Surfactant for Pesticide Formulation.

Supplement Edition, IR & NMR Analysis.

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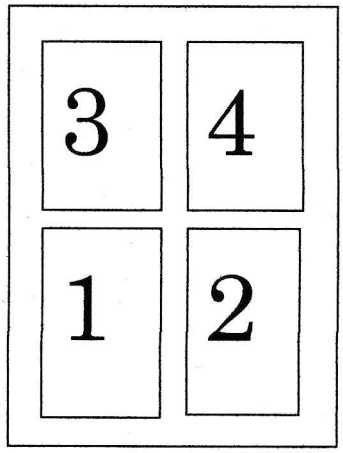
IR, NMR Chart Arrangement.

Following IR Spectrum (Chart) are arranged as follows.



1. Anionic Surfactant

1-11. Salt of Carboxylic acid

IR

1,560cm^{-1}, $\nu_{C=O}$, very strong, characteristic,

Al salt, it shift to 1,590cm^{-1}, half ester of maleic acid also shift to 1,590cm^{-1}

1. K Stearate (ノンサール SK-1)
2. Ca Stearate
3. Al Stearate
4. Na iso Stearate
5. K Oleate
6. Oleic acid TEA salt
7. Na (LL-3) maleate
8. K Stearate (ノンサール TK-1)

1-12. Alkyl sulfonate

IR

1,180～1,200cm^{-1}, $\nu_{S=O}$, very strongest, very characteristic, little broad.

1,050～1,060cm^{-1}, sharp, middle strong

1,120cm^{-1}, in case, weak, sometime it become doublet.

Compare with other Sulfonate, the peak will be shown in low wave number area.

1. Na Isethionate
2. Chloro hydroxy propane sulfonate
3. Di hydroxy propane sulfonate
4. Na Butyl sulfonate
5. Na Octyl sulfonate
6. Na n-Lauryl sulfonate
7. K n-Lauryl sulfonate
8. Na Alkyl sulfonate (マーソラート H)

1-13. Alkyl aryl sulfonate

IR

1,200cm^{-1}, $\nu_{S=O}$, very strongest, very characteristic, little broad.
1,030 (1,050, 1010)cm^{-1}, sharp, middle strong
1,130cm^{-1}, in case, weak, sometime it become doublet.
1,600 (little broad), 830cm^{-1} (sharp, middle strong) are very stable, sometime 760cm^{-1} (weak) observed.

1. Hexylbenzene sulfonate
2. Nonylphenyl sulfonate (NP sulfonate)
3. Na L-Dodecylbenzene sulfonate
4. Ca Dodecylbenzene sulfonate
5. Mg Dodecylbenzene sulfonate
6. DBS-DMC (Lauryl dimethyl amine salt)
7. Di phenyl ether di sulfonate (Dowfax 2A-1)
8. Benzylaminobenzene sulfonic acid NH_4 salt
9. Petro sulfonate (石油スルフォネート ペトロネート K)

NMR

1. DBS-Na
2. L-DBC

1-14. Naphthalene sulfonate

IR

1,200cm^{-1}, $\nu_{S=O}$, very strongest, very characteristic, generally shoulder peaks observed at higher weave number. Based on SO_3 substituted position, absorption at 1,000 to 1,200cm^{-1} is little bit different, but symmetry observed as

follows.

1,200, 1,060, 800, 770cm^{-1}, α substituted, 1,5-di substituted

1,270, 1,240, 1,200, 1,110, 1,060, 920, 840cm^{-1}, β substituted, 2,6-di substituted

1. Na α-Naphthalene sulfonate
2. Na β-Naphthalene sulfonate
3. Na 1, 5-Naphthalene di sulfonate
4. Na 2, 6-Naphthalene di sulfonate
5. Na 2, 7 Naphthalene di sulfonate

1-15. Alkylnaphthalene sulfonate

IR

Almost same as Naphthalene sulfonate, peak will be little broad.

1,380cm^{-1} is very characteristic for Isopropyl group.

In case Butyl group, because of Carbonium ion stabilization, Alkyl group will be Tertiary Butyl.

1. Na tri-isopropyl naphthalene sulfonate (アルカノール XC)
2. Na di-butyl naphthalene sulfonate
3. Na di-octyl naphthalene sulfonate

1-16. Naphthalene sulfonate formalin condensate.

IR

Essentially same as Naphthalene sulfonate, but the peak will be combined and became 3 peaks (1,200, 1,100, 1,030cm^{-1}).

The peak 1,600cm^{-1} became little bit strong.

1. Na Naphthalene sulfonate formalin condensate
2. Ca Naphthalene sulfonate formalin condensate
3. Na Naphthalene sulfonate formalin condensate (ラベリン FH)
4. Na Naphthalene sulfonate formalin condensate (マイティー 150)
5. Na Naphthalene sulfonate formalin condensate (タモール NNO)
6. Na Lignin sulfonate

1-17. Alcoxylated sulfonate

IR

Essentially, alkoxylation originated peak are mainly observed, $\nu_{S=O}$ is not so very clear.

1. NP-5 HPS (NP-5 hydroxy propane sulfonate Na)
2. DNP-30 HPS (Di nonylphenyl ethoxylate (30) hydoroxy propane sulfonate Na)
3. DNP-30 HPS

1-18. Ester sulfonate

IR

1,250cm^{-1}	$\nu_{S=O}$, strong, broad,	·O·C(O)·CH_2·SO_3M,	sulfoacetate
		·O·C(O)·CH(R)·SO_3M,	sulfosuccinate
1,200cm^{-1}	$\nu_{S=O}$, strong broad	·C(O)·O·CH_2CH(OH)·CH_2·SO_3M	(HPS)
1,740cm^{-1}	$\nu_{C=O}$, strongest		
1,600～1,620cm^{-1}	$\nu_{C=O}$, weak,	Carboxylic acid origin	
1,620cm^{-1}	$\nu_{C=O}$, monoester of sulfosuccinate		

1. iso Stearic acid HPS Na
2. DAHPS-Na
3. DAPS-Na
4. COFA-LA-E-HPS-Na
5. Dol_{23}-10 sulfoacetate Na
6. OL-18.5 sulfoacetate Na
7. NP-5 sulfo acetate Na
8. NP-PO_5 sulfo acetate Nasulfo acetate Na
9. NP-P_3E_6 sulfo acetate Na
10. NP-13 sulfo acetate Na
11. LL-3 sulfo propyl acetate Na
12.
13. Di octyl sulfosuccinate Na (ネオコール SWC)
14. Di lauryl sulfosuccinate Na
15. Bis (Ocl-4) sulfosuccinate Na
16. Bis (Dol_{23}-4) sulfosuccinate Na
17. Bis (SL-1) sulfosuccinate Na
18. Bis (SL-3) sulfosuccinate Na
19. Bis (Sof-50) sulfosuccinate Na

20.

21. Di (NP-3) sulfosuccinate Na
22. Di (NP-3) sulfosuccinate NH_4
23. Di (NP-3) sulfosuccinate ethylene diamine salt
24. Di (NP-5) sulfosuccinate Na
25. Di (NP-PO_4) sulfosuccinate Na
26. Di (NP-10) sulfosuccinate Na
27. Di cyclohexyl sulfosuccinate Na (Aerosol A-196)

NMR

1. NP-5 sulfo acetate Na
2. Di octyl sulfosuccinate Na

1-19. Sulphate

IR

1,200～1,250cm^{-1}	ν S=O,	strong, broad,	Ester sulfonate
1,210～1,240cm^{-1}	ν S=O,	strong, broad,	Sulphate
1,200cm^{-1}	ν S=O,	strong, broad,	Alkyl sulfonate

In case Sulphate that contains Phenyl group, the peak (ν S=O) observed in more high wave number (～20cm^{-1}) area.

1. K Lauryl sulphate
2. NH_4 Lauryl sulphate
3. LL-3 sulphate Na
4. LL-5 sulphate Na
5. Dil_{115}-3 sulphate Na (NLES)
6. Oxl-3 sulphate Na
7. ML-3 sulphate NH_4
8. ML-3 sulphate TEA
9. K oleyl sulphate
10. Ca oleyl sulphate
11. OL-5 sulphate Na
12. OL-8 sulphate Na
13. NP-3 sulphate NH_4
14. NP-5 sulphate Na
15. NP-5 sulphate NH_4 (Urea contained)

16. NP-10 sulphate Na
17. TSP-120 sulphate Na
18. TSP-150 sulphate Na
19. TSP-200 sulphate Na
20.
21. Oleic acid sulphate Na
22. Spermaceti sulphate Na
23. Sulphated Tall oil methyl ester Na
24. Pluronic sulphate Na (EO 10%, PO 90%, mw 2,220, EO-PO-EO)

NMR

1. NP-6.3 sulfate NH_4

1-20. Phosphate

IR

In case Surfactant, characteristic $\nu_{P=O}$ was not observed generally. Observed main peak will be shown as original product before Phosphation.

1. 1/2 LL-5 phosphate Ca
2. 1/3 LL-5 phosphate K
3. 1/3 LL-20 phosphate Na
4. 1/2 mono NP-4 phosphate TEA
5.
6. 1/3 LP cholin
7. Sof-3 phosphate K

NMR

1. TSP-EO Phosphate TEA (SK-33SC)

2. Cationic Surfactant

2-111. Short chain Tetra Alkyl

IR

In case short chain Tetra alkyl quaternary compound show different shift based on Counter Ions.

Counter Ion	Wave number cm^{-1}	Peak	Others
Cl^-	950		
ClO_4^-	1,090		
	620	Sharp	
NO_3^-	1,760		
	1,380		
	830	Sharp	
HSO_4^-	1,200		
	1,050, 1080	Doublet	
CH_3-ph-SO_3^-	1,200		Peak will shift to lower
	1,010, 1040	Doublet	wave number than HSO_4^-
	810		
	690		
	570		
CH_3CH_2-SO_4^-	1,230		Peak will shift to higher
	1,030	Doublet	wave number than HSO_4^-
	920	Doublet	
	760		

$(Bu)_4N^+X^-$, $RN^+(CH_3)X^-$ does not show any shift based on Counter Ions.

1. Tetra methyl ammonium chloride
2. Tetra methyl ammonium nitrate
3. Tetra methyl ammonium tosylate
4. Tetra methyl ammonium hydrogen sulphate
5. Tri ethyl methyl ammonium salt
6. Tri ethyl methyl ammonium tosylate
7. Tetra ethyl ammonium ethylsulphate
8.
9. Tetra butyl ammonium chloride
10. Tetra butyl ammonium bromide
11. Tetra butyl ammonium iodide
12. Tetra butyl ammonium hydrogen sulphate
13. Lauryl tri methyl ammonium chloride
14. Lauryl di methyl ethyl ammonium bromide
15. Cetyl tri methyl ammonium bromide
16. Stearyl tri methyl ammonium chloride
17. Stearyl di methyl ethyl ammonium ethylsulphate

18. Tri octyl methyl ammonium chloride
19. Tri octyl methyl ammonium salt
20. Di lauryl di methyl ammonium chloride
21. Lauryl tri methyl ammonium mono chloroacetate

NMR

1. Tetra butyl ammonium bromide
2. Lauryl tri methyl ammonium chloride

2-112. Alkyl aryl

IR

700～800cm^{-1} γ CH characteristic for containing Benzyl group more Benzyl group split the peak to Triple, Quartet. When Alkyl group become longer, γ CH will move to 700cm^{-1}.

1. Tri ethyl benzyl ammonium chloride
2. Tri ethyl benzyl ammonium bromide
3. Tri butyl benzyl ammonium chloride
4. Lauryl di methyl benzyl ammonium nitrate
5. Cetyl di methyl benzyl ammonium chloride
6. Di benzyl di methyl ammonium chloride
7. TMPDA/Benzyl chloride quaternized
8. Lauryl di benzyl hydroxyethyl ammonium chloride

NMR

1. Octyl di methyl benzyl ammonium chloride

2-113. Hydroxy ethyl

IR

1. Lauryl di methyl hydroxyethyl ammonium perchlorate
2. Lauryl di methyl hydroxyethyl ammonium nitrate
3. Lauryl di methyl hydroxyethyl ammonium salt
4. Lauryl di methyl hydroxyethyl ammonium DBS
5. Di lauryl methyl hydroxyethyl ammonium salt (D12M·EO·DBS)
6. Di lauryl methyl hydroxyethyl ammonium salt (L_2NCH_3·EO·ClO_4)
7.

8.

9. Lauryl di hydroxyethyl methyl ammonium chloride
10. Lauryl di hydroxyethyl methyl ammonium perchlorate
11. Lauryl ethyl di hydroxyethyl ammonium bromide
12. Lauryl tri hydroxyethyl ammonium perchlorate
13. Bis (poly (10) ethoxylated) lauryl methyl ammonium chloride
14. Octyl thioethyl di methyl hydroxyethyl ammonium chloride
15. Tri butyl hydroxyethyl ammonium perchlorate

NMR

1. Bis (hydoxyethyl) lauryl dimethyl ammonium chloride

2-121. Pyridine

IR

3,000cm^{-1} ν_{CH} hetero ring absorbed in 3,000cm^{-1}, compare with Aliphatic compound, shift move to high wave number side (100～200cm^{-1})

1,210cm^{-1} ν_{CH} as same as normal aromatic ring, absorbed in 1,600 to 1,200cm^{-1}.

1,170cm^{-1}

770cm^{-1} γ_{CH} very characteristic

620cm^{-1} γ_{CH} very characteristic

1. Benzyl pyridinium chloride
2. Butyl pyridinium bromide
3. Lauryl pyridinium chloride
4.
5. N-methyl piperazine salt

2-122. Morpholine

IR

1,110～1,130cm^{-1} $\nu_{C=O}$, doublet

(970cm^{-1}) γ CH

920～930cm^{-1} γ CH

890～900cm^{-1} γ CH

850cm^{-1} γ CH

Compare with Pyridine derivative, γ_{CH} will be move to high wave number side (900cm^{-1}).

1. Lauryl methyl morpholinium bromide
2. Lauryl ethyl morpholinium ethylsulphate
3. Di methyl morpholinium salt
4. Lauryl hydroxyethyl morpholinium perchlorate

2-123. Imidazoline

IR

1. 1-hydroxyethyl 2-lauryl imidazolin・methyl mono chloroacetate quaternized.
2. 1-hydroxyethyl 2-oleyl imidazoline・di ethyl sulphate quaternized

2-124. Oxazoline

2-213. Others.

IR

1. DMAP-LD・CH_3Cl quaternized
2. DMAP-SD-EO$^+H_2PO_4^-$

2-22. Quaternary Phosphonium Compound.

IR

1. Cetyl tri butyl phosphonium bromide
2. Tri phenyl butyl phosphonium bromide

3. Betain

IR

1. Octyl di methyl betain
2. Lauryl di methyl betain
3.
4.
5. 1-hydroxyethyl 2-lauryl imidazolinium betain
6.
7.
8.
9. DMAP-LD hydroxy sulfo betain

4. Nonionic Surfactant

4-11. Alkoxylated Silicone

IR

Beside typical peak such as normal Nonionic surfactant,

844 cm^{-1}, $\nu_{si\text{-}o}$, sharp, middle strong peak, very stable.

1. Ethoxylated silicone (SK-48S, PEG, LL-10)
2. Ethoxylated silicone (DS-5211)
3. Ethoxylated silicone (OFX5211)
4. Alkoxylated silicone (Silwet 806)
5. Ethoxylated silicone (XF)

NMR

TMS as internal standard was not contained.

1. Ethoxylated silicone (SK-48S, PEG, LL-10)
2. Ethoxylated silicone (DS-5211)
3. Ethoxylated silicone (OFX5211)
4. Alkoxylated silicone (Silwet 806)
5. Ethoxylated silicone (XF)

4-12. Alcoxylated Modified Phenol

IR, Styrene

700cm^{-1}, sharp, middle strong peak, very stable.

1. Alcoxylated Styrylphenol (TSP-EO/PO-EO, CP-80)
2. Ethoxylated styrylphenol (TSP-EO, TSP-150)
3. Ethoxylated styrylphenol formalin condensate (TSPFR-100)

NMR, Styrene

CH_3 of PO, CH_3 and CH of Styrylphenyl, CH_2 of Benzylphenyl are clearly distinct.

1. Ethoxylated Styrylphenol (TSP-EO, TSP-50)
2. Alcoxylated Styrylphenol (TSP-EO/PO-EO, CP-80)
3. Ethoxylated styrylphenol formalin condensate (TSPFR-100)
4. Alcoxylated Benzylphenol (TBP-10-120)

IR, Alkylphenol (Nonyl, Octyl)

1. Ethoxylated nonylphenol
2. Ethoxylated octylphenol (585cm^{-1}, triplet)
3. Ethoxylated octylphenol formalin condensate

NMR, Alkylphenol (Nonyl, Octyl)

Nonyl and Octyl group were clearly distinct, and it looks rather special.

1. Ethoxylated nonylphenol (NP-5)
2. Ethoxylated octylphenol (OP-8)
3. Ethoxylated octylphenol formalin condensate (OPFR-150)

4-13. Alkoxylated Aliphatic alcohol

IR

720cm^{-1}, little broad, weak, more than C_6 chain.

1. Ethoxylated higher alcohol (TDL-3)
2. Ethoxylated higher alcohol (LL-10)
3. Ethoxylated higher alcohol (OL-4)

NMR

Alkyl group of its different origin, branched situation was very clearly distinct.

1. Ethoxylated higher alcohol (TDL-3)
2. Ethoxylated higher alcohol (LL-10)
3. Ethoxylated higher alcohol (OL-4)

4-14. *Ester type Nonionic surfactant*

IR

1,735～1740cm^{-1}, $\nu_{C=O}$, very strong

1. Ethoxylated higher fatty acid (OA-13)
2. Ethoxylated castor oil (COG-12)
3. Poly oxyethylene sorbitan mono oleate (SMO-20)
4. Poly oxyethylene sorbitan tri oleate (STO-20)

NMR

1. Ethoxylated higher fatty acid (OA-13)
2. Ethoxylated castor oil (COG-12)
3. Poly oxyethylene sorbitan mono oleate (SMO-10)

4. Poly oxyethylene sorbitan tri oleate (STO-75)