

Appendix C. Properties of Surfactants

Table C.1a Compositions of Natural Triglycerides (shorter chain)

from Hilditch and Williams [ref list]

Material	Percent Distribution of Acid Components									
	Acid Chain Length ^a -->	8	10	12	14	16	18	20	18	18
Double Bonds -->	0	0	0	0	0	0	0	0	1	2
coconut oil	8	7	46	15	9	2	-	6	1	
palm kernel oil	3	5	47	15	7	2	-	14	1	
beef tallow	-	-	-	5	28	21	-	40	3	
mutton tallow	-	-	-	2	25	27	-	41	4	
olive oil	-	-	-	0.4	18	0	-	68	12	
peanut (ground nut) oil	-	-	-	-	6	3	6	60	25	
cottonseed oil	-	-	-	-	20	2	-	24	50	
sunflower oil	-	-	-	-	6	2	-	25	66	

a -- common names are caprylic, capric, lauric, myristic, palmitic, stearic, arachidic, oleic, and linoleic, respectively.

Table C.1b Compositions of Natural Triglycerides (longer chain)

from Linfield [ref list], page 90.

Material	Percent Distribution of Acid Components							
	Acid Chain Length ^a -->	14	16	18	18	18	18	22
Double Bonds -->	0	0	0	1	1	2	3	1
lard	1	26	11	49	-	12	1	-
soybean oil	-	11	4	25	-	50	8	-
corn oil	-	12	2	27	-	57	1	-
castor oil	-	-	-	8	88	4	-	-
rapeseed oil	-	3	2	32	-	19	1	24
mustard seed oil	-	-	-	32	-	18	3	42

a -- common names are myristic, palmitic, stearic, oleic, ricinoleic, linoleic, linolenic, and euricic, respectively.

Table C.2 Area Covered by Adsorbed Surfactant

Surfactant	M g/mol	z_n m ² /mmol	A_f	Ref.
sodium dodecanoate	222	2	277	b
sodium perfluoro-octanate	488	2	319	b
sodium dodecyl sulfonate	272	2	391	b
sodium dodecylbenzene sulfonate	348	2	301	b
sodium dodecyl sulfate	288	2	379	b
sodium salt of highly branched alcohol sulfate (Tergitol 4)	292	2	813	a
ethoxylated octyl phenol (\approx 9 EtO's) (Triton X-100)	577	1	313	a
octaethoxylated nonylphenol	556	1	482	b
octaethoxylated nonylphenol phosphate	653	1	361	b
octadecyl trimethylammonium bromide	392	1	385	b
trimethylamino dodecanoate	257	1	397	b
sodium salt of di-2-ethylhexyl sulfosuccinate (Aerosol OT)	444	2	927	a
sodium salt of di-hexyl sulfosuccinate (Aerosol MA)	388	2	711	a
ethylene oxide condensate of dodecyl mercaptan (Nonic 218)	562	1	320	a

a -- Osipow [ref list] page 280

b -- Rosen [ref list] pages 62-69 lists many more.

Table C.3 HLB Contributions from Structural Features

from Davies [ref list]

Group	HLB Contribution
STARTING VALUE for the summation	7.0
HYDROPHILIC GROUPS	
R(CO)OH (acid)	2.1
R(CO)OK (potassium salt of acid)	21.1
R(CO)ONa (sodium salt of acid)	19.1
RSO ₄ Na (sodium salt of sulfate)	38.7
RSO ₃ H (sulfonic acid)	11.0
R(NR')R'' (tertiary amine)	9.4
ROR' (ether)	1.3
ROH (alcohol)	1.9
R(CO)OR' (ester)	2.4
SoOH (sorbitan ring alcohol)	0.5
SoO(CO)R (sorbitan ring ester)	6.8
-CH ₂ CH ₂ O- (ethoxy link)	0.33
HYDROPHOBIC GROUPS	
-CH ₂ - (methylene link)	-0.475
-CH ₃ (methyl group)	-0.475
-CH=(CH)- (ethylene link)	-0.475
-CH ₂ CH(CH ₃)O- (propoxy link)	-0.15
R(CR')R'' (branch in chain)	-0.475

Table C.4 Enthalpy and Entropy of Micelle Formation in Water near 298K

Surfactant	M g/mol	ΔH_{mic} kJ/mol	ΔS_{mic} J/(mol K)	Ref.
methyl(α -dimethylamino)tetradecanoate				
	285.46	2.3	97	b
hexa(ethoxy) decanol	350.61	15.1	142	a
hexa(ethoxy) dodecanol	78.66	-3.6	44	b
dodecyl dimethyl phosphite	246.36	8.3	127	b
decyl methyl sulfite	204.39	3.0	106	b
dodecyl pyridinium bromide	328.28	-4.06	57	a
sodium dodecyl sulfate	288.38	2.51	82	b
N,N-dimethyl dodecylamine oxide	229.40	7.1	110	b

a -- Hiemenz [ref list], page 445

b -- Rosen [ref list], pages 116-117 lists more compounds.

Table C.5 Theta Temperatures of Polymer Chains

from Napper [ref list], pages 116-117. See also Barton [ref list] page 275.

Repeat Unit	Vehicle	Salt	C _{salt} mol/m ³	Θ K
-CH ₂ CH ₂ O-	water	MgSO ₄	390	315 _u
-CH ₂ (CHOH)-	water	NaCl	2000	300 _u
-CH ₂ (CHCOOH)-	water	HCl	200	287 _l
-CH ₂ (CHCONH ₂)-	water	(NH ₄) ₂ SO ₄	2100	290 _l
-CH ₂ (CHC ₆ H ₅)-	cyclopentane	-	-	293 _l
ditto	ditto	-	-	427 _u
-CH ₂ (CCH ₃ C ₆ H ₅)-	n-butyl chloride	-	-	263 _l
ditto	ditto	-	-	412 _u
-CH ₂ CH ₂ CH(CH ₃)-	2-methylbutane	-	-	325 _u
-O[Si(CH ₃) ₂]-	n-heptane/ethanol	-	-	340 _l

Repeat units are poly(ethylene oxide), poly(vinyl alcohol), poly(acrylic acid), poly(acrylamide), poly(styrene), poly α-methyl styrene, poly(isobutylene), and poly(dimethylsiloxane) respectively.

u = upper flocculation temperature

l = lower flocculation temperature

Table C.6 Critical Micelle Concentration, Aggregation Number in water near 298K

Surfactant	M g/mol ³	C _{NaCl} mol/m ³	CMC mol/m ³	Agg. No.	Ref.
sodium dodecyl sulfate	288.38	100	1.39	112	a
dodecylamine hydrochloride	221.81	15.7	10.4	93	a
dodecyl trimethylammonium bromide	308.34	13	10.7	56	a
hexa(ethoxy)dodecanol	350.61	0	0.05	400	b

a -- Hiementz [ref list], page 432.

b -- Rosen [ref list], page 90.

Rosen [ref list], pages 90-99 and Mukerjee and Mysels [ref list] list more.

C.1 Selecting Surfactants for Testing

The procedures and data required to design and operate a distillation tower or a reaction synthesis are (for many compounds) readily available. The procedures and data required to design a process to disperse a specific solid in a specific vehicle are NOT so available. There are thousands of surfactants that might be tried, and there are many criteria beyond adsorption and repulsion to constrain the selection.

All too often manufacturers claim so many applications for their surfactants that cross-indexing by claimed application is of little help in selecting candidates for testing. At the same time so little fundamental information is provided that we have no basis for computing surfactant compatibility or dose and thus cannot predict which surfactant would be suitable for an application beyond their claims.

The following two pages are intended to help you chart a path toward identifying those surfactants that are most likely to succeed in dispersing a particular solid in a particular liquid with typical constraints. You may add specific surfactants (columns), and information or constraints (rows) to suit your particular needs.

1. Make a copy of the table and use a yellow highlighting marker to draw a horizontal line through each criterion row that fits the intended application.
2. Circle any surfactant classes (top row) that have all Y's (and the desired sign for surfactant charge) in the marked lines. If no surfactant classes have been circled, circle those that have the most Y's and no N's.
3. Read the detailed discussions of each class circled to see if there are any problems that would eliminate that class from further consideration.
4. For each selected class, refer to a comprehensive listing of surfactants (McCutcheons\dag, Ashe and Ashe\dag) and gather further information to help you predict surfactant CMC and tail group solubility in the liquid, adsorption on the solid, repulsion of the coated particles, and the effects of impurities or additives. Use this information to select the specific commercial surfactants to be tested.
5. Refer to Chapter 7 for tests to aid in making the final selection.

Table C.7 Nonionic and Cationic Class Characteristics

class --->	Al	Fa	Fe	Gr	Ge	Ao	Ag	Aa	Pm	So	Pp	Fc	Si	An	Qa	Im	Da
CHARGE OF SURFACTANT IN WATER																	
low pH	0	0	0	0	0	0	0	0	0	0	0	0	0	+	+	+	+
mid pH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	+	Z	+
high pH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	.	-	0
SOLUBILITY OF SURFACTANT IN LIQUID																	
acid water	Y	Y	Y	Y	.	.	Y	.	.	.	Y	.	Y	Y	Y	.	N
base water	Y	Y	Y	Y	.	.	Y	.	.	.	Y	.	Y	N	Y	.	Y
H-b org	.	.	Y	Y	Y
polar	Y	.	Y	Y	Y
nonpolar	Y	.	Y	Y	.	Y	.	.	.	Y	Y	Y	Y
fluoroc	Y
DISPERSING AGENT FOR PARTICLE (SURFACE)																	
metal	.	Y	Y	Y	.	.	.
carbon	Y	.	.	Y
salt	Y	Y	.	.
oxide/h	.	Y	Y	Y	.	.	.	Y	Y	.
H-b org	Y	.	Y	Y	Y	Y
protein	Y	.	Y	Y
polar	Y	Y	.	.	.	Y	.	.	.	Y	.	Y
nonpola	Y	Y	.	Y	Y	.	Y
fluoroc	Y
STABILITY AND BEHAVIOR																	
high IS OK	Y	Y	.
di cat OK	Y	.	.	Y
foams	.	N	.	N	.	.	N	Y	N	Y
STABLE TOWARD																	
biodeg	N	N	.	.	.	Y	.	.	.	N	.	Y	.	.	Y	.	.
oxidatio	.	N	N	.	.	Y
reduction	Y
hot acid	.	Y	N	.	.	.	N	.	N	.	.	Y	.	.	.	Y	.
warm acid	.	Y	N	.	N	.	.	Y	.	Y	.	Y	.
cold acid	.	Y	N	.	N	.	.	Y	.	Y	.	Y	.
cold base	Y	Y	Y	Y	.	.	Y	.	.	N	Y	.
warm base	Y	Y	Y	Y	.	.	Y	.	.	N	Y	.
hot base	Y	Y	N	Y	Y	.	.	Y	.	.	N	Y	.

Table C.8 Anionic Class Characteristics

chemical class -->	Sf	Sd	To	Ab	Is	Ss	Ta	As	St	Ap	Ip	Ai	Pl
CHARGE OF SURFACTANT IN WATER													
low pH	0	--	+	.
mid pH	-	--	--	--	--	--	--	--	--	--	--	Z	--
high pH	-	--	--	--	--	--	--	--	--	--	--	--	--
SOLUBILITY OF SURFACTANT IN LIQUID													
acid water	Y	Y	Y	Y	Y	Y	Y	.	.	Y	Y	Y	Y
base water	N	Y	Y	Y	Y	Y	N	.	.	Y	Y	N	Y
H-b org	Y
polar	Y
nonpolar	Y
fluoroc	.	Y	.	.	Y	.	Y
DISPERSING AGENT FOR PARTICLE (SURFACE)													
metal	Y
carbon
salt
oxide/h	.	.	.	Y	Y	.	.
H-b org	Y	.	.	Y	Y	Y
proteins	.	.	Y	Y	.	.	Y	Y	Y
polar	.	.	.	Y	Y	.	Y	Y	Y	Y	.	Y	Y
nonpolar	.	.	.	Y	Y	.	Y	Y	.	Y	.	.	.
fluoroc
STABILITY AND BEHAVIOR													
high IS OK	N	.	.	Y	.	.	Y	.	.	Y	.	Y	.
di cat OK	N	Y	Y	Y	Y	.	Y	.	.	Y	N	.	.
foams	Y	Y	.	Y	Y	Y	Y	Y	N	N	.	.	.
STABLE TOWARD													
biodeg	.	.	.	N	.	.	.	N	N	.	.	Y	.
oxidation
reduction
hot acid	.	.	.	Y	.	.	Y	N	N	.	N	.	.
warm acid	.	.	.	Y	.	N	Y	.	.	.	N	Y	.
cold acid	.	.	.	Y	.	.	Y	Y	.	.	N	Y	.
cold base	.	.	.	Y	.	.	Y	Y	.	Y	Y	Y	.
warm base	.	.	.	Y	.	.	Y	Y	.	Y	Y	Y	.
hot base	.	.	.	Y	N	N	Y	Y	N	Y	Y	.	.

ABBREVIATIONS for Table C.7 and C.8

. = no information on this item
Aa = alkanolamides
Ab = alkylbenzene sulfonates (LAS, SAS, AOS)
Ag = acetylenic glycols
Ai = amino and imino acids
Al = fatty alcohols
An = alkyl amines
Ao = alkyl phenols
Ap = alcohol phosphates
As = alcohol sulfates
biodeg = biodegradation
Da = dialkylamine oxides
di cat OK = works in presence of moderate concentrations of divalent cations

Fa = fatty acids
Fc = fluorocarbons
Fe = fatty esters
fluoroc = fluorocarbons
foams = high foaming tendency in water
Ge = glycol esters
Gr = glycerol esters
H-b org = hydrogen-bonding organics
high IS = works in high ionic strength solutions

Im = imidazolines
Ip = inorganic phosphates
Is = isethionates
N = no
nonpolar = nonpolar organics
oxide/h = metal oxides or hydroxides
Pl = phospholipids
Pm = PEO mercaptans
polar = polar organics
Qa = quaternary amines

Sd = sarcosine derivatives
Sf = salts of fatty acids
Si = siloxanes
So = sorbitol derivatives
Ss = sulfosuccinates
St = sulfated triglycerides
Ta = taurates
To = salts of tall oil acids
Y = yes
Z = zwitterionic