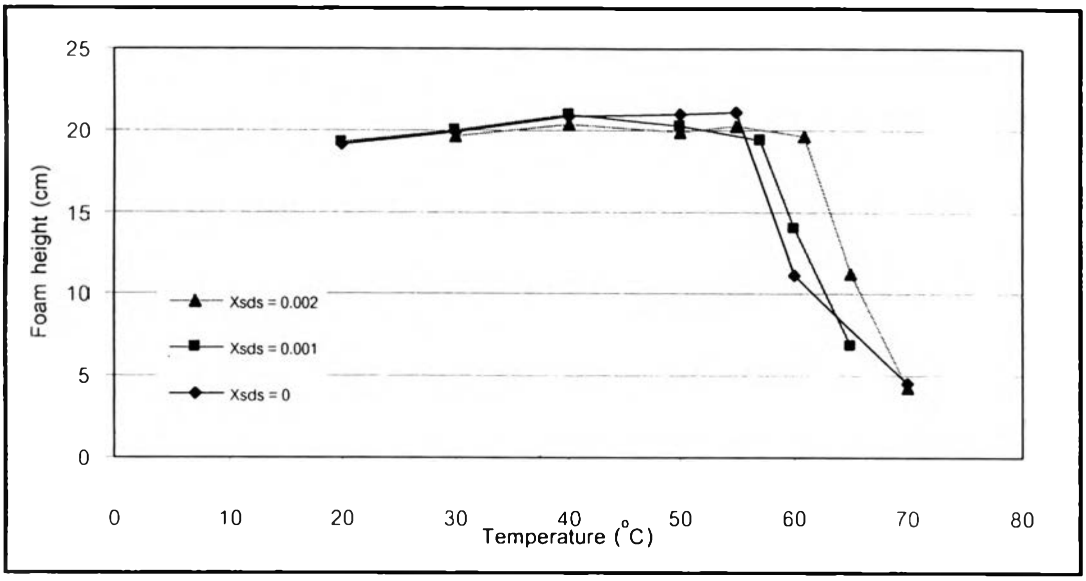

Figure 4.18 Relationship between foam height of 0.01 M $NP(EO)_9/SDS$ at varying mole ratio and temperature by the Ross-Miles method.

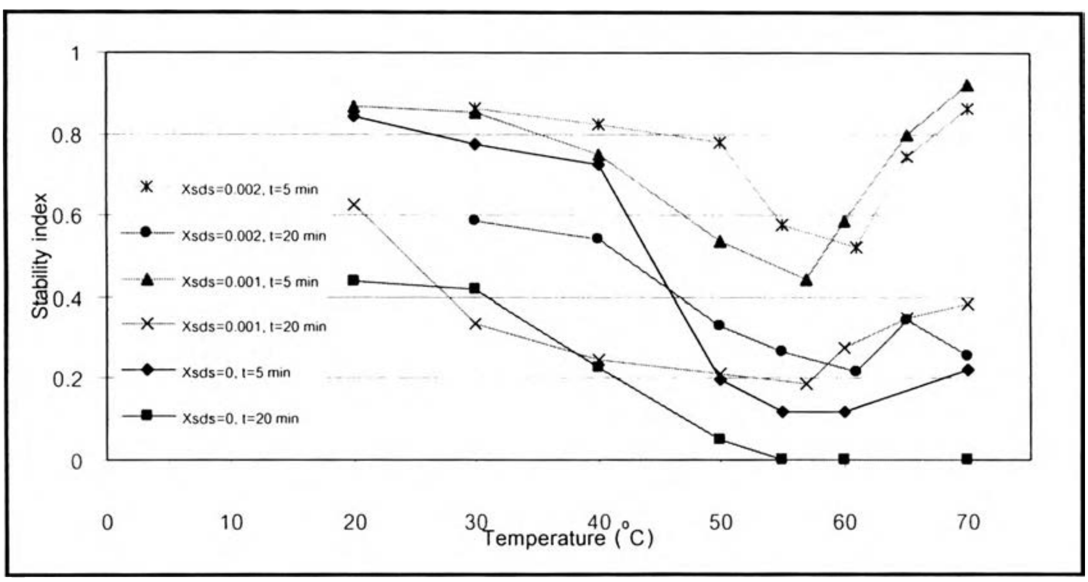

Figure 4.19 Relationship between stability index of 0.01 M $NP(EO)_9/SDS$ at varying mole ratio and temperature by the Ross-Miles method.

The results in Figures 4.20 - 4.22 show that foamability of the mixtures remained constant regardless of temperature below the cloud point. There is however a sharp decrease of foam height above the cloud point of the mixture. The results show that the cloud point plays an important role in the foamability of the mixed systems even though the cloud point temperature changes with the addition of anionic surfactant and electrolyte. Above the cloud point, the mixed systems behave like pure nonionic surfactant with the separation of the solutions into two phases; a mixed micellar-rich phase and a mixed micellar-poor phase. The mixed micellar-rich which is immicible with the mixed micellar-poor phase is believed to act as antifoam causing a dramatic decrease in foamability above the cloud point. The same qualitative results were also obtained by earlier workers (Bonfillon-Colin and Langevin, 1997).

4.3.3 Comparison of the Foaming of Systems in the Absence and Presence of Electrolyte

In general, the electrolytes change (decrease or increase) the cloud point of nonionics, but the relevant electrolyte concentrations are usually high, exceeding 0.1 M (Sadaghiania and Khan, 1991). The electrolytes were also found to suppress the cloud point of mixed ionic-nonionic surfactants at much lower concentrations than do the nonionic ones (Marszall, 1988).

The results in Figures 4.23 and 4.24 show foamability of NP $(EO)_8$ /SDS and NP$(EO)_9$/SDS solutions at different ratios in the absence and presence of electrolyte. The total concentration was fixed at 0.01 M. The temperature was varied to cover the range below and above the specific cloud point of the mixture as shown in Figures 4.1 and 4.2.

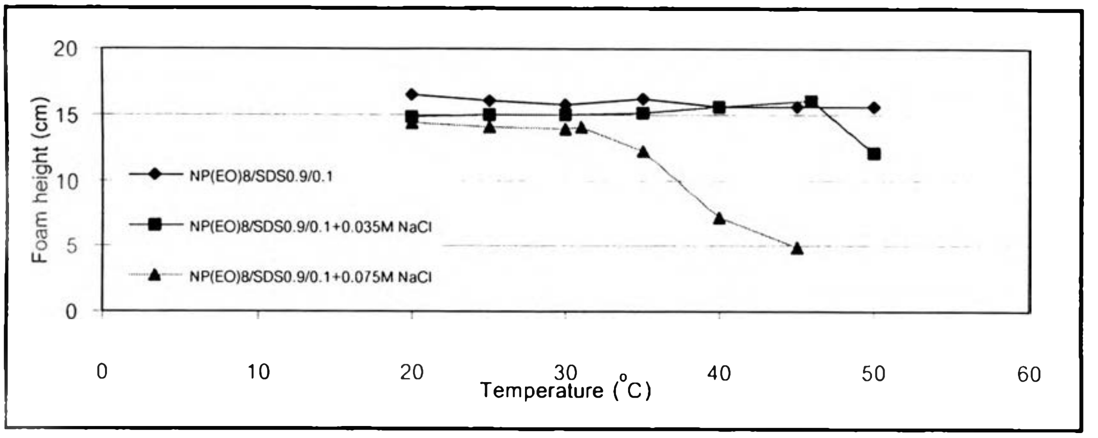

Figure 4.20 Relationship between foam height of 0.01 M $NP(EO)_8$/SDS ratio 0.9/0.1 with and without NaCl and temperature by the Ross-Miles method

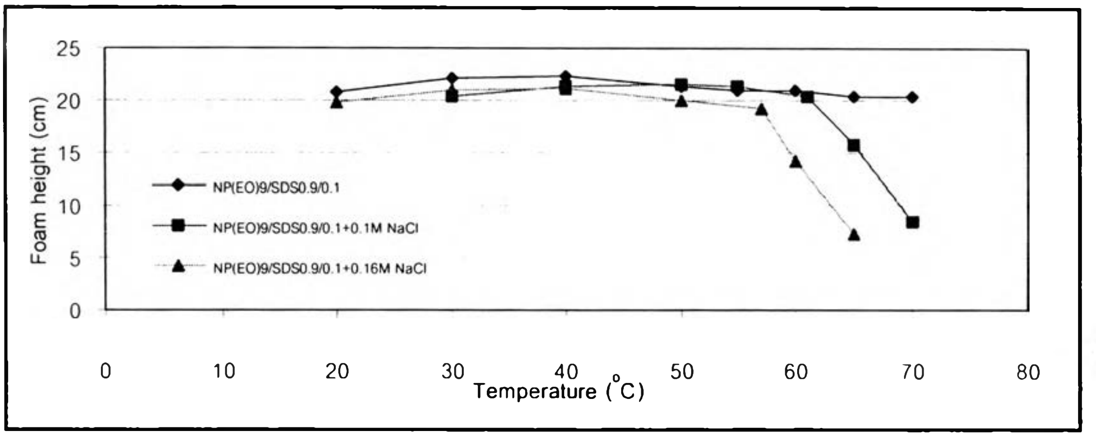

Figure 4.21 Relationship between foam height of 0.01 M $NP(EO)_9$/SDS ratio 0.9/0.1 with and without NaCl and temperature by the Ross-Miles method.

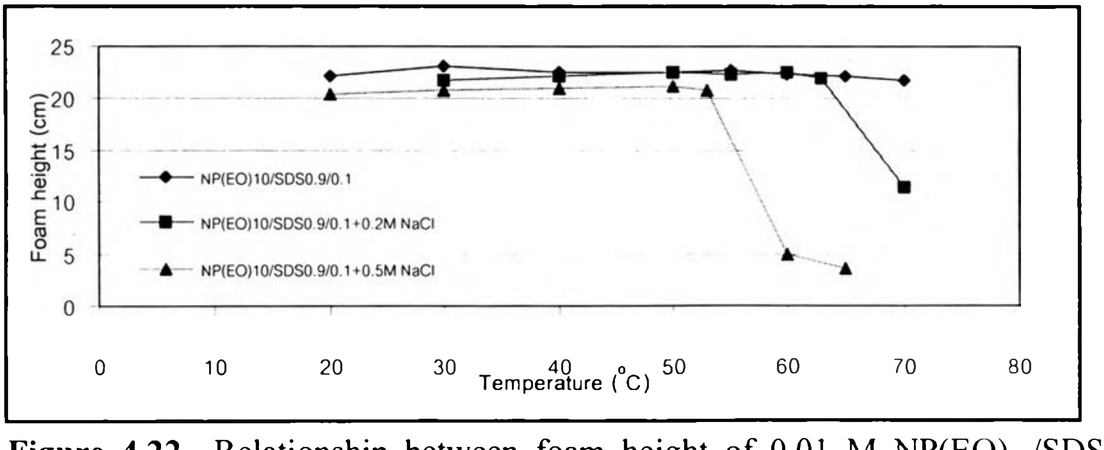

Figure 4.22 Relationship between foam height of 0.01 M $NP(EO)_{10}$/SDS ratio 0.9/0.1 with and without NaCl and temperature by the Ross-Miles method.

The foamability of $NP(EO)_8$/SDS solutions slowly increased with an increase in the amount of SDS. It is also interesting to note that in all cases, the foam height decreases sharply above the cloud point. The results therefore confirm the important role of the cloud point on the foaming properties of mixed nonionic/anionic systems. The presence of electrolyte leads to the reduction of the cloud point. The same qualitative results were obtained with the $NP(EO)_9$/SDS as shown in Figure 4.24.

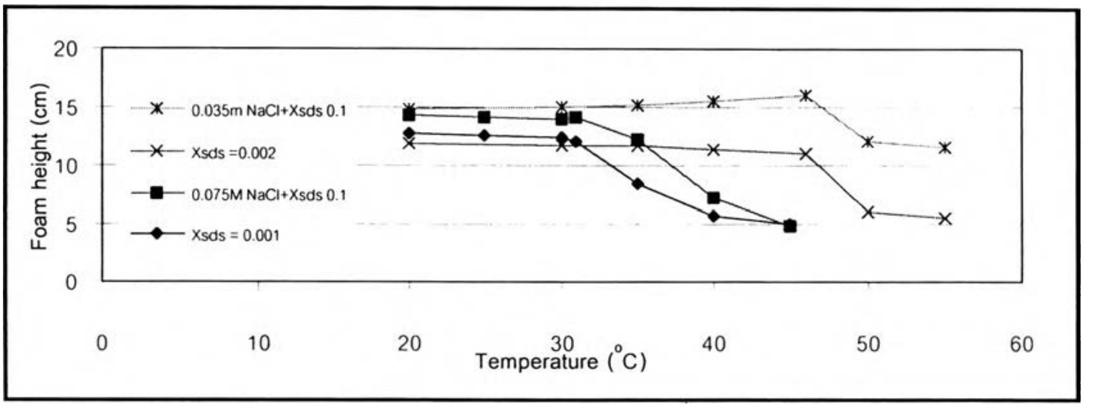

Figure 4.23 Relationship between foam height of 0.01 M $NP(EO)_8$/SDS with and without NaCl at varying mole ratio and temperature by the Ross-Miles method.

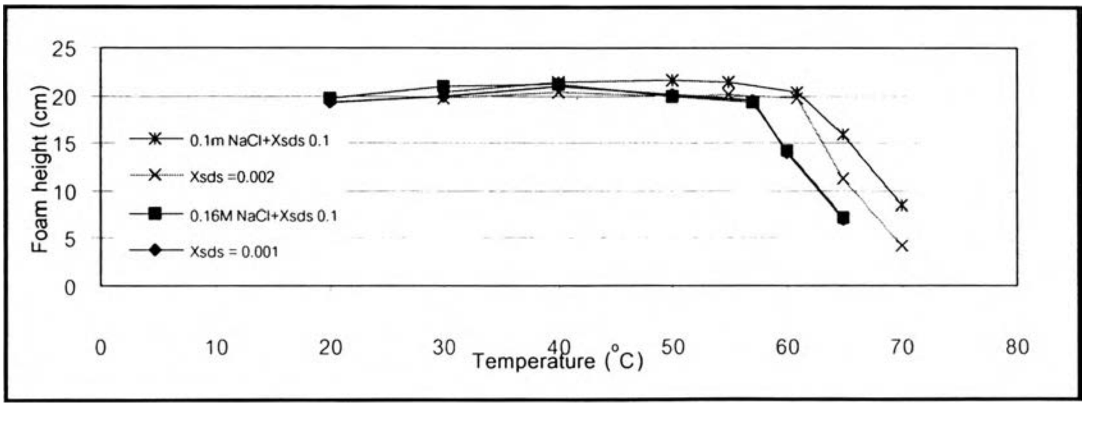

Figure 4.24 Relationship between foam height of 0.01 M $NP(EO)_9$/SDS with and without NaCl at varying mole ratio and temperature by the Ross-Miles method.

4.3.4 Systems with Different Mole Ratios of Nonionic/Anionic Mixtures

The effect of mole ratios of $NP(EO)_8$/SDS on foaming properties was further investigated by varying mole ratio of $NP(EO)_8$/SDS from 1.0/0.1, 0.8/0.2, to 0.6/0.4. The total concentration was fixed at 0.01 M. The temperature was varied to cover the region below and above the specific cloud point of the mixture. The clouding temperature remained constant with the addition of the electrolyte.

The results in Figure 4.25 show that foamability and foam stability of the mixtures decrease dramatically above the cloud point. The sharp change occurs similar to the clouding phenomena of pure nonionic surfactants. As the mole ratio of SDS increases, the foam height of the solution increases even in the presence of the electrolyte. Generally, the foamability depends on both its effectiveness in reducing the surface tension of the foaming solution and on the magnitude of its intermolecular cohesive forces. In the nonionic-anionic mixed system, CMC values exhibit a negative deviation from ideality due to a decrease in electrostatic repulsion between the charged head groups in the mixed micelle (Hongpaya, 1998) and since the reduction in mole ratio of nonionic leads to smaller surface area per molecule and the presence of highly charged surface films in these foams, these lead consequently to the increase in the foam height.

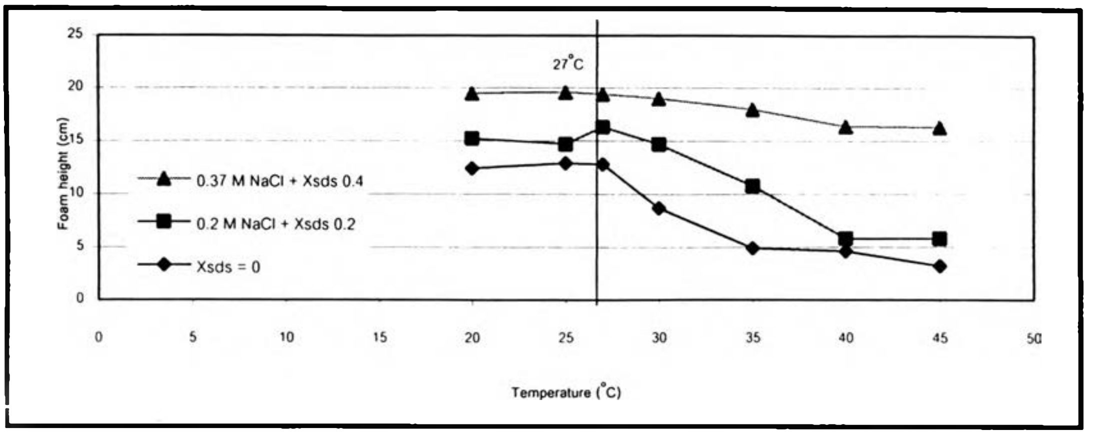

Figure 4.25 Relationship between foam height of 0.01 M $NP(EO)_8/SDS$ with and without NaCl at varying mole ratio and temperature by the Ross-Miles method.