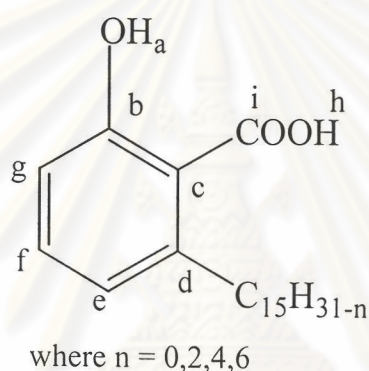


## CHAPTER IV

### RESULT AND DISCUSSION

#### 4.1 Preparation of cardanol from CNSL

The major component of CNSL was anacardic acid, whose structure is shown below



The structure was characterized by IR spectrometer and NMR spectrometer. The results are shown in Figures A1- A3 (Appendix A).

The infrared spectrum of CNSL showed absorption peaks at 3390  $\text{cm}^{-1}$  (O-H stretching of phenol), 3006  $\text{cm}^{-1}$  (=C-H stretching of aromatic), 2940  $\text{cm}^{-1}$  and 2846  $\text{cm}^{-1}$  (C-H stretching of aliphatic) 1649  $\text{cm}^{-1}$  (C=O stretching of carboxylic acid) , 1602  $\text{cm}^{-1}$  (C=C ring stretching of aromatic), and 1221  $\text{cm}^{-1}$  and 1160  $\text{cm}^{-1}$  (C-O stretching ). The assignments are concluded in Table 4.1.

The  $^1\text{H-NMR}$  spectrum of CNSL showed signals at  $\delta_H$  7.0, 7.4, 6.9 and 9.4 ppm, which belonged to protons at e, f, g and i respectively. In addition, the spectrum also demonstrated signals of methylene protons adjacent to the aromatic at  $\delta_H$  2.4-2.8, double bonds in side chain at  $\delta_H$  4.9-5.4 and methyl protons at  $\delta_H$  0.83-0.93 ppm. The assignments are concluded in Table 4.2.

The  $^{13}\text{C}$ -NMR spectrum of CNSL showed signals at  $\delta_{\text{C}}$  159, 118, 132, 121, 135, 116 and 172 ppm, which belonged to carbons at b, c, d, e, f, g and h respectively. In addition, the spectrum also demonstrated signals of methylene and methyl groups at  $\delta_{\text{C}}$  13-35 and double bonds in the aromatic ring and side chain at  $\delta_{\text{C}}$  126-136 ppm. The assignments are concluded in Table 4.3.

**Table 4.1 Infrared spectroscopic data of CNSL**

Wave number, $\text{cm}^{-1}$	Functional groups
3390	O-H stretching of phenol(PhOH)
3006	=C-H stretching of aromatic(Ph-H)
2940 and 2846	C-H stretching of aliphatic( $-\text{CH}_2-$ , $-\text{CH}_3$ )
1649	C=O stretching of carboxylic group
1602	C=C stretching of aromatic
1451	C-H deformation of alkane
1301	C-H deformation of alkene
1244	O-H deformation of phenol
1221 and 1160	C-O stretching
990	C-H deformation of aromatic
908	C-H deformation of alkene ( $\text{R}-\text{CH}=\text{CH}_2$ )
824	C-H deformation of 1,3,5-trisubstituted benzene
718	C-H deformation of 1,2,3-disubstituted benzene

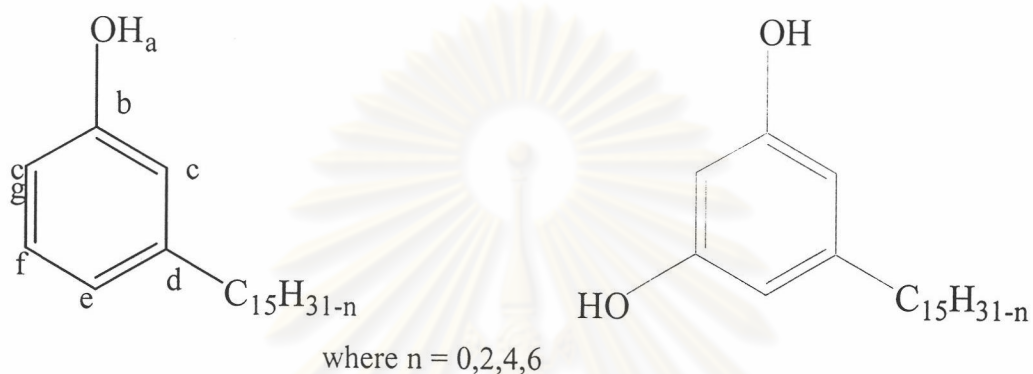
Table 4.2  $^1\text{H-NMR}$  spectroscopic data of CNSL

Position	$\delta_H$ (ppm.)
c	7.0
f	7.4
g	6.9
i	9.4

Table 4.3  $^{13}\text{C-NMR}$  spectroscopic data of CNSL

Position	$\delta_C$ (ppm.)
b	159
c	118
d	132
e	121
f	135
g	116
h	172

CNSL was decarboxylated by heating at 135-140°C for 2-3 hours using TLC (silica gel) to monitor the progress of reaction and the product was investigated by IR and NMR spectrometers. The results are shown in Figure A4-A6 (Appendix A). The TLC revealed two major products; these were cardanol and cardol, whose structures are depicted below.



The infrared spectrum of decarboxylated CNSL showed absorption peaks at 3390  $\text{cm}^{-1}$  (O-H stretching of phenol), 3006  $\text{cm}^{-1}$  (=C-H stretching of aromatic), 2940  $\text{cm}^{-1}$  and 2846  $\text{cm}^{-1}$  (C-H stretching of aliphatic), 1592  $\text{cm}^{-1}$  (C=C stretching of aromatic), 1160  $\text{cm}^{-1}$  (C-O stretching of phenol). No C=O absorption at 1649  $\text{cm}^{-1}$  (C=O stretching of carboxylic acid) was observed. The assignments are concluded in Table 4.4

The  $^1\text{H-NMR}$  spectrum of decarboxylated CNSL showed signals at  $\delta_H$  6.7, 7.0, 7.1 and 6.8 ppm, which belonged to protons at a, c, e, f and g respectively. In addition, the spectrum also demonstrated signals of methylene protons adjacent to the aromatic at  $\delta_H$  2.5-2.8 ppm, double bonds in side chain at  $\delta_H$  4.9-5.8 ppm and methyl protons at  $\delta_H$  0.8-0.9 ppm. The assignments are concluded in Table 4.5.

The  $^{13}\text{C}$ -NMR spectrum of decarboxylated CNSL show signals at  $\delta_{\text{C}}$  157, 116, 130, 121, 130 and 116 ppm, which belong to carbons at b, c, d, e, f and g respectively. In addition, the spectrum demonstrate signals of methylene and methyl groups at  $\delta_{\text{C}}$  14-38 ppm and double bonds in the aromatic ring and side chain at  $\delta_{\text{C}}$  126-136 ppm. The assignments are concluded in Table 4.6. It may be confirmed that anacardic acid was completely decarboxylated to cardanol.

**Table 4.4 Infrared spectroscopic data of decarboxylated CNSL**

Wave number, $\text{cm}^{-1}$	Functional groups
3390	O-H stretching of phenol (PhOH)
3006	=C-H stretching of aromatic (Ph-H)
2940 and 2846	C-H stretching of aliphatic(-CH <sub>2</sub> -, -CH <sub>3</sub> )
1592	C=C stretching of aromatic
1451	C-H deformation of alkane
1348	C-H deformation of alkene
1263 and 1160	C-O stretching
990	C-H deformation of aromatic
908	C-H deformation of alkene (R-CH=CH <sub>2</sub> )
868 and 779	C-H deformation of 1,3-disubstituted benzene

**Table 4.5  $^1\text{H}$ -NMR spectroscopic data of decarboxylated CNSL**

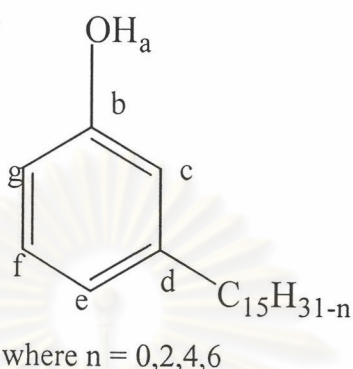
Position	$\delta_H$ (ppm.)
c	6.7
e	7.0
f	7.1
g	6.8

**Table 4.6  $^{13}\text{C}$ -NMR spectroscopic data of decarboxylated CNSL**

Position	$\delta_C$ (ppm.)
b	157
c	116
d	130
e	121
f	130
g	116

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Cardanol was isolated from the decarboxylated residue by Tyman's method [ref.5] in 80 % w/w from CNSL. The results are shown in Figures A7-A9 (Appendix A).



The infrared spectrum of purified cardanol showed absorption peaks at  $3390\text{ cm}^{-1}$  (O-H stretching of phenol),  $3006\text{ cm}^{-1}$  (=C-H stretching of aromatic),  $2940\text{ cm}^{-1}$  and  $2846\text{ cm}^{-1}$  (C-H stretching of aliphatic),  $1592\text{ cm}^{-1}$  (C=C ring stretching of aromatic),  $1160\text{ cm}^{-1}$  (C-O stretching). The assignments are concluded in Table 4.7.

The  $^1\text{H-NMR}$  spectrum of purified cardanol showed signals at  $\delta_H$  6.7, 7.0, 7.1 and 6.8 ppm, which belonged to protons at c, e, f and g respectively. In addition, the spectrum also demonstrated signals of methylene protons adjacent to the aromatic at  $\delta_H$  2.5-2.7 ppm, olefinic protons in side chain at  $\delta_H$  4.9-5.8 ppm and methyl protons at  $\delta_H$  0.8-0.9 ppm. The assignments are concluded in Table 4.8.

The  $^{13}\text{C-NMR}$  spectrum of purified cardanol showed signals at  $\delta_C$  157, 116, 130, 121, 130 and 116 ppm, which belonged to carbons at b, c, d, e, f and g respectively. In addition, the spectrum also demonstrated signals of methylene and methyl groups at  $\delta_C$  13-36 and double bonds in the aromatic ring and side chain at  $\delta_C$  127-137 ppm. The assignments are concluded in Table 4.9. It confirmed that the decarboxylated CNSL was purified to cardanol.

**Table 4.7 Infrared spectroscopic data of purified cardanol**

Wave number, $\text{cm}^{-1}$	Functional groups
3390	O-H stretching of phenol (PhOH)
3006	=C-H stretching of aromatic (Ph-H)
2940 and 2846	C-H stretching of aliphatic(-CH <sub>2</sub> -, -CH <sub>3</sub> )
1592	C=C stretching of aromatic
1451 and 1348	C-H deformation of alkane
1263 and 1160	C-O stretching
1080 and 990	C-H deformation of aromatic
908	C-H deformation of alkene (R-CH=CH <sub>2</sub> )
868 and 779	C-H deformation of 1,3-disubstituted benzene

**Table 4.8 <sup>1</sup>H-NMR spectroscopic data of purified cardanol**

Position	$\delta_H$ (ppm.)
c	6.7
e	7.0
f	7.1
g	6.8



**Table 4.9**  $^{13}\text{C}$ -NMR spectroscopic data of purified cardanol

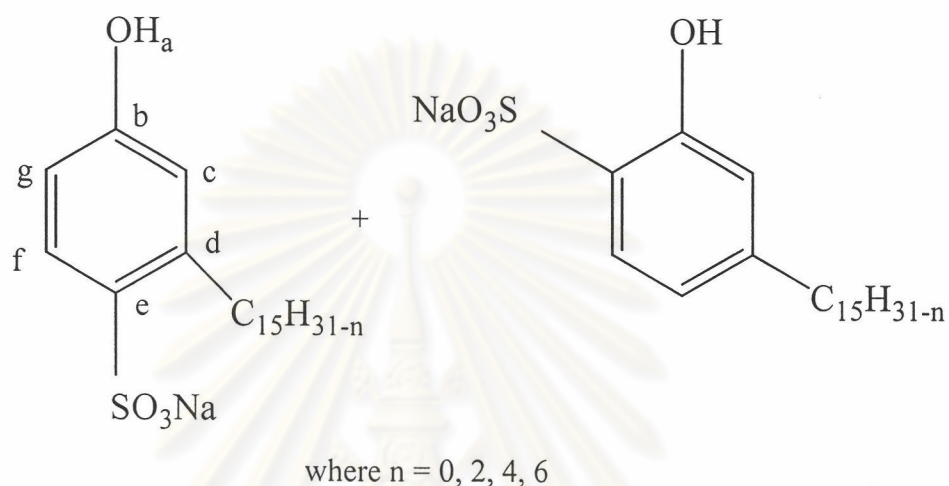
Position	$\delta_c$ (ppm.)
b	157
c	116
d	130
e	121
f	130
g	116



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## 4.2 Sulfonation of cardanol

Cardanol was sulfonated by [Exp.3.4.2]. The sulfonation gave cardanol sulfonate in 86 % by mole. The results are shown in Figures A10-A12 (Appendix A). The structure of cardanol sulfonate are shown below.



The infrared spectrum of cardanol sulfonate showed absorption peaks at  $3465\text{ cm}^{-1}$  (O-H stretching of phenol),  $2921\text{ cm}^{-1}$  and  $2846\text{ cm}^{-1}$  (C-H stretching of aliphatic),  $1635\text{ cm}^{-1}$  (C=C ring stretching of aromatic),  $1174\text{ cm}^{-1}$  ( $\text{SO}_2$  stretching) and  $1056\text{ cm}^{-1}$  (S=O stretching). The assignments are concluded in Table 4.10.

The  $^1\text{H-NMR}$  spectrum of cardanol sulfonate showed signals at  $\delta_H$  6.7, 7.1 and 6.8 ppm, which belonged to protons at c, f and g respectively. In addition, the spectrum also demonstrated signals of methylene protons adjacent to the aromatic at  $\delta_H$  2.3-2.8 ppm, olefinic protons in side chain at  $\delta_H$  4.9-5.8 ppm, methyl protons at  $\delta_H$  0.7-0.8 ppm. The assignments are concluded in Table 4.11.

The  $^{13}\text{C-NMR}$  spectrum of cardanol sulfonate showed signals at  $\delta_C$  157, 116, 130, 121, 130 and 116 ppm, which belonged to carbons at b, c, d, e, f and g respectively. In addition, the spectrum also demonstrated signals of methylene and methyl groups at  $\delta_C$  22-36 ppm and double bonds in the aromatic ring and side chain at  $\delta_C$  127-137 ppm. The assignments are concluded in Table 4.12. It confirmed that cardanol was sulfonated to cardanol sulfonate.

**Table 4.10 Infrared spectroscopic data of cardanol sulfonate**

Wave number, $\text{cm}^{-1}$	Functional groups
3465	O-H stretching of phenol(PhOH)
2921 and 2846	C-H stretching of aliphatic( $-\text{CH}_2-$ , $-\text{CH}_3$ )
1635	C=C stretching of aromatic
1456 and 1371	C-H deformation of alkane
1174	SO <sub>2</sub> stretching
1056	S=O stretching
868	C-H deformation of 1,3-disubstituted benzene

**Table 4.11 <sup>1</sup>H-NMR spectroscopic data of cardanol sulfonate**

Position	$\delta_H$ (ppm.)
c	6.7
f	7.1
g	6.8

**Table 4.12** The  $^{13}\text{C}$ -NMR spectroscopic data of cardanol sulfonate

Position	$\delta_c$ (ppm.)
b	157
c	116
d	130
e	121
f	130
g	116



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### **4.3 Physical Properties of cardanol sulfonate compared with dodecylbenzene sulfonate**

#### **4.3.1 Determination of stability in hard water**

Solubility in hard water of dodecylbenzene sulfonate, cardanol sulfonate were determined by an ISO method. The results are shown in Table 4.13.

From Table 4.13, it was shown by the score of solubility in hard water of dodecylbenzene sulfonate and cardanol sulfonate. The results demonstrated that the solubility of these salts were not different from dodecylbenzene sulfonate.



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**Table 4.13 Solubility in hard water**

Materials	Dodecylbenzene sulfonate	Score	Cardanol sulfonate	Score
5 ml of				
300mg of Ca <sup>+2</sup>	Clear	5	Clear	5
450mg of Ca <sup>+2</sup>	Clear	5	Clear	5
600mg of Ca <sup>+2</sup>	Opalescent	4	Opalescent	4
2.5 ml of				
300 mg of Ca <sup>+2</sup>	Opalescent	4	Opalescent	4
450 mg of Ca <sup>+2</sup>	Opalescent	4	Opalescent	4
600 mg of Ca <sup>+2</sup>	Opalescent	4	Opalescent	4
1.2 ml of				
300 mg of Ca <sup>+2</sup>	Opalescent	4	Opalescent	4
450 mg of Ca <sup>+2</sup>	Opalescent	4	Opalescent	4
600 mg of Ca <sup>+2</sup>	Opalescent	4	Opalescent	4
0.6 ml of				
300 mg of Ca <sup>+2</sup>	Opalescent	4	Opalescent	4
450 mg of Ca <sup>+2</sup>	Opalescent	4	Opalescent	4
600 mg of Ca <sup>+2</sup>	Opalescent	4	Opalescent	4

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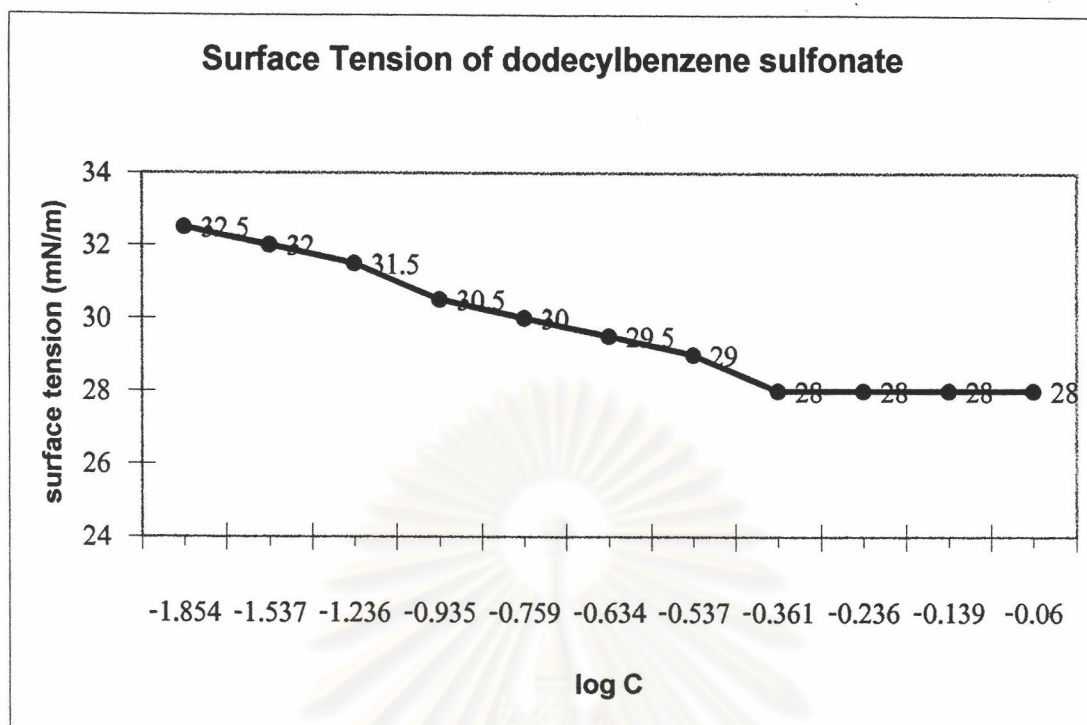
### 4.3.2 Determination of surface tension

Surface tension of dodecylbenzene sulfonate and cardanol sulfonate were determined by ISO method. The results are shown in Figures 4.1-4.2. (Table B.1-B2, Appendix B).

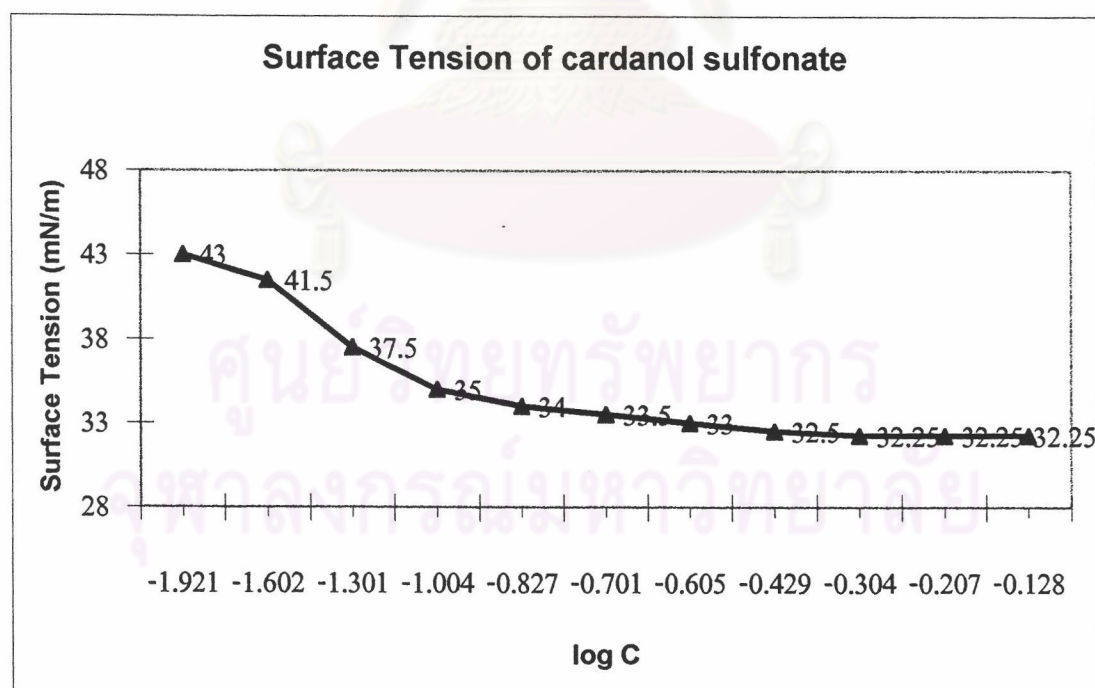
Surface tensions of dodecylbenzene sulfonate and cardanol sulfonate were reduced as the concentration of solution of surfactant increased until the minimum surface tension was reached and which this value remained unchanged. Dodecylbenzene sulfonate gave the minimum surface tension (28 mN/m.) at -0.361 (15% w/v) and cardanol sulfonate gave the minimum surface tension (32.25 mN/m.) at -0.304 (20% w/v). From this result demonstrated that the surface tension reduction of cardanol sulfonate was not significantly different from dodecylbenzene sulfonate and was acceptable to use in commercial application like common anionic surfactants.



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**Figure 4.1 Surface Tension of sodium dodecylbenzene sulfonate.**



**Figure 4.2 Surface Tension of cardanol sulfonate.**



### 4.3.3 Determination of C.M.C.

C.M.C. of dodecylbenzene sulfonate and cardanol sulfonate were determined by an ISO method. Surface tension of detergent – log C plot illustrating the surface tension reduction. The result showed that surface tension of a solution of cardanol sulfonate decreased steadily as the concentration of cardanol sulfonate is increased until the concentration reaches a value known as the critical micelle concentration (C.M.C.), above which the surface tension remained virtually unchanged. The surface tension of cardanol sulfonate at this concentration is therefore very close to the minimum surface tension. From the surface tension of the two cases, C.M.C. values of dodecylbenzene sulfonate and cardanol sulfonate were found to be 0.435 and 0.372 mol/l, respectively. These results indicates that the C.M.C. of two surfactants were not different. Therefore cardanol sulfonate may be used in place of dodecylbenzene sulfonate properly.

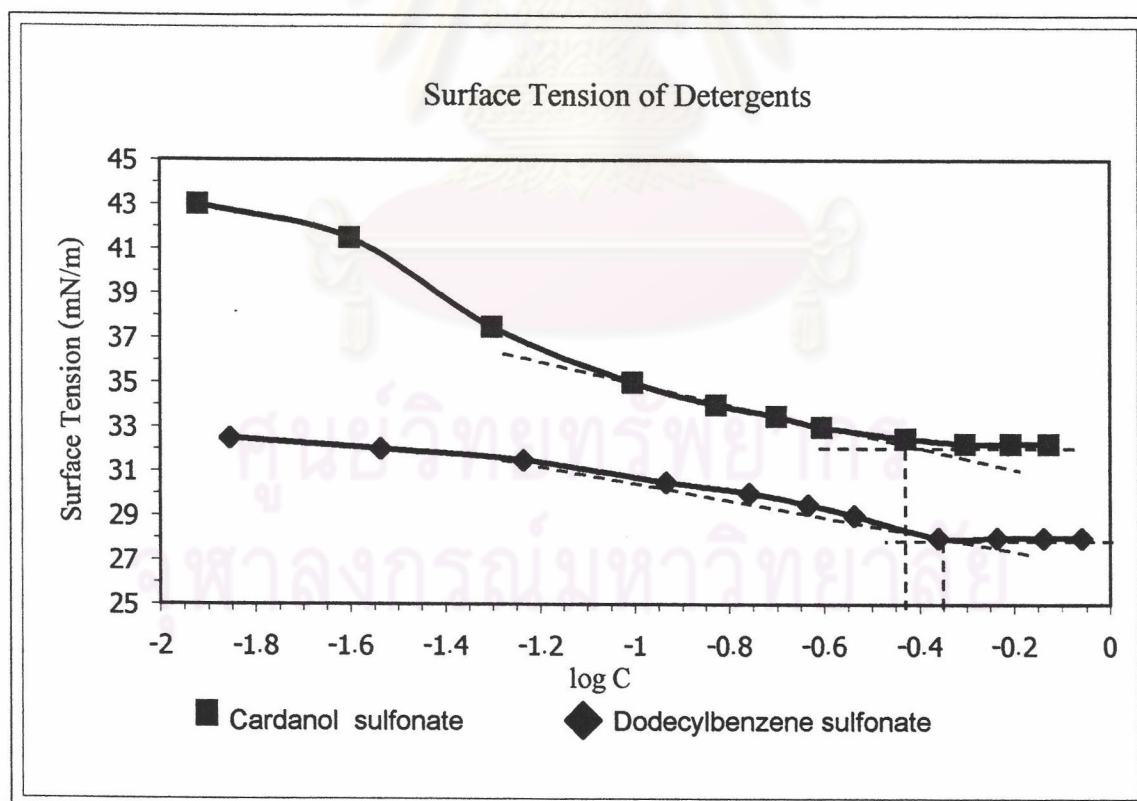


Figure 4.3 Surface Tension of Detergents.

#### 4.3.4 Determination of % detergency

Detergency of dodecylbenzene sulfonate and cardanol sulfonate were determined by an ICS method. The results are shown in Table B.3.

Reflectance of dodecylbenzene sulfonate and cardanol sulfonate were found to be 78.1% and 73.2%, respectively. Using the dodecylbenzene sulfonate as reference, % Detergency of cardanol sulfonate was calculated to be 93.7%. These results were meet with ICS standard, which specified that washing powder should have over 80% detergency when compared with reference [18]. Therefore, cardanol sulfonate is acceptable to be used as a detergent.



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