

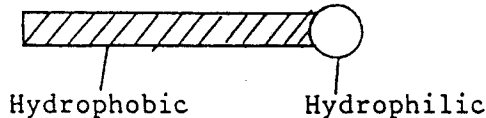
계면활성제의 분석기술

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ANALYSIS OF SURFACE ACTIVE AGENT

1. Surface active agent. (= Surfactant)

Surfactant Hydrophilic group - Lipophobic group.
 Hydrophobic group - Lopophilic group.



Soluble in water

Soluble in oil (Solvent)

2. Classification of Surfactant.

2. 1. Anionic Surfactant.

- | | | |
|----------|----------------------|--|
| 2. 1. 1. | Carbonate, Soap | RCOONa (A-I) |
| 2. 1. 2. | Alkyl Sulfate Salt | ROSO_3Na (A-II) |
| 2. 1. 3. | Alkyl Sulfonate Salt | RSO_3Na (A-III) |
| 2. 1. 4. | Alkyl phosphate salt | $\begin{array}{c} \text{O} \qquad \qquad \text{O} \\ \parallel \qquad \qquad \parallel \\ \text{ROP} - \text{ONa}(\text{RO})_2\text{P} - \text{ONa} \\ \\ \text{ONa} \end{array}$ (A-IV) |

2. 2. Cationic Surfactant.

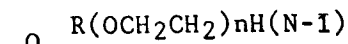
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|----------|--------------------------------|--|
| 2. 2. 1. | Alkyl Amine Salt | $\text{RNH}_2\text{-HCl}$ (C-I) |
| 2. 2. 2. | Alkyl Quaternary Ammonium Salt | $\begin{array}{c} \text{R}_2 \\ \\ \text{R}_1\text{N-R}_3\text{.Cl} \\ \\ \text{R}_4 \end{array}$ (C-II) |

2. 3. Amphoteric Surfactant

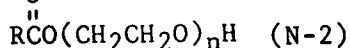
- | | | |
|----------|----------------------|------------------------------|
| 2. 3. 1. | Carbonate amino acid | RNHCOONa (Am - 1) |
|----------|----------------------|------------------------------|

2. 4. Nonionic Surfactant

2. 4. 1. Alkyl polyethylene oxide



2. 4. 2. Fatty acid ester



3. History of Sample

3. 1. Name

3. 2. Maker

3. 3. Catalogue - (MC Cutcheon's Detergent and Emulsifier)

3. 4. Other technical information.

4. Preliminary test

4. 1. Appearance (liquid, solid, powder)

4. 2. Mixture or pure compound - TLC

4. 3. Color (APHA. Gardener)

4. 4. Odor

	C ₈	C ₁₀	C ₁₂	C ₁₄	C ₁₆	C ₁₈	C _{18F}
Fatty alcohol							
Fatty acid							
Fatty amine							

* IPA. DMF. Benzene. Acetone. Chloroform.

4. 5. Solid Content

4. 6. Specific gravity

4. 7. Ionic Character (Anionic, Cationic, Nonionic, Amphoteric.)

4. 8. Cloud point and acetic acid titration

4. 9. Solubility (water, methanol, benzene, n-hexane)

4. 10. PH (1% Solution, 5% Solution)

4. 11. Cl⁻ Detect

4. 12. SO₄⁼ Detect

4. 13. Sample 1g/100CC of 5% H₂SO₄. boiling.

4. 14. Sample 1g/100CC of 5% NaOH. boiling.

5. Hydrophilic group analysis.

5. 1. Volumetric determination of surfactant with dyes as an indicator.

5.1.1 Diphasic titration method.

methylene blue - indicator (cationic)

chloroform - Solvent

Determination of anionic surfactant.

Table 1. Determination of anionic Surfactant by Epton Method

Sample Anionic Surfactant (ml)	Methylene blue indicator. (ml)	Chloroform (ml)	Cationic Surfactant C mM=5.920	Sample m mol
10	25	15	5.30	2.98
20	25	15	10.38	3.07
30	25	15	15.73	3.10

Color indicator.

Basic (for anionic)

Methylene blue, Methyl green, Fuchsin, Toluidine blue, Neutral Red, Potamine Fast Red.

Acid (for cationic)

Bromphenol blue, Dichlorofluorescein, Eosin, Ethylthrosine, Bromcresol purple, Orange II

Solvent

Small dielectric constant

CCl₄, benzene, ethyl acetate.

@ Not Soluble The Surfactant - Dye Complex

Large dielectric constant

Nitrobenzene, n-butanol

@ Not Soluble The dye.

Table 2

Analysis of amphoteric surfactant by the alkaline Epton method

Amphoteric Surfactant	Concentration (m mol/l)	Purity (%)	m mol/l	Purity
○ N-lauryl- -alanine	2.003	98.2	0.953	99.5
○ N-Sodium lauryl taurine	2.134	99.5	2.130 2.124	99.8 99.5
○ 3-heptadecyl 3- (2' sodium ethyl Sulfate) imidazoliue	2.152	96.0	2.077 2.091	96.5 97.2

6. Hydrophobic group analysis

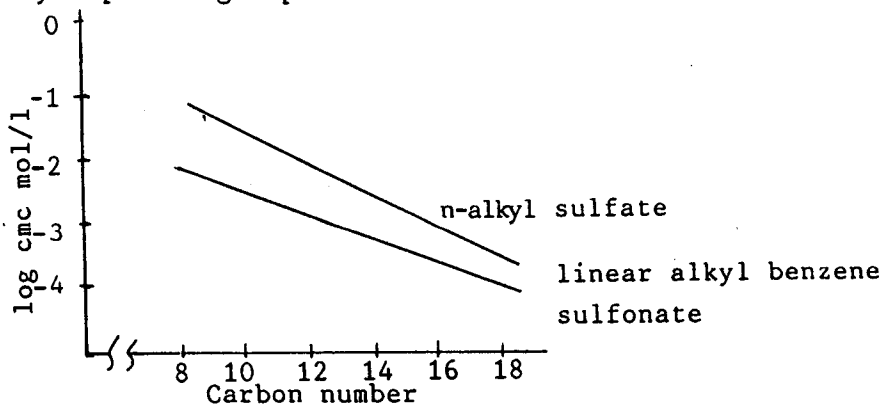
Paraffine

Alkyl benzene

-Olefin

Fatty alcohol

6. 1. Hydrophobic group - c.m.c



6. 2. Gaschromatography.

Sample → Deconposition → GC

* Deccmposition method

Alkyl benzene Sulfonate - heating in the conc
Acid Solution
(60-70% H₂SO₄ X 140-190% C-S bond)

Alkyl sulfate - heating in the diluted Acid solution
(1N HCl 100°C X 7hr)

Soap - Boiling with acid Solution

Cationic Surfáctant - heating with conc
alkaline, amine detect

Nonionic Surfáctant - Direct GC

7. Analysis of surfactant - classical method (Example I)

7. 1. Preliminary test.

	method	Results
Appearance		yellow paste
Ionic	Bromphenol blue	Cationic
PH (1% Soln)	PH - meter	5.7
Amine value (Dry)	Total amine value	13.
Solid content	Kett	20%
Odor		amine, Fat, oleyl
Solubility		
Water		Turbid
Isopropyl alcohol		Soluble
CL ⁻		negative
SO ₄ ⁻		negative

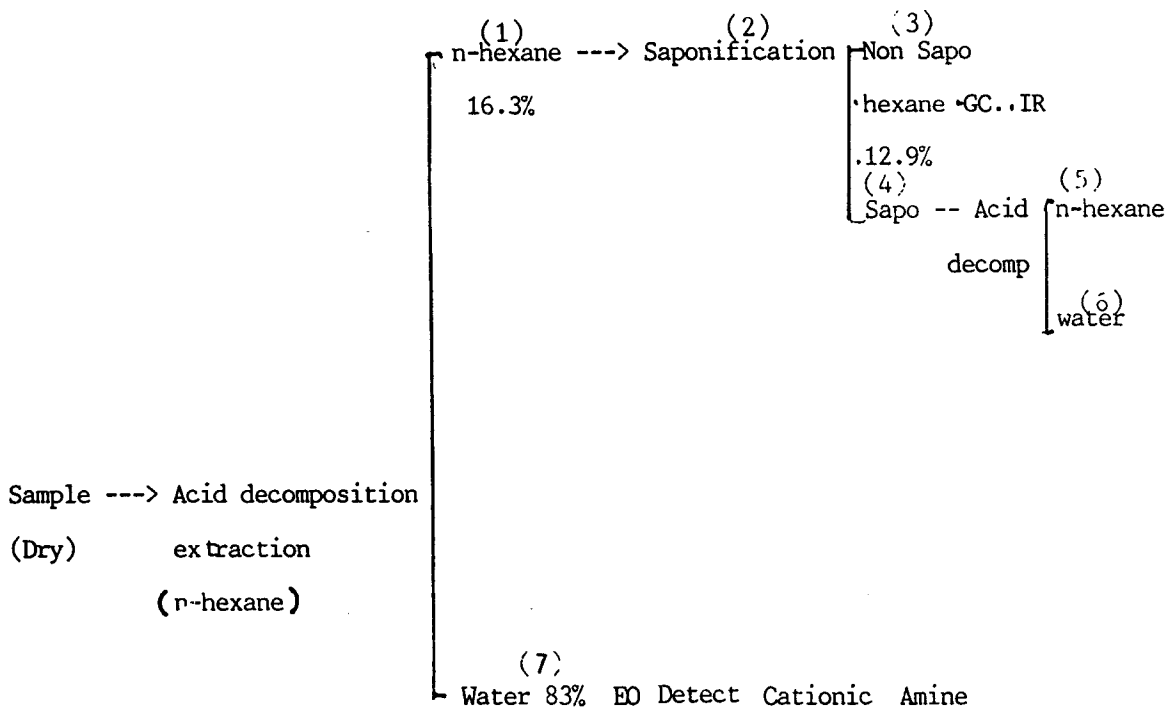
* Sample : Commercial product (Reported July, 1971)

7. 2. Column Chromatograph

First fraction	n-hexane
Second fraction	CCL ₄
Third fraction	Benzene
Fourth fraction	Isopropanol
Fifth fraction	methanol

Fraction	IR	Appea-	mp	Solubility		Ionic	S.V.	
				Water	CCl ₄			
1 St n-hexane	2980-3000cm ⁻¹ -CH ₂ - 1730 - C - O 1460 -CH ₂ - 1380 CH ₃	Cololess Liquid	-	-	+	Nonionic	-	RCOOR
2 nd CCl ₄	2980-3000cm ⁻¹ -CH ₂ - 1730 " - C - O 1460 " -CH ₂ - 1120, 1070 - O -	Cololess Liquid	-	-	+	-		RCOOR
3 rd Isopropyl Alcohol	3200Cm -OH 1980-3000Cm ⁻¹ -CH ₂ - 1470 Cm ⁻¹ 1370 Cm ⁻¹ -CH ₃ 1070-1120Cm ⁻¹ -CH ₃	Yellow Solid	-	-	+	Cationic	62.545	RCOOR
4 th Acetone	3200-1 OH 2980-3000Cm ⁻¹ -CH ₂ - 1720 Ester 1630 -NH ₂ 1120-1070 -OH	Yellow Solid	-	-	+	Nonionic	-	RN $\begin{matrix} \diagup \text{EO} \\ \diagdown \text{EO} \end{matrix}$
5 th Methanol	3200 Cm ⁻¹ OH 2980-3000Cm ⁻¹ -CH ₂ - 1630 Cm ⁻¹ NH ₂ 1120,1060 OH	White Solid	57°C	+	-	Nonionic	-	HO(CH ₂ CH ₂ O) _n H

7.3. Systematic analysis



7.4. Ion exchange Resin Column Chromatograph.

Sample	Cationic	79,8%	Cationic
Ben - Al Soln(1:1)			
IR 130.	Nonionic	12%	EO Detect

7.4. Determination of Cationic Surfactant(Epton Method)

Standard Cationic - Cetylpyridinium Chloride (C.P.C)

Standard Anionic - Sodium Alkylbenzene Sulfonate (ABS)

C, P, C Consumption 0.01. g

7.5. Summerization

7.5.1. Column Chromatography, IR detection

Fatty Acid Ester

Fatty Amine ethylene Oxide Adduct

polyoxy ethylene.

7.5.2. Hydrolysis Acidic Medium

ether layer 16.8

Saponification Value 97.6

Oleic Acid = $\frac{97.6}{180.7} \times 100 = 54\%$

7.5.3 Ion-exchange Resin

Cationic Surfactant 79%

7.5.4. Determination of Cationic Surfactant.

CPC - ABS Titration

$$\frac{0.05027 \times 3 \times 0.7983}{\lambda} = \frac{0.01 \times 1.12}{357.5}$$

$$\lambda = 3842$$

< Result >

1.	$R - N \begin{cases} (EO)_m \\ (EO)_n \end{cases}$	$m + n = 75$	80%
2.	R - OH (oleyl)		13%
3.	R COOR (oleyl)		7%
4.	PEG		-

8. TLC/FID method.

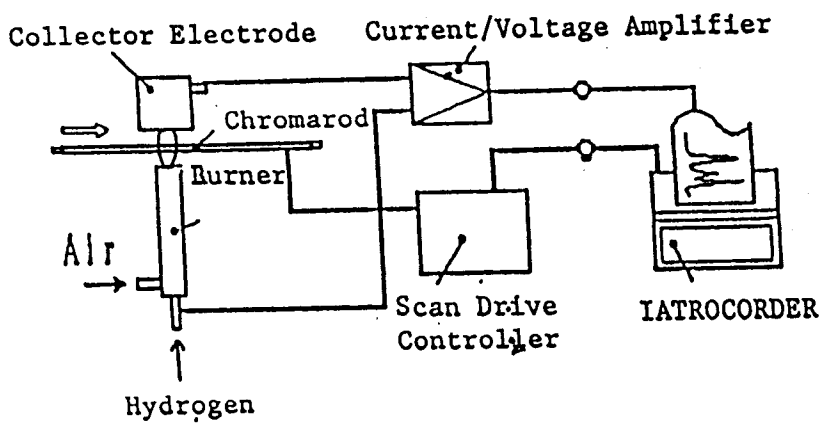


Fig. 1.2b

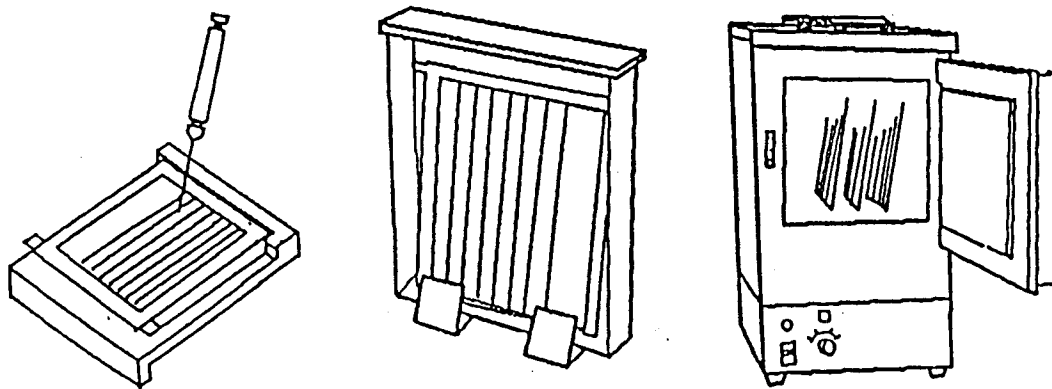


Fig. 1.2a

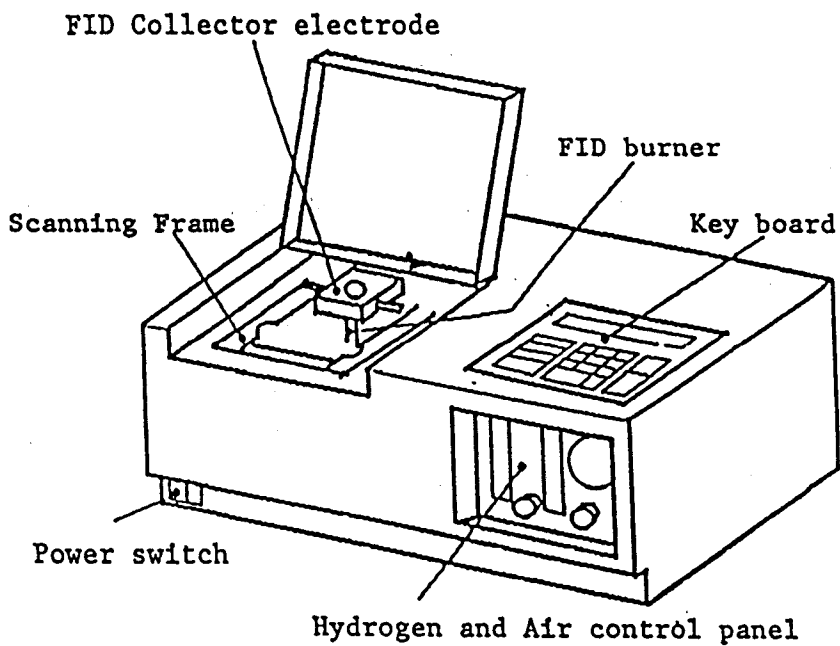


Fig. 2.2a

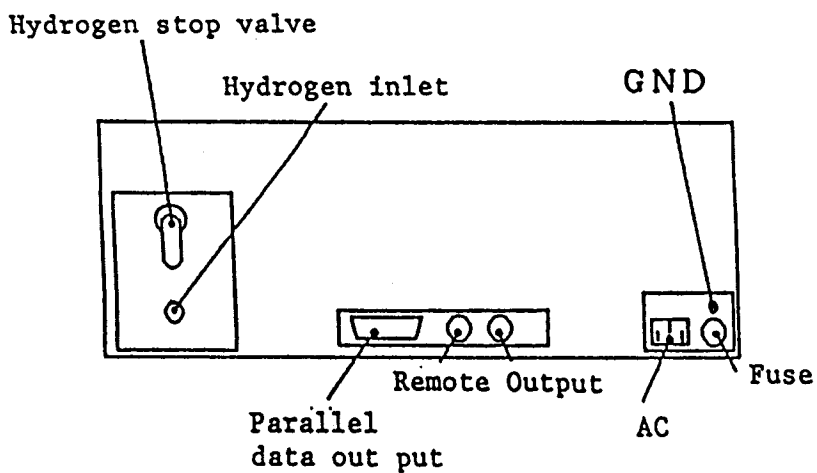


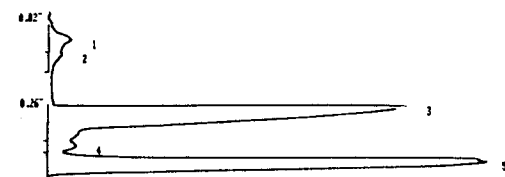
Fig. 2.2b

1) カチオン活性剤

Fig 1-1. Monoalkyl ammoniumchloride

Mobile phase :

Acetone : Water : conc Ammonia (63 : 6 : 1)

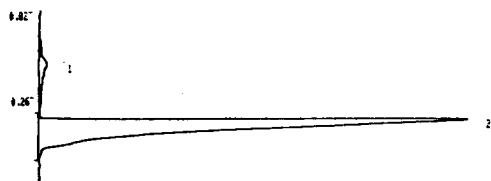


NO.	NAME	RT	H	OR	H	PK	CONC
1		0.101	4101			M	2.9583
2		0.141	1799			M	1.2375
3		0.303	68735			M	49.5745
4		0.405	3154			M	2.2751
5		0.465	60860			M	43.8943
TOTAL			138651				100.0000

Fig 1-3. Stearoyl amidoethyl diethyl amine

Mobile phase :

Acetone : Water : conc Ammonia (63 : 6 : 1)



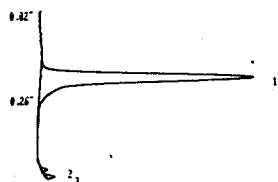
NO.	NAME	RT	H	OR	H	PK	CONC
1		0.173	1318			M	4.2546
2		0.343	23951			M	95.6453
TOTAL			30269				100.0000

2) アニオン活性剤

Fig 2-1. Sodium alkyl benzene sulfate

Mobile phase :

Chloroform : Methanol : Formic acid (30 : 30 : 1)

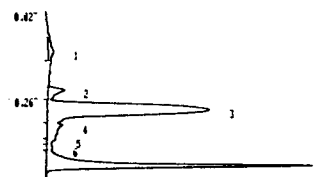


NO.	NAME	RT	H	OR	H	PK	CONC
1		0.317	24733			M	37.5143
2		0.480	250			M	0.3333
3		0.502	331			M	1.5023
TOTAL			25425				100.0000

Fig 1-2. Dialkyl ammoniumchloride

Mobile phase :

Acetone : Water : conc Ammonia (63 : 6 : 1)

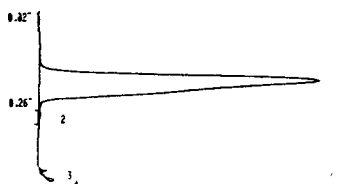


NO.	NAME	RT	H	OR	H	PK	CONC
1		0.133	1851			M	2.5614
2		0.244	1302			M	3.1838
3		0.303	21412			M	52.1327
4		0.346	1524			M	4.6397
5		0.386	401			M	0.9791
6		0.412	362			M	0.8650
7		0.467	14574			M	35.5182
TOTAL			41033				100.0000

Fig 2-2. α -Olefin sulfonate

Mobile phase :

Chloroform : Methanol : Formic acid (30 : 30 : 1)

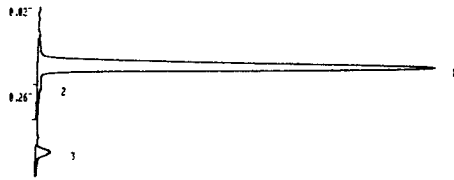


NO.	NAME	RT	H	OR	H	PK	CONC
1		0.222	54120			M	35.0769
2		0.313	151			M	0.2072
3		0.478	140			M	0.2064
4		0.503	234			M	0.4286
TOTAL			54644				100.0000

Fig 2-3. Sodium N-palmitoyl sarcosinate

Mobile phase :

Chloroform : Methanol : Formic acid (50 : 10 : 1)

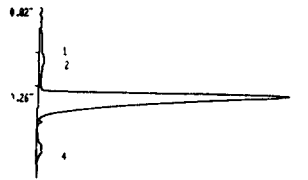


NO.	NAME	RT	A OR H	NK	CONC
1		0.189	19466	M	94.1387
2		0.248	492	M	1.9453
3		0.474	796		3.8558
TOTAL			20665		100.0000

Fig 2-4. Sodium N-lauroyl methyltaurate

Mobile phase :

Chloroform : Methanol : Formic acid (50 : 10 : 1)

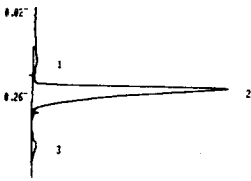


NO.	NAME	RT	A OR H	NK	CONC
1		0.132	509	M	1.7920
2		0.171	592	M	2.2746
3		0.271	16193		32.1909
4		0.431	470		0.9323
TOTAL			17565		100.0000

Fig 2-5. Sodium lauryl sulfate

Mobile phase :

Chloroform : Methanol : Formic acid (50 : 10 : 1)



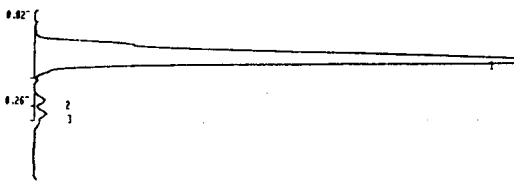
NO.	NAME	RT	A OR H	NK	CONC
1		0.170	414		3.1722
2		0.252	12134	M	92.2945
3		0.418	596		3.8324
TOTAL			13055		100.0000

3) ノニオン活性剤

Fig 3-1. POE(2) Monostearate

Mobile phase :

Ethyl acetate : Acetone : Water (45 : 20 : 3)

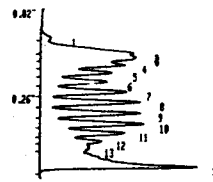


NO.	NAME	RT	A OR H	NK	CONC
1		0.146	21157	M	37.4232
2		0.276	252	M	1.1613
3		0.316	307	M	1.4153
TOTAL			21717		100.0000

Fig 3-2. POE(10) Monostearate

Mobile phase :

Ethyl acetate : Acetone : Water (45 : 20 : 3)



NO.	NAME	RT	A OR H	NK	CONC
1		0.104	176	M	0.7977
2		0.148	1294	M	5.9974
3		0.157	1716	M	7.7557
4		0.179	1329	M	6.3104
5		0.201	1193	M	5.3476
6		0.228	1176	M	5.3150
7		0.256	1513	M	6.8422
8		0.285	1496	M	6.8661
9		0.317	1726	M	7.8018
10		0.348	1739	M	8.1350
11		0.373	1552	M	7.0149
12		0.398	1920	M	8.6104
13		0.420	1359	M	6.1796
14		0.472	4131	M	18.9457
TOTAL			22126		100.0000

SAMPLE 73 14112 HHR. 02 1983

Fig 3-3. Diglycerol monooleate

Mobile phase :

Ethyl acetate : Acetone : Water (52 : 15 : 3)

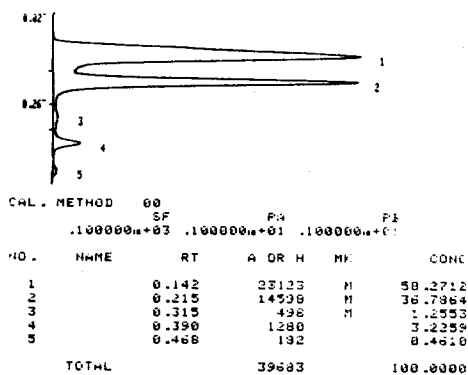


Fig 3-5. Solbitan monooleate

Mobile phase :

Chloroform : Methanol : Formic acid (65 : 2 : 1)

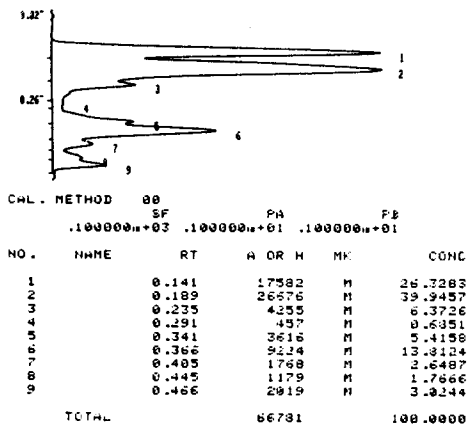


Fig 3-7. ED(4) Alkyl ether

Mobile phase :

Ethyl acetate : Acetone : Water (52 : 15 : 3)

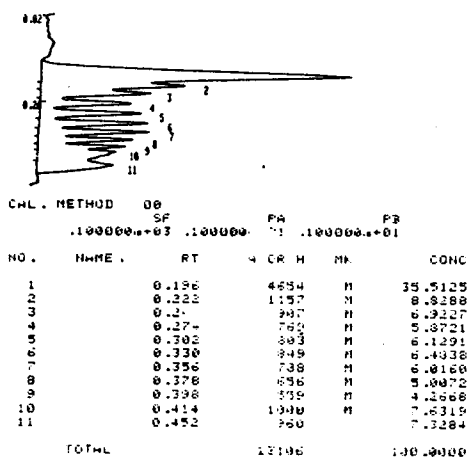


Fig 3-4. Diglycerol dioleate

Mobile phase :

Ethyl acetate : Acetone : Water (52 : 15 : 3)

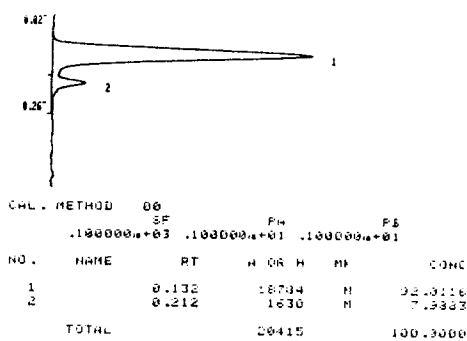


Fig 3-6. Solbitan tristearate

Mobile phase :

Chloroform : Methanol : Formic acid (65 : 2 : 1)

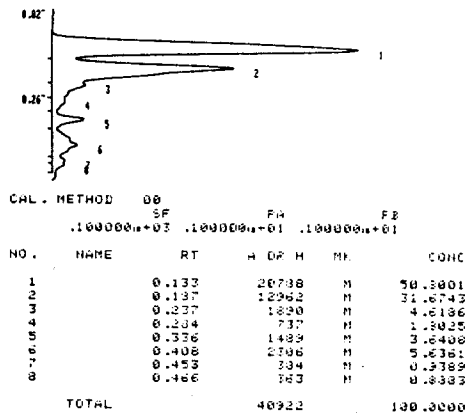


Fig 3-8. ED(10) Nonyl phenyl ether

Mobile phase :

Ethyl acetate : Acetone : Water (52 : 15 : 3)

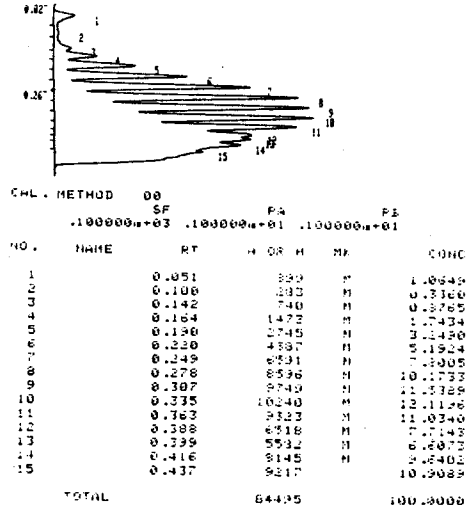
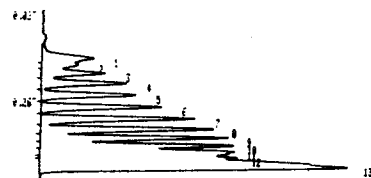


Fig. 3-9. POE(9) Lauryl ether

Mobile phase :

Ethyl acetate : Acetone : Water (52 : 15 : 3)

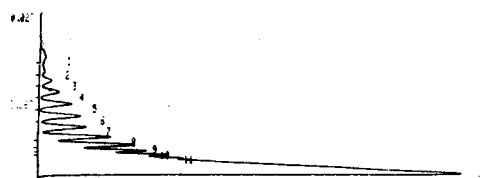


NO.	NAME	RT	H OR H	PK	CONC
1		0.155	1120	M	3.7407
2		0.172	591	M	1.7945
3		0.186	1318	M	3.2168
4		0.225	1248	M	4.1048
5		0.258	1437	M	4.3449
6		0.292	1733	M	5.6676
7		0.325	3231	M	7.3555
8		0.354	2547	M	6.0521
9		0.376	2613	M	3.2630
10		0.409	2336	M	8.2065
11		0.419	4946	M	12.7382
12		0.437	1503	M	4.7512
13		0.462	6923	M	26.2297
TOTAL			31674		100.0000

Fig 3-10. POF(15) Oleyl ether

Mobile phase :

Ethyl acetate : Acetone : Water (52 : 15 : 3)

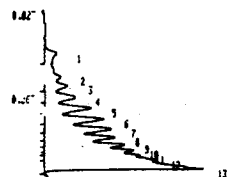


NO.	NAME	RT	H OR H	PK	CONC
1		0.141	400	M	0.3242
2		0.132	133	M	0.3260
3		0.211	452	M	1.3211
4		0.243	396	M	1.2775
5		0.272	351	M	2.2302
6		0.310	1290	M	2.2912
7		0.342	1491	M	3.1254
8		0.371	1322	M	4.4222
9		0.392	2430	M	5.2034
10		0.409	2366	M	5.7422
11		0.421	2329	M	5.4402
12		0.428	2200	M	56.3682
TOTAL			44110		100.0000

Fig 3-11. POE(9) Secondary alkyl ether

Mobile phase :

Ethyl acetate : Acetone : Water (52 : 15 : 3)

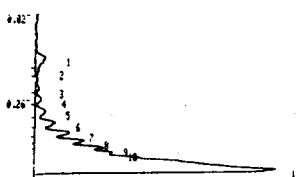


NO.	NAME	RT	H OR H	PK	CONC
1		0.145	409	M	2.7095
2		0.210	379	M	2.2434
3		0.239	524	M	3.4771
4		0.271	731	M	4.3481
5		0.303	985	M	6.5348
6		0.333	1232	M	8.1722
7		0.362	1332	M	8.8340
8		0.386	1237	M	6.8055
9		0.407	1370	M	6.1582
10		0.423	1224	M	8.1122
11		0.438	320	M	5.4407
12		0.453	1631	M	10.8199
13		0.476	3224	M	22.8336
TOTAL			15091		100.0000

Fig 3-12. POE(12) Secondary alkyl ether

Mobile phase :

Ethyl acetate : Acetone : Water (52 : 15 : 3)

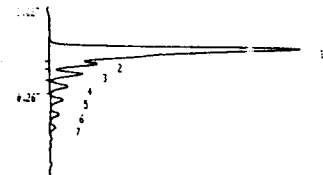


NO.	NAME	RT	H OR H	PK	CONC
1		0.143	301	M	2.1750
2		0.151	36	M	0.4101
3		0.236	72	M	0.2120
4		0.265	172	M	0.3260
5		0.299	181	M	1.2341
6		0.321	432	M	2.1249
7		0.361	385	M	4.2423
8		0.382	700	M	5.2006
9		0.403	271	M	1.2310
10		0.416	1312	M	7.2402
11		0.462	2472	M	58.2442
TOTAL			1385		100.0000

Fig 3-13. POE(2) Cetyl ether

Mobile phase :

Ethyl acetate : Acetone : Water (52 : 15 : 3)

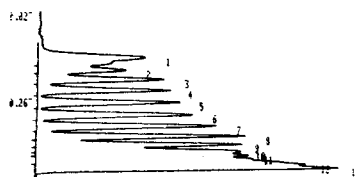


NO.	NAME	RT	H	OR	H	IB	CONC
1		0.146	6175	N			75.3301
2		0.184	733	N			0.3558
3		0.212	474	N			0.5281
4		0.248	235	N			3.5881
5		0.287	114				2.6211
6		0.328	148				1.3081
7		0.385	90				1.0296
TOTAL			8132				100.0000

Fig 3-14. POE(7) Cetyl ether

Mobile phase :

Ethyl acetate : Acetone : Water (52 : 15 : 3)



NO.	NAME	RT	H	OR	H	IB	CONC
1		0.150	3211	N			0.1511
2		0.167	1473	N			0.2509
3		0.213	1092	N			0.2541
4		0.244	2901	N			0.2506
5		0.277	1813	N			0.2560
6		0.312	1536	N			0.2559
7		0.345	1736	N			0.2474
8		0.372	2929	N			0.2411
9		0.397	2246	N			0.2411
10		0.416	1738	N			0.2411
11		0.428	1971	N			0.2361
12		0.453	5741	N			0.2361
13		0.462	4905	N			0.2361
TOTAL			37137				100.0000

Fig 3-15 POE(15) Cetyl ether

Mobile phase :

Ethyl acetate : Acetone : Water (52 : 15 : 3)

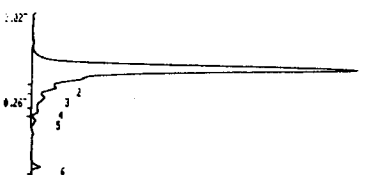


NO.	NAME	RT	H	OR	H	IB	CONC
1		0.133	723	N			1.1046
2		0.141	329	N			1.1257
3		0.156	407	N			1.3205
4		0.208	142	N			0.4386
5		0.241	123				0.4371
6		0.278	155	N			0.5296
7		0.316	170	N			0.5237
8		0.347	329	N			1.3629
9		0.373	571	N			1.3513
10		0.463	26526	N			30.6357
TOTAL			29225				100.0000

Fig 3-16 POE(1) POP(4) Cetyl ether

Mobile phase :

Ethyl acetate : Acetone : Water (52 : 15 : 3)



NO.	NAME	RT	H	OR	H	IB	CONC
1		0.178	5000	N			53.9141
2		0.238	503	N			4.5220
3		0.265	793	N			3.7841
4		0.302	122	N			1.1426
5		0.332	81				0.7262
6		0.467	122	N			0.2827
TOTAL			10226				100.0000

Fig 3-17. POE(20) POP(6) Cetyl ether

Mobile phase :

Ethyl acetate : Acetone : Water : Formic acid
(30 : 30 : 3 : 1)

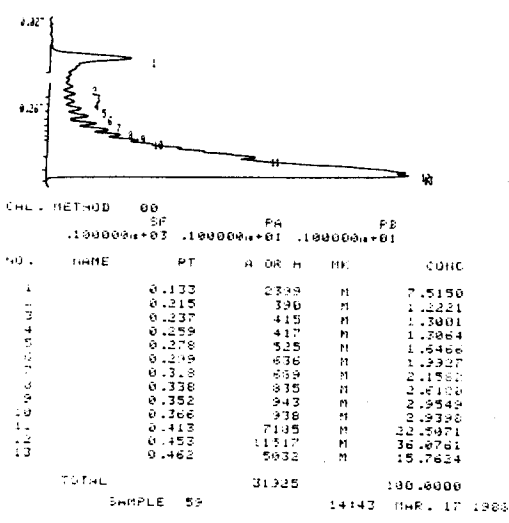


Fig 3-18. Sodium POE(3) alkyl ether sulfate

Mobile phase :

Chloroform : Methanol : Formic acid (50 : 10 : 1)

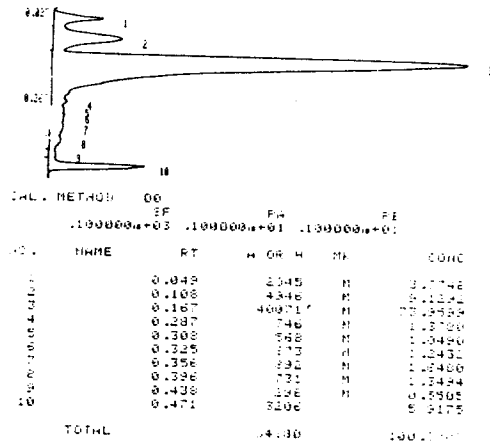
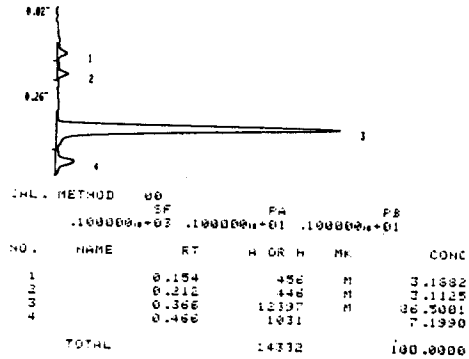


Fig 3-19. Glycerol monostearate

Mobile phase :

Chloroform : Methanol : Formic acid (70 : 1 : 0.3)

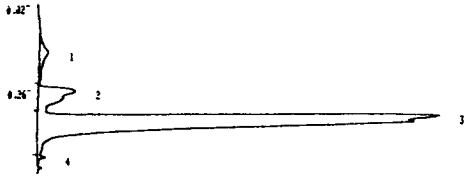


4) 両性活性剤

Fig 4-1. Lauryl dimethyl aminoacetic acid
betaine

Mobile phase :

Chloroform : Methanol : Formic acid (50 : 20 : 1)



NO.	NAME	RT	H OR H	PK	CONC
1		0.158	198	N	2.1481
2		0.271	197	N	8.4446
3		0.357	3119	N	35.7332
4		0.462	197		0.4748
TOTAL					35261 100.0000

Fig 4-2. Cocoyl amido propyl dimethyl aminoacetic
acid betaine

Mobile phase :

Chloroform : Methanol : Formic acid (50 : 20 : 1)



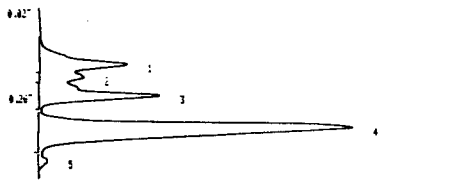
NO.	NAME	RT	H OR H	PK	CONC
1		0.085	125	N	0.6272
2		0.157	1171	N	5.1425
3		0.245	730	N	1.2514
4		0.291	476	N	1.2722
5		0.314	833	N	3.1161
6		0.388	126	N	0.6228
7		0.422	1719	N	15.1069
TOTAL					20056 100.0000

5) その他の活性剤

Fig 5-1. Sugar ester

Mobile phase :

Chloroform : Methanol : Formic acid (50 : 10 : 1)



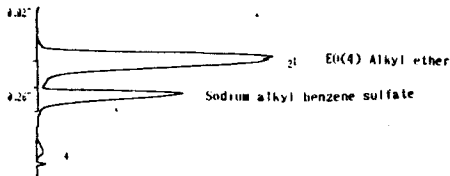
NO.	NAME	RT	H OR H	PK	CONC
1		0.102	6220	N	14.1181
2		0.112	2154	N	5.0759
3		0.174	7624	N	17.3778
4		0.371	26342	N	31.7712
5		0.452	432		1.1527
TOTAL					42245 100.0000

6) 活性剤混合物

Fig 6-1. Sodium alkyl benzene sulfate
+ EO(4) Alkyl ether

Mobile phase :

Chloroform : Methanol : Formic acid (60 : 10 : 1)



NO.	NAME	RT	H OR H	PK	CONC
1		0.171	11212	N	15.1006
2		0.190	12092	N	37.8332
3		0.276	8212	N	19.6247
4		0.426	432		1.1372
TOTAL					31364 100.0000