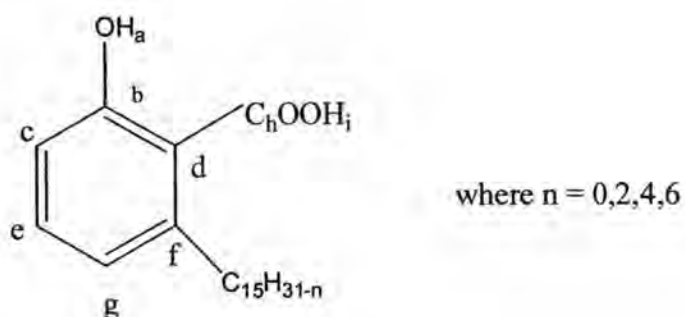


CHAPTER IV

RESULTS 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 characterised by IR spectrometer and NMR spectrometer. The results are shown in Figures 1-3 (Appendix A).

The infrared spectrum of CNSL showed absorption peaks at 3371 cm^{-1} (O-H stretching of phenol), 3009 cm^{-1} (=C-H stretching of aromatic), 2921 cm^{-1} and 2859 cm^{-1} (C-H stretching of aliphatic), 1596 cm^{-1} (C=C ring stretching of aromatic), 1698 cm^{-1} (C=O stretching of carboxylic acid) and 1161 cm^{-1} and 1267 cm^{-1} (C-O stretching of phenol) [24]. The assignments are concluded in Table 4.1.

The $^1\text{H-NMR}$ spectrum of CNSL showed signals at δ_H 6.61, 6.71, 6.75, 7.07-7.15 and 9.37 ppm, which belonged to protons at a, c, e g and i respectively. In addition, the spectrum also demonstrated signals of methylene protons adjacent to the

aromatic at δ_H 2.4-2.8, double bonds in side chain at δ_H 4.9-5.4 and methyl protons at δ_H 0.83-0.93 ppm. The assignments are concluded in Table 4.2.

The ^{13}C -NMR spectrum of CNSL showed signals at δ_C 155, 112, 118, 129 and 130, 144, 120 and 171 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 δ_C 13-35 and double bonds in the aromatic ring and side chain at δ_C 126-136 ppm. The assignments are concluded in Table 4.3.

Table 4.1 The infrared spectroscopic data of CNSL

Wave number, cm^{-1}	Functional groups
3371	O-H (PhOH)
3009	C-H (Ph-H)
2921 and 2859	C-H (-CH ₂ -, -CH ₃)
1698	C=O(carboxylic group)
1596	Phenyl
1460	CH ₃
1362	CH ₃
1275	C-OH(PhOH)
1267 and 1157	C-O(Ph-O)
911	R-CH=CH ₂
876	1,3,5-trisubstituted benzene
841	1,2,3-trisubstituted benzene
722	1,3-disubstituted benzene

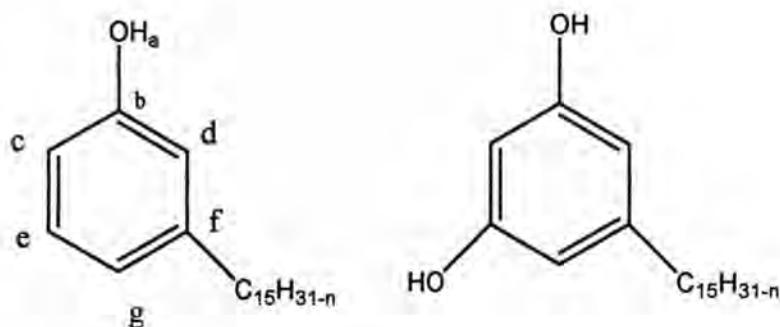
Table 4.2 The ^1H -NMR spectroscopic data of CNSL

Position	δ_H (ppm.)
a	6.61
c	6.71
e	6.75
g	7.07, 7.11 and 7.15
i	9.37

Table 4.3 The ^{13}C -NMR spectroscopic data of CNSL

Position	δ_C (ppm.)
b	155
c	112
d	118
e	129 and 130
f	144
g	120
h	171

CNSL was decarboxylated by heating in the presence of $\text{Ca}(\text{OH})_2$ (Exp. 3.4.1). It was then modified by Tyman's method [7] at $120\text{ }^\circ\text{C}$. The carboxylation process was monitored by TLC and the product was investigated by IR and NMR spectrometers. The results are shown in Figures 4-6 (Appendix A). The TLC revealed two major products; these were cardanol and cardol, whose structures are depicted below.



where $n = 0, 2, 4, 6$

The infrared spectrum of decarboxylated CNSL showed absorption peaks at 3375 cm^{-1} (O-H stretching of phenol), 3006 cm^{-1} (=C-H stretching of aromatic), 2929 cm^{-1} and 2852 cm^{-1} (C-H stretching of aliphatic), 1588 cm^{-1} (C=C ring stretching of aromatic), 1163 cm^{-1} (C-O stretching of phenol). No C=O absorption at 1698 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 δ_H 6.51, 6.71, 6.64, 6.75 and 7.07-7.15 ppm, which belonged to protons at a, c, d, e and g respectively. In addition, the spectrum also demonstrated signals of methylene protons adjacent to the aromatic at δ_H 2.49-2.80, double bonds in side chain at δ_H 4.94-5.87 and methyl protons at δ_H 0.83-0.92 ppm. The assignments are concluded in Table 4.5.

The ^{13}C -NMR spectrum of decarboxylated CNSL showed signals at δ_{C} 155.65, 112.61, 114.75, 129.34, 144.76 and 120.76 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 δ_{C} 13.84-38.72 and double bonds in the aromatic ring and side chain at δ_{C} 126.83-136.84 ppm. The assignments are concluded in Table 4.6. They confirmed that anacardic acid was completely decarboxylated to cardanol.

Table 4.4 The infrared spectroscopic data of decarboxylated CNSL

Wave number, cm^{-1}	Functional groups
3375	O-H (PhOH)
3006	C-H (Ph-H)
2929 and 2852	C-H (-CH ₂ -, -CH ₃)
1588	Phenyl
1460	CH ₃
1375	CH ₃
1275	C-OH(PhOH)
1163	C-O(Ph-O)
911	R-CH=CH ₂
876	1,3,5-trisubstituted benzene
778	1,3-disubstituted benzene

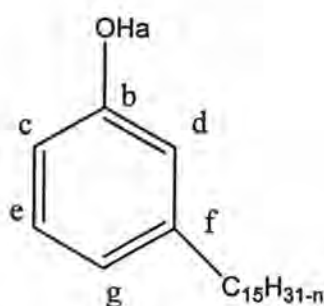
Table 4.5 The ^1H -NMR spectroscopic data of decarboxylated CNSL

position	δ_H (ppm.)
a	6.51
c	6.71
d	6.64
e	6.75
g	7.07, 7.11 and 7.15

Table 4.6 The ^{13}C -NMR spectroscopic data of CNSL

position	δ_C (ppm.)
b	155.65
c	112.61
d	114.74
e	129.34
f	144.76
g	120.76

Cardanol was isolated from the decarboxylated residue by Tyman's method [20] in 80 % w/w from CNSL. The results are shown in Figures 7-9 (Appendix A).



where $n = 0, 2, 4, 6$

IR spectrum of purified cardanol showed absorption peaks at 3395 cm^{-1} (O-H stretching of phenol), 3009 cm^{-1} (=C-H stretching of aromatic), 2921 cm^{-1} and 2859 cm^{-1} (C-H stretching of aliphatic), 1596 cm^{-1} (C=C ring stretching of aromatic), 1156 cm^{-1} (C-O stretching of phenol). The assignments are concluded in Table 4.7.

The $^1\text{H-NMR}$ spectrum of purified cardanol showed signals at δ_H 6.61, 6.71, 6.65, 6.75 and 7.07-7.15 ppm, which belonged to protons at a, c, d, e and g respectively. In addition, the spectrum also demonstrated signals of methylene protons adjacent to the aromatic at δ_H 2.49-2.78, double bonds in side chain at δ_H 4.95-5.83 and methyl protons at δ_H 0.87-0.93 ppm. The assignments are concluded in Table 4.8.

The $^{13}\text{C-NMR}$ spectrum of purified cardanol showed signals at δ_C 155.62, 112.58, 114.73, 129.35, 144.86 and 120.79 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 δ_C 12.68-35.86 and double bonds in the aromatic ring

and side chain at δ_C 126.87-136.84 ppm. The assignments are concluded in Table 4.9.

It confirmed that decarboxylated CNSL was purified to cardanol.

Table 4.7 The infrared spectroscopic data of purified cardanol

Wave number, cm^{-1}	Functional groups
3395	O-H (PhOH)
3009	C-H (Ph-H)
2921 and 2859	C-H (-CH ₂ -, -CH ₃)
1596	Phenyl
1461	CH ₃
1374	CH ₃
1277	C-OH(PhOH)
1156	C-O(Ph-O)
919	R-CH=CH ₂
784	1,3-disubstituted benzene

Table 4.8 The ^1H -NMR spectroscopic data of purified cardanol

position	δ_H (ppm.)
a	6.61
c	6.71
d	6.65
e	6.75
g	7.07, 7.11 and 7.15

Table 4.9 The ^{13}C -NMR spectroscopic data of purified cardanol

position	δ_C (ppm.)
b	155.62
c	112.58
d	114.73
e	129.35
f	144.86
g	120.79

4.2 Hydrogenation of cardanol

Hydrogenation of cardanol was carried out using the modified Tyman's method (Exp. 3.4.3) [21, 22]. The cardanol in ethyl acetate was treated with hydrogen (250 psi.) in the presence of 10% Pd/C at 200 °C for 8 hours. The hydrogenation process gave the hydrogenated cardanol in 100 % w/w. The IR and NMR spectroscopic results showed that the olefinic carbons of the side chain of cardanol were completely eliminated. The results are shown in Figures 10-12 (Appendix A). And the structure is shown below.



IR spectrum of hydrogenated cardanol showed absorption peaks at 3386 cm^{-1} (O-H stretching of phenol), 2929 cm^{-1} and 2853 cm^{-1} (C-H stretching of aliphatic), 1664 cm^{-1} , 1621 cm^{-1} and 1589 cm^{-1} (C=C ring stretching of aromatic), 1250 cm^{-1} (C-O stretching of phenol). The assignments are concluded in Table 4.10.

The $^1\text{H-NMR}$ spectrum of hydrogenated cardanol showed signals at δ_H 6.61, 6.71, 6.65, 6.70 and 7.11 ppm, which belonged to protons at a, c, d, e and g respectively. In addition, the spectrum also demonstrated signals of methylene protons adjacent to the aromatic at δ_H 2.49-2.56 and methyl protons at δ_H 0.83-0.86 ppm. The assignments are concluded in Table 4.11.

The ^{13}C -NMR spectrum of hydrogenated cardanol showed signals at δ_{C} 155.77, 112.55, 115.39, 129.28, 144.84 and 120.61 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 δ_{C} 21.04-35.87 ppm. The assignments are concluded in Table 4.12. It confirmed that cardanol was hydrogenated to hydrogenated cardanol.

Table 4.10 The infrared spectroscopic data of hydrogenated cardanol

Wave number, cm^{-1}	Functional groups
3386	O-H (PhOH)
2929 and 2853	C-H (-CH ₂ -, -CH ₃)
1664, 1621 and 1589	Phenyl
1465	CH ₃
1379	CH ₃
852 and 798	1,3-disubstituted benzene

Table 4.11 The ^1H -NMR spectroscopic data of hydrogenated cardanol

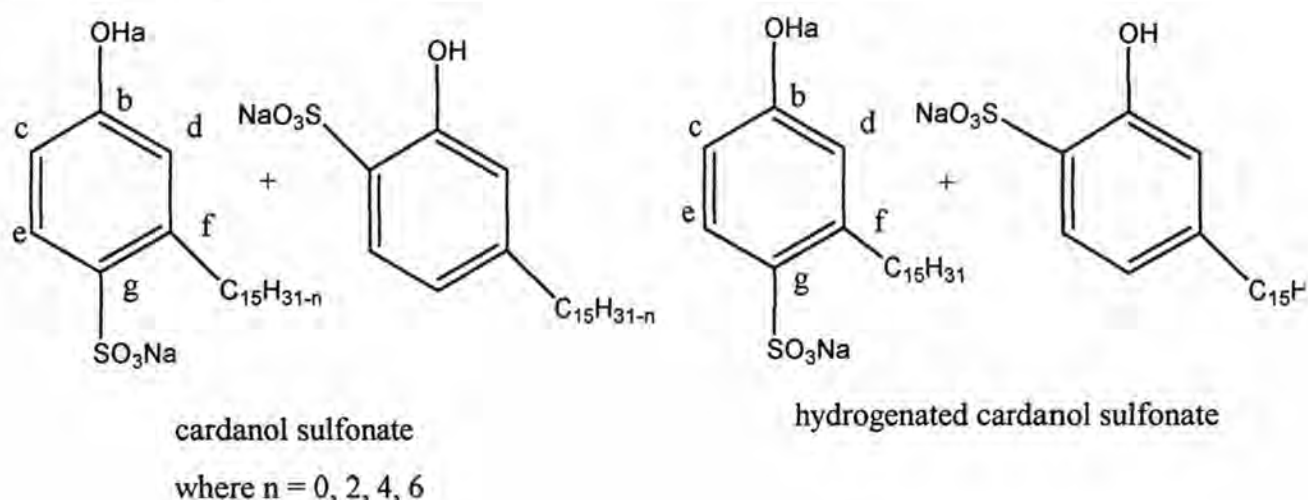
Position	δ_H (ppm.)
a	6.61
c	6.70
d	6.65
e	6.75
g	7.11

Table 4.12 The ^{13}C -NMR spectroscopic data of hydrogenated cardanol

Position	δ_C (ppm.)
b	155.77
c	112.55
d	114.84
e	129.28
f	144.84
g	120.61

4.3 Sulfonation of cardanol and hydrogenated cardanol

Cardanol and hydrogenated cardanol were sulfonated by Loza's method [Exp.3.4.4] [23]. The sulfonation gave cardanol sulfonate and hydrogenated cardanol sulfonate in 61% by mole and 71% by mole, respectively. The results are shown in Figures 13-18. The structures of cardanol sulfonate and hydrogenated cardanol sulfonate are shown below.



IR spectrum of cardanol sulfonate showed absorption peaks at 3445 cm^{-1} (O-H stretching of sulfonic acid), 3009 cm^{-1} (=C-H stretching of aromatic), 2924 cm^{-1} and 2864 cm^{-1} (C-H stretching of aliphatic), 1650 cm^{-1} (C=C ring stretching of aromatic), 1239 cm^{-1} and 1158 cm^{-1} (SO_3^-). The assignments are concluded in Table 4.13.

The $^1\text{H-NMR}$ spectrum of cardanol sulfonate showed signals at δ_H 6.61, 6.72, 6.64 and 7.07-7.15 ppm, which belonged to protons at a, c, d and e respectively. In addition, the spectrum also demonstrated signals of methylene protons adjacent to the aromatic at δ_H 2.34-2.77, double bonds in side chain at δ_H 4.95-5.83, methyl protons at δ_H 0.71-0.85 and proton of sulfonic group at 6.32 ppm. The assignments are concluded in Table 4.14.

The ^{13}C -NMR spectrum of cardanol sulfonate showed signals at δ_{C} 155.45, 112.48, 114.70, 120.89, 144.89 and 146.84 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 δ_{C} 22.67-35.86 and double bonds in the aromatic ring and side chain at δ_{C} 126.81-136.82 ppm. The assignments are concluded in Table 4.15. It confirmed that cardanol was sulfonated to cardanol sulfonate.

Table 4.13 The infrared spectroscopic data of cardanol sulfonate

Wave number, cm^{-1}	Functional groups
3445	O-H (PhOH)
3009	C-H (Ph-H)
2924 and 2864	C-H (-CH ₂ -, -CH ₃)
1650	Phenyl
1470	CH ₃
1239 and 1158	Sulfonic acid
1070	S=O
912	R-CH=CH ₂
886	1,3-disubstituted benzene

Table 4.14 The ^1H -NMR spectroscopic data of cardanol sulfonate

position	δ_H (ppm.)
a	6.51
c	6.74
d	6.64
e	7.11

Table 4.15 The ^{13}C -NMR spectroscopic data of cardanol sulfonate

position	δ_C (ppm.)
b	155.45
c	112.48
d	114.70
e	120.89
f	144.89
g	146.84

IR spectrum of hydrogenated cardanol sulfonate showed absorption peaks at 3447 cm^{-1} (O-H stretching of phenol), 2924 cm^{-1} and 2863 cm^{-1} (C-H stretching of aliphatic), 1650 cm^{-1} (C=C ring stretching of aromatic), 1239 cm^{-1} and 1158 cm^{-1} (SO_3^-). The assignments are concluded in Table 4.16.

The $^1\text{H-NMR}$ spectrum of hydrogenated cardanol showed signals at δ_H 6.60, 6.74, 6.64, 6.24 and 7.11 ppm, which belonged to protons at a, c, d, g and e respectively. In addition, the spectrum also demonstrated signals of methylene protons adjacent to the aromatic at δ_H 2.49-3.27 and methyl protons at δ_H 0.82-0.88 ppm. The assignments are concluded in Table 4.17.

The $^{13}\text{C-NMR}$ spectrum of hydrogenated cardanol sulfonate showed signals at δ_C 155.49, 112.45, 115.30, 120.86, 144.92 and 146.92 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 δ_C 22.69-35.83 ppm. The assignments are concluded in Table 4.18. It confirmed that hydrogenated cardanol was sulfonated to hydrogenated cardanol sulfonate.

Table 4.16 The infrared spectroscopic data of hydrogenated cardanol sulfonate

Wave number, cm^{-1}	Functional groups
3447	O-H (PhOH)
2924 and 2863	C-H (-CH ₂ -, -CH ₃)
1650	Phenyl
1471	CH ₃
1239 and 1158	Sulfonic acid
1070	S=O
886 and 784	1,3-disubstituted benzene

Table 4.17 The ¹H-NMR spectroscopic data of hydrogenated cardanol sulfonate

Position	δ_H (ppm.)
a	6.60
c	6.74
d	6.64
g	6.24
e	7.11

Table 4.18 The ^{13}C -NMR spectroscopic data of hydrogenated cardanol sulfonate

Position	δ_{C} (ppm.)
b	155.49
c	112.45
d	115.30
e	120.86
f	144.92
g	146.92

4.4 Physical Properties of sodium salts compared with dodecylbenzene sulfonate

4.4.1 Determination of solubility in hard water

Solubility in hard water of dodecylbenzene sulfonate, cardanol sulfonate and hydrogenated cardanol sulfonate were determined by ISO method. The results are shown in Table 4.19.

From Table 4.19, it was shown by the score of solubility in hard water of dodecylbenzene sulfonate, cardanol sulfonate and hydrogenated cardanol sulfonate. The results demonstrated that the solubility of these salts were not significantly different from dodecylbenzene sulfonate.

Table 4.19 Solubility in hard water

materials	dodecylbenene sulfonate	score	cardanol sulfonate	score	hydrogenated cardanol sulfonate	score
5ml of						
300mg of Ca ²⁺	clear	5	clear	5	clear	5
450mg of Ca ²⁺	clear	5	clear	5	clear	5
600mg of Ca ²⁺	opalescent	4	opalescent	4	opalescent	4
2.5ml of						
300mg of Ca ²⁺	opalescent	4	opalescent	4	opalescent	4
450mg of Ca ²⁺	opalescent	4	opalescent	4	opalescent	4
600mg of Ca ²⁺	opalescent	4	opalescent	4	opalescent	4
1.2ml of						
300mg of Ca ²⁺	opalescent	4	opalescent	4	opalescent	4
450mg of Ca ²⁺	opalescent	4	opalescent	4	opalescent	4
600mg of Ca ²⁺	opalescent	4	opalescent	4	opalescent	4
0.6ml of						
300mg of Ca ²⁺	opalescent	4	opalescent	4	opalescent	4
450mg of Ca ²⁺	opalescent	4	opalescent	4	opalescent	4
600mg of Ca ²⁺	opalescent	4	opalescent	4	opalescent	4

4.4.2 Determination of surface tension

Surface tension of dodecylbenzene sulfonate, cardanol sulfonate and hydrogenated cardanol sulfonate were determined by ISO method. The results are shown in Figures a-c. (Tables b.1-b.3, Appendix B.)

Surface tension of dodecylbenzene sulfonate was different from cardanol sulfonate and hydrogenated cardanol sulfonate. Dodecylbenzenesulfonate gave the minimum surface tension (28 mN/m.) at -0.542 (10 % w/v), cardanol sulfonate gave the minimum surface tension (32 mN/m.) at -1.002 (4 % w/v.) and hydrogenated cardanol sulfonate gave the minimum surface tension (32 mN/m.) at -1.002 (4 % w/v.).

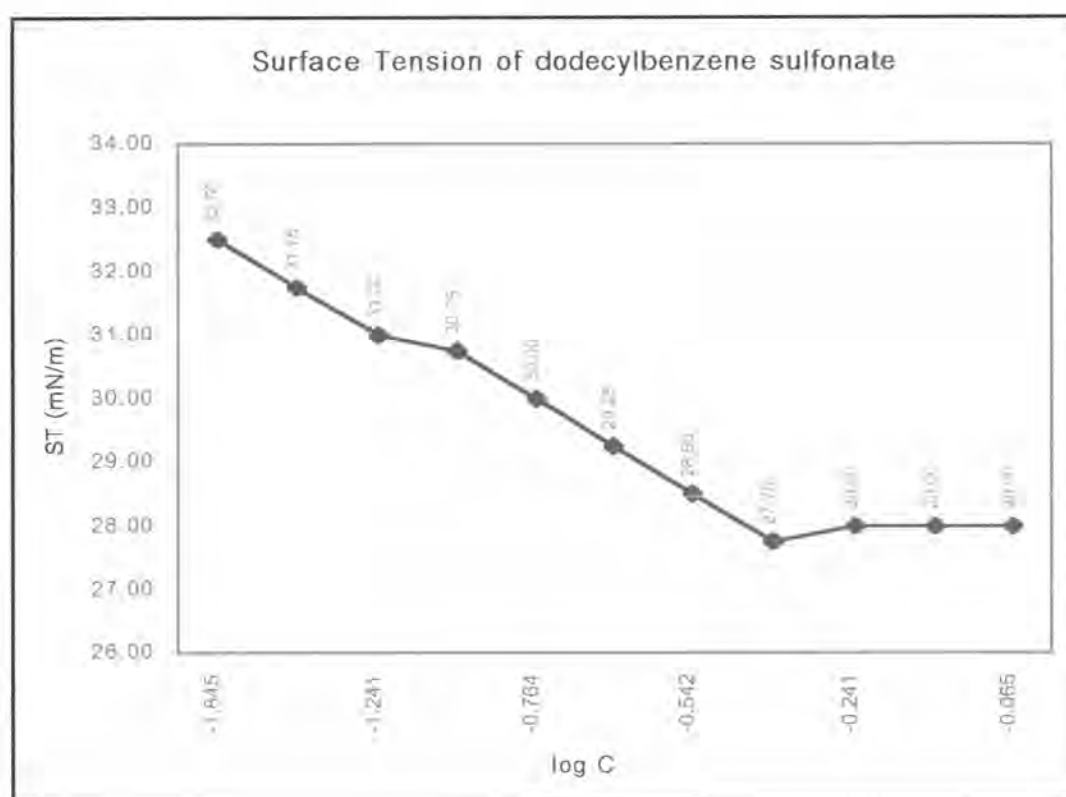


Figure a. Surface tension of sodium dodecyl benzene sulfonate

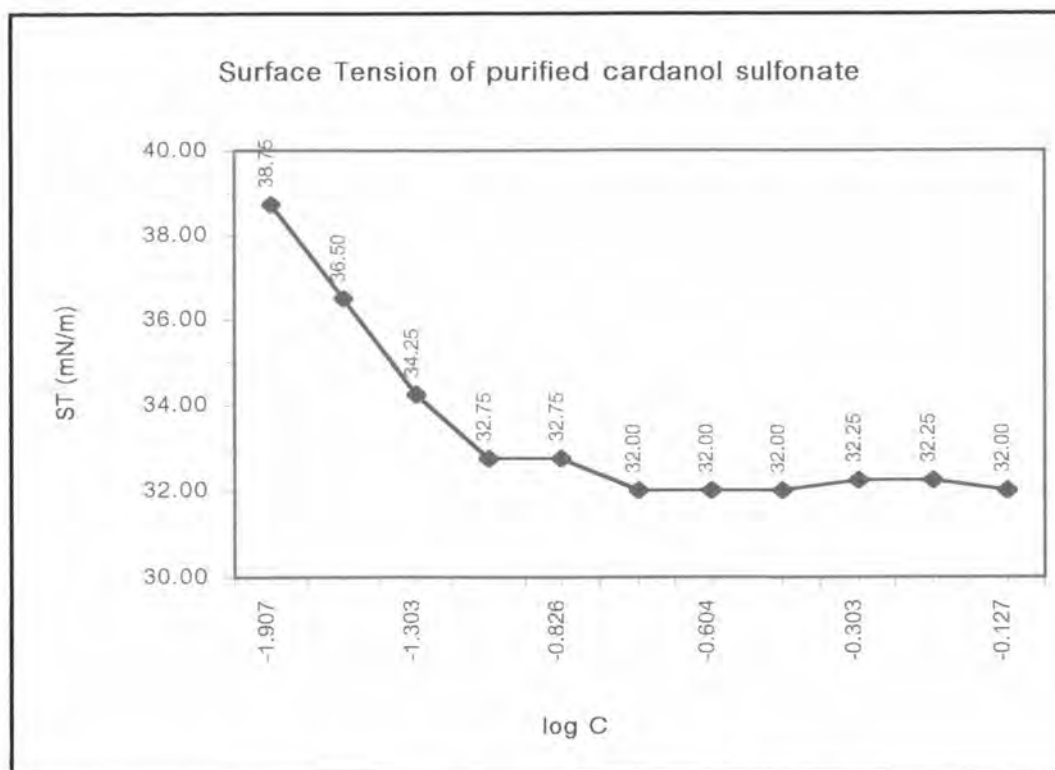


Figure b. Surface tension of cardanol sulfonate

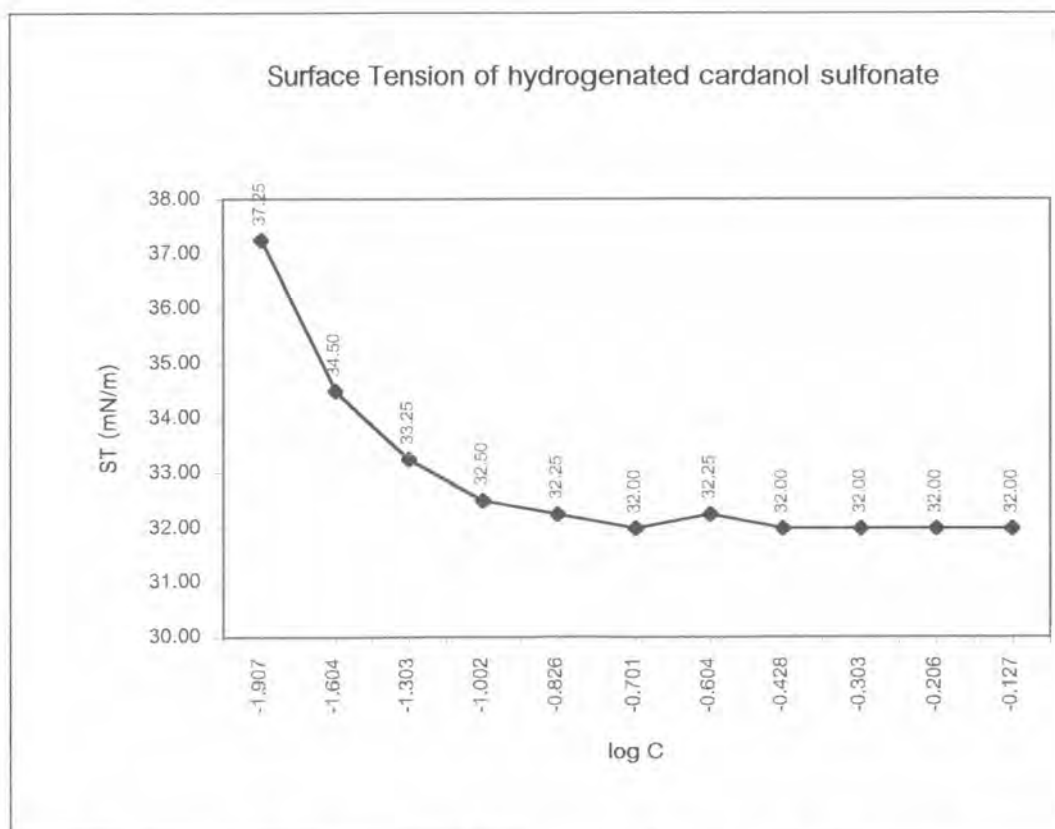


Figure c. Surface tension of hydrogenated cardanol sulfonate

4.4.3 Determination of C.M.C.

C.M.C. of dodecylbenzene sulfonate, cardanol sulfonate and hydrogenated cardanol sulfonate were determined by ISO method. The results are shown in Figure d.

From the surface tension of the three cases, the C.M.C. of dodecylbenzene sulfonate was 0.4304 mol/l, C.M.C. of purified cardanol sulfonate was 0.0936 mol/l and of hydrogenated cardanol sulfonate was 0.0465 mol/l.

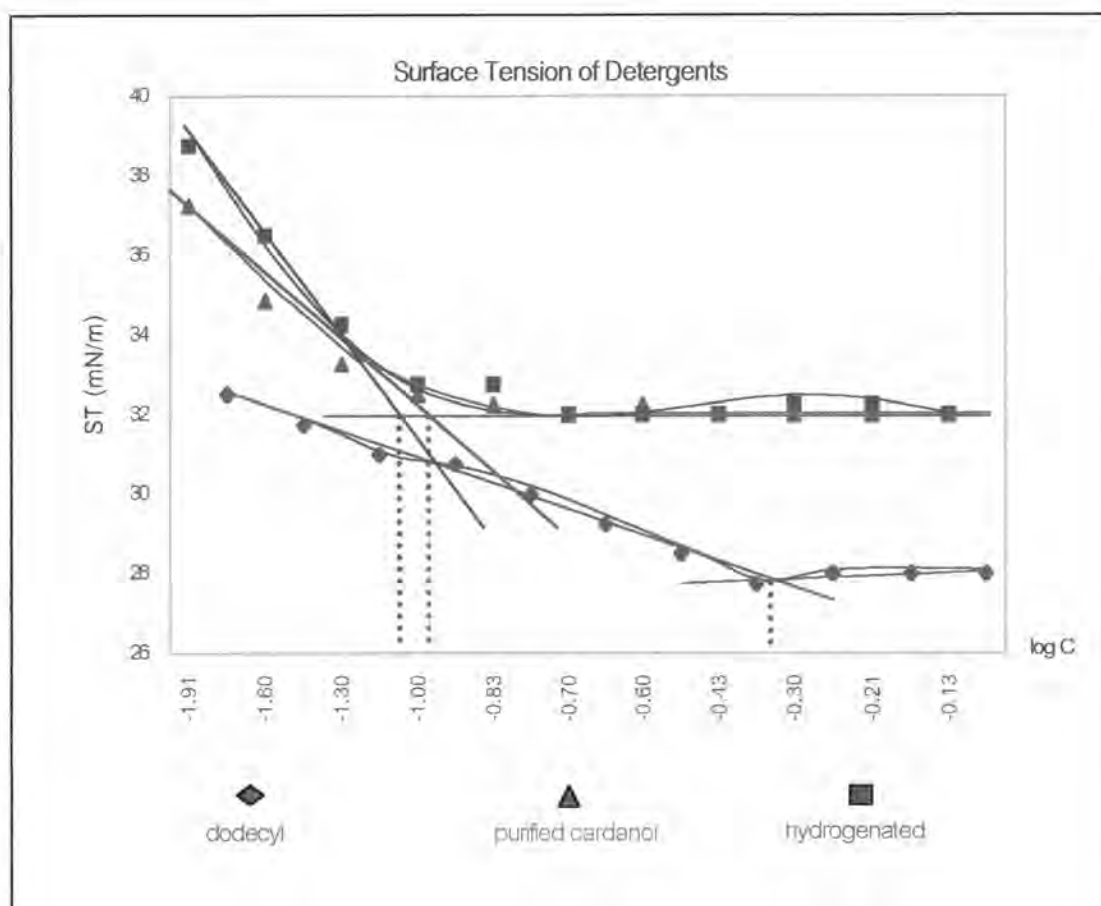


Figure d. Surface tension of detergents

4.4.4 Determination of % detergency

Detergency of dodecylbenzene sulfonate, cardanol sulfonate and hydrogenated cardanol sulfonate were determined by ICS method. The results are shown in Table b.4 (Appendix B.) and % detergency of each salt is shown in Table b.5. (Appendix B.)

Reflectance of dodecylbenzene sulfonate, cardanol sulfonate and hydrogenated cardanol sulfonate were 68.91, 66.74 and 67.97, respectively. % Detergency of cardanol sulfonate and hydrogenated cardanol sulfonate using the dodecylbenzene sulfonate as reference was 87.81 and 94.09 %, respectively. (Table 4.20.)

Table 4.20. % Detergency of cardanol and hydrogenated cardanol sulfonate using dodecylbenzene sulfonate as a reference

	Dodecylbenzene	Cardanol sulfonate	Hydrogenated cardanol sulfonate
% detergency	100	87.58	93.84