

Lysine-Based Silicone Surfactants

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Supporting information

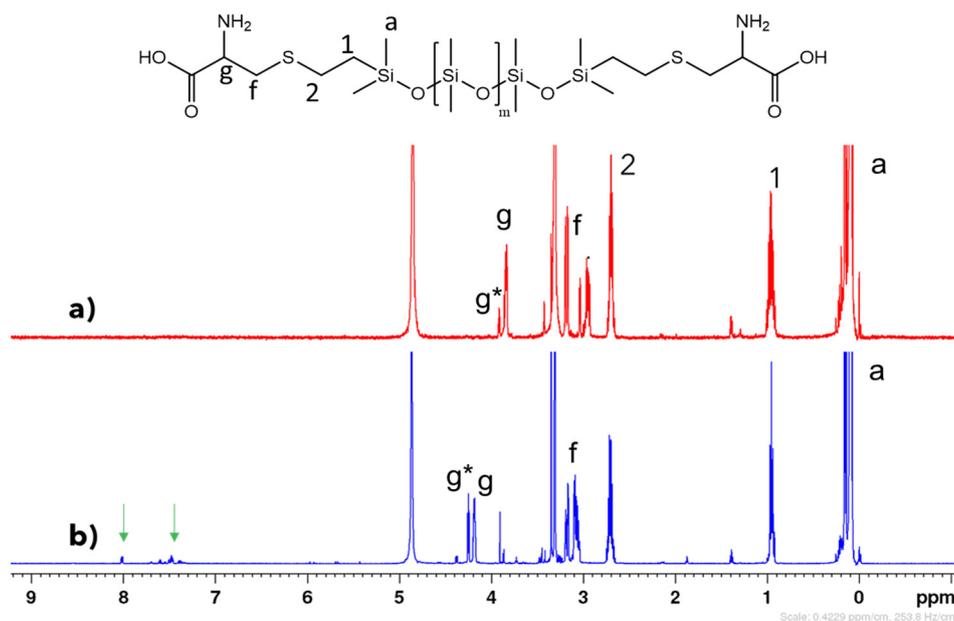


Figure S1. ¹H NMR spectrum of CYS10 a) after and b) before purification by dialysis. It can be seen that in the spectrum a) the shifts between 8 and 7 ppm that correspond to the catalyst of DMPA have been removed after dialysis purification. Moreover, it is possible to observe that the signal g exhibited a shift after purification due to the absence of hydrochloride in CYS10. On the other hand, the g*-signal was associated with the remaining L-cysteine hydrochloride and L-cysteine free of hydrochloride before and after purification respectively.

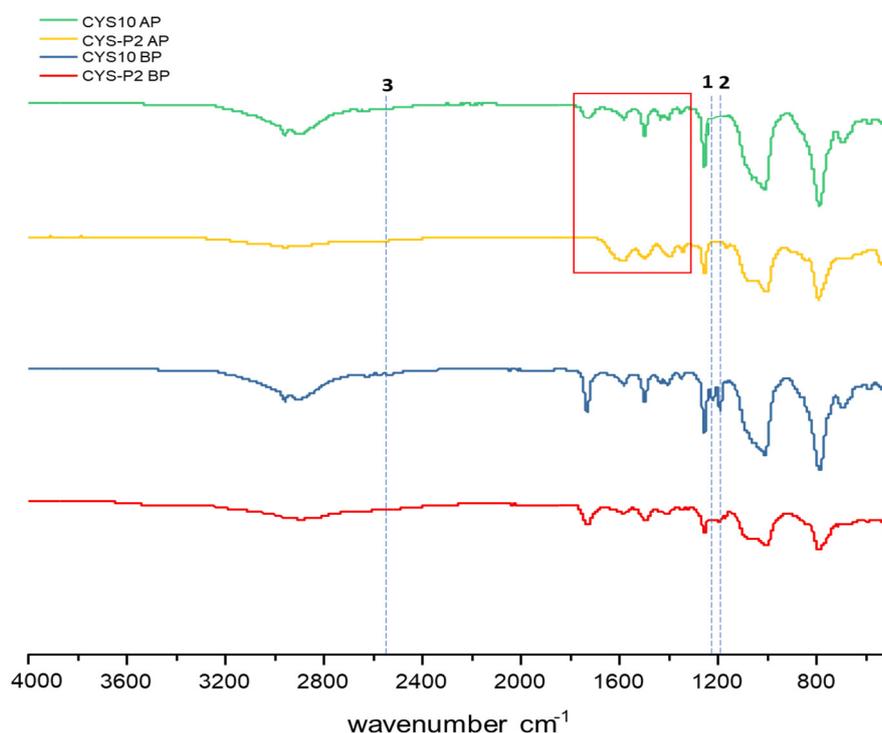


Figure S2. IR spectra of CYS10 and CYS-P2. It can be seen that the absorption bands 1 and 2 due to asymmetrical C-O-C stretching (1220 cm^{-1}) and symmetrical (1190 cm^{-1}) bands of DMPA disappear after dialysis purification for CYS10 and CYS-P2. Moreover, the absence of weak band 3 around 2550 and 2560 cm^{-1} in CYS10 AP and CYS-P2 AP associated with the S-H group of L-cysteine, is attributed to the successful coupling between L-cysteine and Vi10 and Vi2. The absorption peaks at 1614 , 1590 , and 1400 cm^{-1} were attributed to the stretching vibration of the COO^- group and NH_3^+ (red trace). In addition, the peaks at 1730 , 1260 , 1070 and 1015 , and 790 cm^{-1} were attributed to C=O, C-H symmetric bending in Si-CH₃, siloxane bond (Si-O-Si) and CH₃ rocking in Si-CH₃ respectively. BP (before purification); AP (after purification).

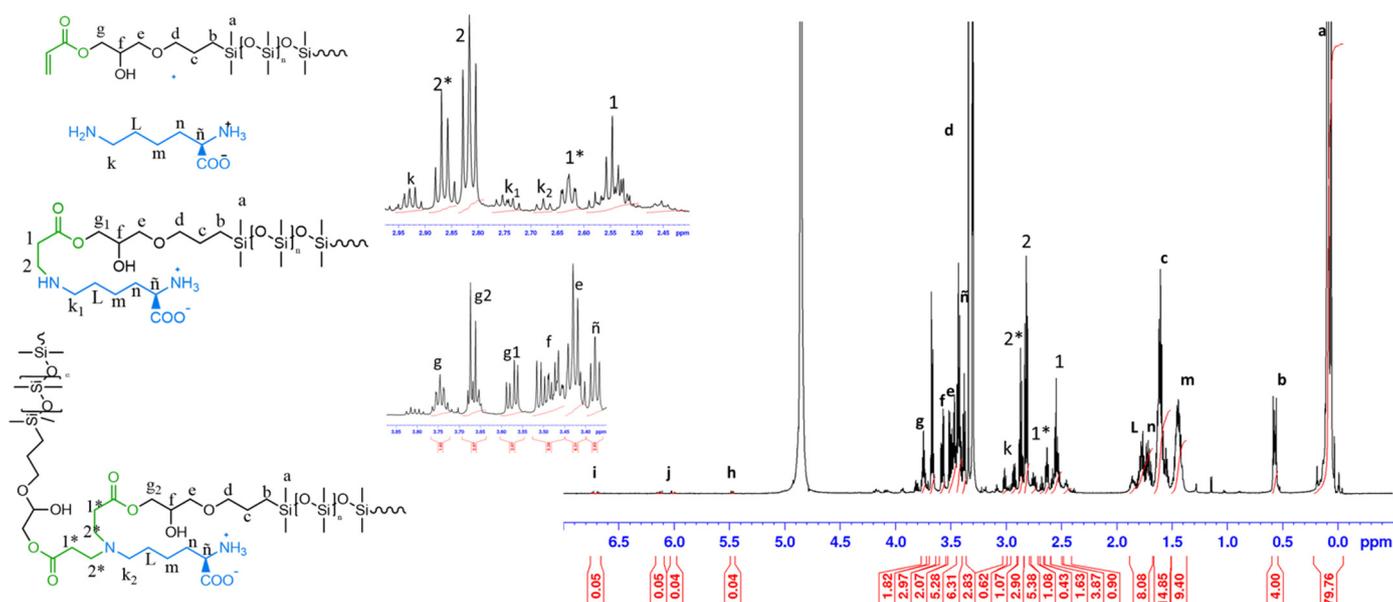


Figure S3. ^1H NMR spectrum of LYS10 (1:2). Trace of starting material acrylate are seen at i,j,h.

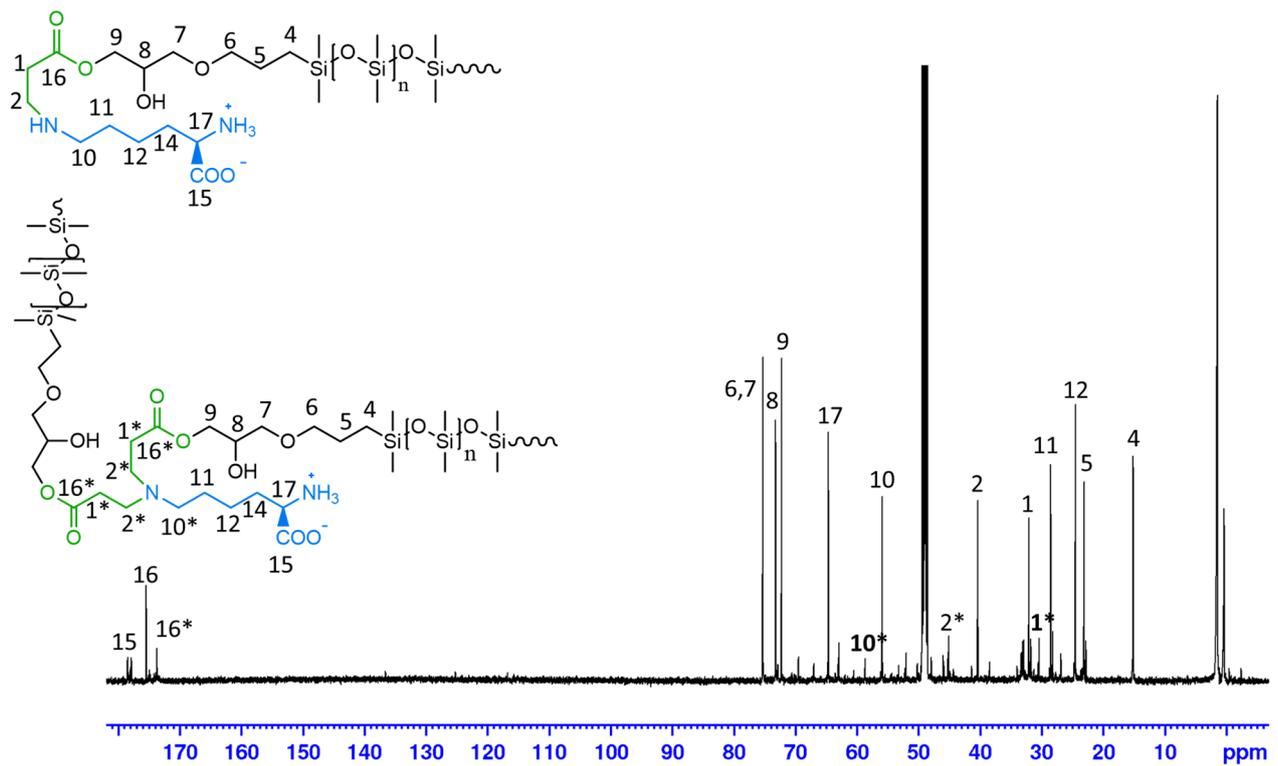


Figure S4. ^{13}C NMR spectrum of LYS10 (1:2).

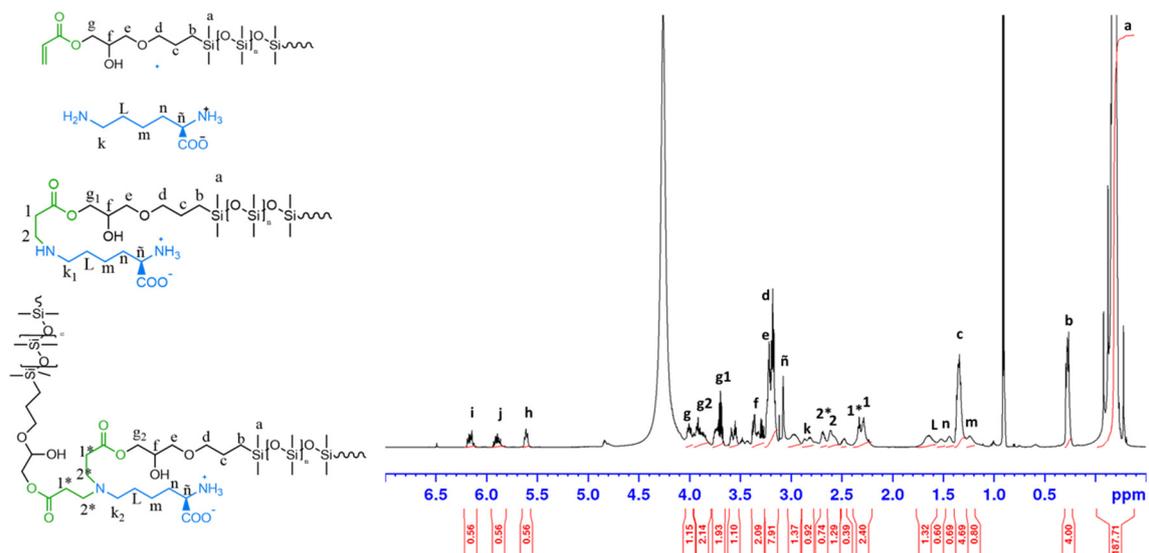


Figure S5. ^1H NMR spectrum of LYS50 (3:1). Trace of starting material acrylate are seen at i,j,h.

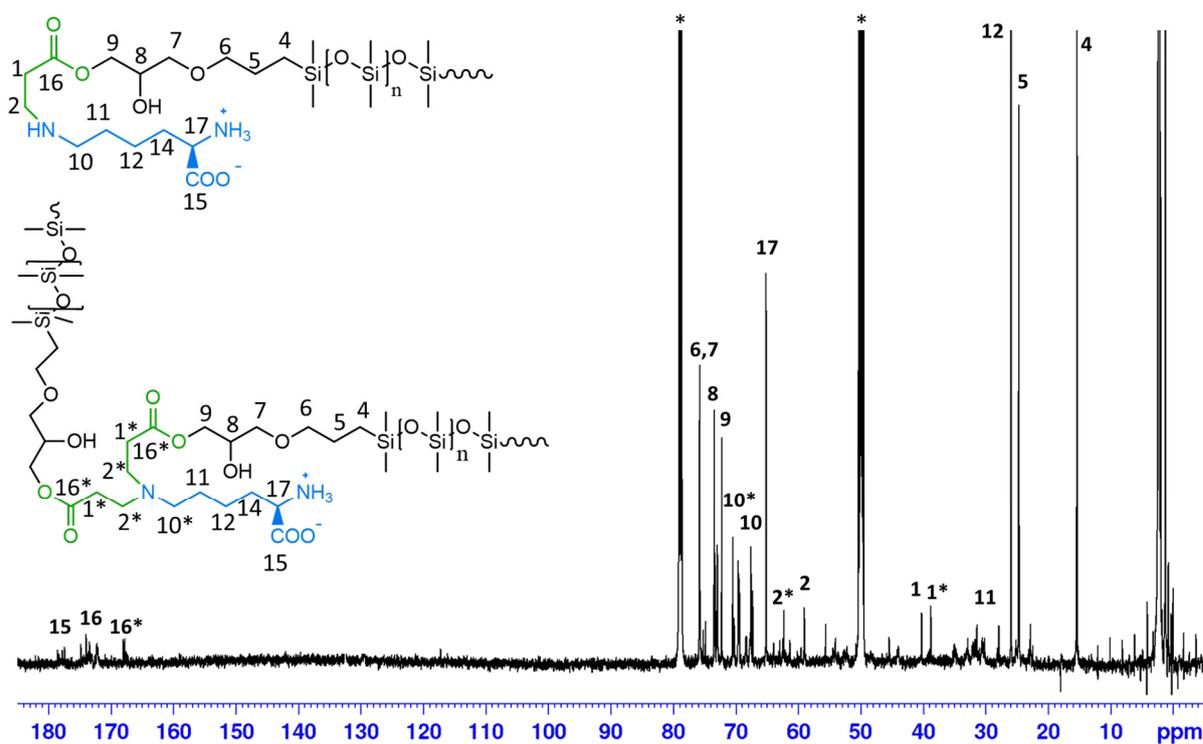


Figure S6. ^{13}C NMR spectrum of LYS25 (3:1).

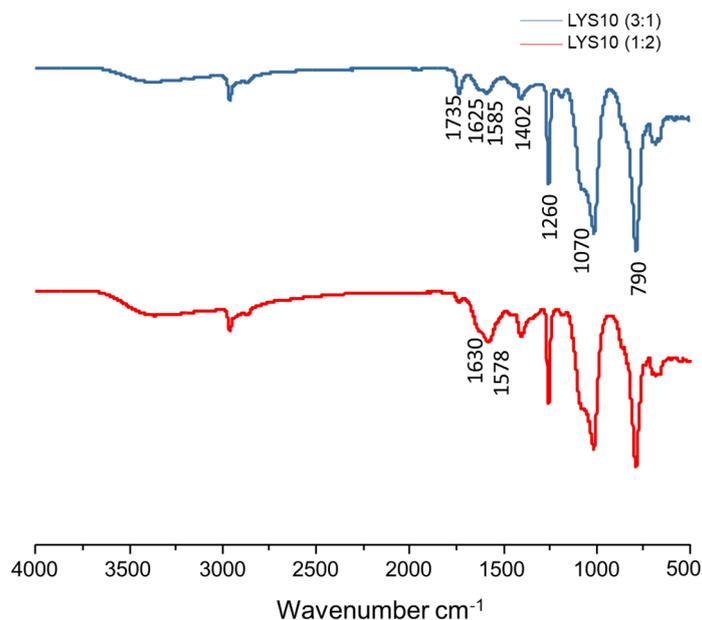


Figure S7. IR spectra of LYS10 at a) 3:1 and b) 1:2 molar ratio. The broad band in the region of 3700 at 3000 cm^{-1} is associated to stretching vibrations of the hydroxyl and amine group of LYS10. The absorption peaks of 1630, 125, 1578, 1585 and 1402 cm^{-1} was attributed to the stretching vibration of the COO^- group and NH_3^+ . In addition, the peaks at 1735, 1260, 1070 and 1015, and 790 cm^{-1} were attributed to $\text{C}=\text{O}$, $\text{C}-\text{H}$ symmetric bending in $\text{Si}-\text{CH}_3$, siloxane bond ($\text{Si}-\text{O}-\text{Si}$) and CH_3 rocking in $\text{Si}-\text{CH}_3$ respectively.

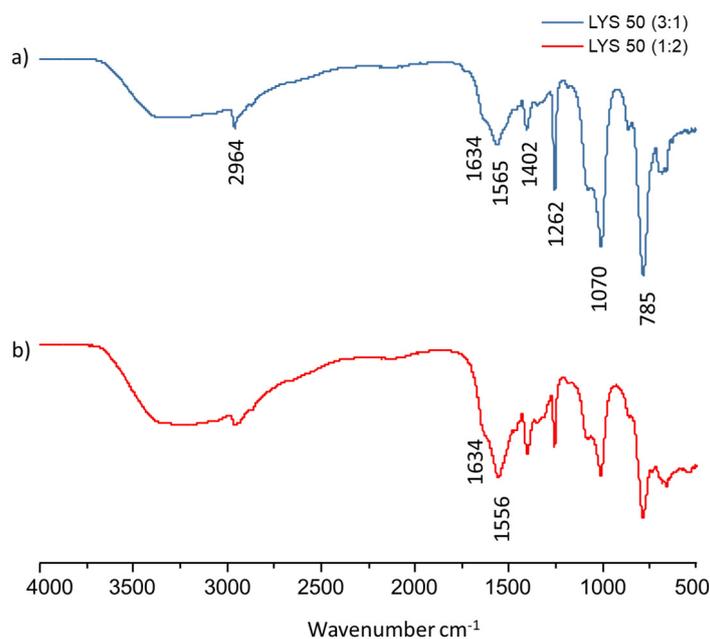


Figure S8. IR spectra of LYS50 at a) 3:1 and b) 1:2 molar ratio. The broad band in the region of 3700 at 3000 cm^{-1} is associated to stretching vibrations of the hydroxyl and amine group of LYS50. The absorption peaks of 1630, 125, 1578, 1585 and 1402 cm^{-1} were attributed to the stretching vibration of the COO^- group and NH_3^+ . In addition, the peaks at 1735, 1260, 1070 and 1015, and 790 cm^{-1} were attributed to $\text{C}=\text{O}$, C-H symmetric bending in Si-CH_3 , siloxane bond (Si-O-Si) and CH_3 rocking in Si-CH_3 respectively.

Table S1. Preparation quantities for surfactants.

Sample (molar ratio)	Silicone	g silicone (mmol C=C)	g amino acid (mmol)	Solvent (volume mL)	Product description
CYS10	DMS-V05	4 (5.66)	2.23 (14.2)	THF (20) ^a	White powder
CYS-P2	VDT-5035	2 (12.5)	2.95 (18.8)	MeOH:THF (1:3)	White powder
ARG10 (1:2)	Di10	0.25 (0.454)	0.160 (0.909)	$\text{H}_2\text{O}:\text{MeOH}:\text{EtOH}$ (1.5:3:20)	White solid
ARG10 (3:1)	Di10	1.50 (2.727)	0.160 (0.909)	$\text{H}_2\text{O}:\text{MeOH}:\text{EtOH}$ (1.5:3:30)	Viscous Liq ^b
LYS10 (1:2)	Di10	0.25 (0.454)	0.130 (0.889)	$\text{H}_2\text{O}:\text{MeOH}$ (0.25, 0.25)	Viscous Liq
LYS10 (3:1)	Di10	1.50 (2.727)	0.130 (0.889)	$\text{H}_2\text{O}:\text{MeOH}$ (0.25, 0.25)	Viscous Liq
LYS25 (1:2)	Di25	0.25 (0.227)	0.066 (0.454)	$\text{H}_2\text{O}:\text{IPA}$ (0.25, 0.25)	Viscous Liq
LYS25 (3:1)	Di25	1.50 (1.363)	0.066 (0.454)	$\text{H}_2\text{O}:\text{IPA}$ (0.25, 0.25)	Solid
LYS50 (1:2)	Di50	0.25 (0.125)	0.036 (0.250)	$\text{H}_2\text{O}:\text{IPA}$ (0.25, 0.25)	Semisolid
LYS50 (3:1)	Di50	1.50 (0.750)	0.036 (0.250)	$\text{H}_2\text{O}:\text{IPA}$ (0.25, 0.25)	Semisolid

^a Small amounts of MeOH were also added to obtain a transparent solution. ^b Liq = liquid.



Figure S9. Photographs of the amino acid/silicone surfactants prepared.

Table S2. Formation of emulsions.

D ₄ /water	100/0	90/10	80/20	70/30	60/40	50/50	40/60	30/70	20/80	10/90	0/100
LYS10 (1:2)											
5%	-	-	-	-	-	-	-	-	-	-	-
1%	-	P	P	P	P	P	P	P	P	P	-
0.5%	-	P	P	P	P	P	P	P	P	P	-
(3:1) 0.1%	-	P	P	P	P	P	P	P	P	P	-
LYS10 (3:1)											
5%	-	-	-	-	-	-	-	-	-	-	-
1%	-	P	P	P	P	P	P	P	P	P	-
0.5%	-	P	P	P	P	P	P	P	P	P	-
0.1%	-	P	P	P	P	P	P	P	P	P	-
LYS25 (1:2)											
5%	-	-	-	-	-	-	-	-	-	-	-
1%	-	P	P	P	P	P	P	P	E	E	-
0.5%	-	P	P	P	P	P	P	P	E	G	-
0.1%	-	P	P	P	P	P	P	P	P	G	-
LYS25 (3:1)											
5%	-	-	-	-	-	-	-	-	-	-	-
1%	-	P	P	P	P	P	P	P	E	E	-
0.5%	-	P	P	P	P	P	P	P	E	G	-
0.1%	-	P	P	P	P	P	P	P	G	G	-
LYS50 (1:2)											
5%	-	-	-	-	-	-	-	-	-	-	-
1%	-	P	P	P	P	P	P	P	E	G	-
0.5%	-	P	P	P	P	P	P	P	E	G	-
0.1%	-	P	P	P	P	P	P	P	E	G	-
LYS50 (3:1)											
5%	-	P	P	P	P	P	P	P	E	E	-
1%	P	P	P	P	P	P	P	P	E	E	-
0.5%	P	P	P	P	P	P	P	P	E	G	-
0.1%	P	P	P	P	P	P	P	P	G	E	-

These description refer to stability 'by eye' after an emulsion was obtained: - = no emulsion formed; P = phase separation began within 5 minutes; E=excellent stability (no observed phase separation for days); and G=slightly less stable than E samples. The **ARG10** (1:2) and (3:1) were evaluated using 1% at all D₄/H₂O, however, immediately after solvent removal the samples showed phase separation. The samples **CYST10-VT2** (1:2) and **LYS10** exhibited the same behavior.

Table S3. Droplet size after and before freeze/thaw (F/T) cycles temperature.

Emulsion		Before Stress	After F/T Cycle 1	After F/T Cycle 2	
LYS50 (10:90) ^{a)}	3:1	Size (nm)	Size (nm)	Size (nm)	
		1%	280.12 ± 6.08	306.57 ± 3.41	362.26 ± 8.93
		0.5%	217.16 ± 1.79	301.84 ± 4.17	394.22 ± 4.61
		245.23 ± 9.67	257.64 ± 6.87	284.68 ± 8.01	
LYS50 (10:90)	1:2	Size (nm)	Size (nm)	Size (nm)	
		1%	279.12 ± 0.84	304.81 ± 2.23	325.96 ± 4.02
		0.5%	315.23 ± 0.84	299.05 ± 5.07	364.77 ± 2.69
		288.56 ± 7.56	EB		
LYS25 (10:90)	3:1	229.23 ± 3.78	266.12 ± 1.34	248.12 ± 3.19	
		305.78 ± 4.76	302.02 ± 1.35	316.97 ± 1.49	
		367.12 ± 2.45	467.21 ± 3.45	435.68 ± 1.49	
LYS25 (10:90)	1:2	327.13 ± 8.56	378.23 ± 2.45	343.17 ± 3.42	
		358.5 ± 2.20	336.23 ± 9.55	346.54 ± 12.08	
		287 ± 5.43	EB ^{b)}	NE ^{c)}	
LYS50 (20:80)	3:1	216.8 ± 7.16	246.23 ± 7.34	319.34 ± 2.24	
		235.89 ± 9.47	289.23 ± 3.12	284.17 ± 2.81	
		267.78 ± 6.45	323.45 ± 4.67	367.73 ± 4.67	
LYS50 (20:80)	1:2,	392 ± 6.39	381.19 ± 18.62	484.61 ± 5.01	
		409.93 ± 14.77	413.59 ± 4.56	434.91 ± 7.34	
		323.41 ± 1.77	345.18 ± 7.56	EB	
LYS25 (20:80)	3:1	312.17 ± 7.66	479.26 ± 4.05	484.21 ± 6.22	
		341.56 ± 2.44	EB	NE	
		328.12 ± 3.54	EB	NE	
LYS25 (20:80)	1:2	311.85 ± 1.29	334 ± 1.29	320.43 ± 10.7	
		372.16 ± 6.49	EB	NE	
		281.92 ± 9.51	EB	NE	

a) The ratio refers to D₄:water. ^{b)} EB Emulsion broke into two distinct phases. ^{c)} NE No emulsion formed.

Table S4. Droplet size at different pHs.

pH	LYS50	LYS25	LYS50	LYS25
	(3:1, 1%, 10:90)	(3:1, 1%, 10:90)	(3:1, 1%, 20:80)	(3:1, 1%, 20:80)
	Size (nm)	Size (nm)	Size (nm)	Size (nm)
3	213.50 ± 5.9	571.78 ± 2.69	269.15 ± 2.71	452.67 ± 3.66
4	219.90 ± 4.56	390.02 ± 5.21	215.30±3.15	472.67 ± 8.57
5	254.30 ± 2.78	328.15 ± 4.71	208.60±2.25	439.11 ± 3.66
7	280.00± 3.41	409.93 ± 4.77	215.10±3.71	468.4 ± 4.60
8	307.45± 6.38	432.00 ± 7.63	215.10±3.71	455.48 ± 8.57
10	239.10± 6.78	383.41 ± 3.03	340.15 ± 3.25	483.27 ± 7.42

Table S5. Emulsion preparation using Lys50 (3:1) by high energy methods.

Surfactant	Emulsion (D ₄ :H ₂ O) ^a	Time (min)	Emulsion Formed
Lys50 (3:1) ^b	10:90	3	Yes
	20:80	3	Yes
	10:90	6	Yes
	20:80	6	Yes
	10:90	12	Yes
	20:80	12	Yes
Lys50 (3:1) ^c	10:90	5	Yes
	20:80	5	Yes
	10:90	30	Yes
	20:80	30	Yes

^a Emulsions formed in all cases based on visual observation. ^b Emulsion obtention by ultrasonication in continuous mode at 40% amplitude. ^c Emulsion obtained using an overhead mechanical stirrer with 3 blades at 1600 rpm.

HLB vs 3D-HLB

The hydrophilic-lipophilic balance (HLB system) is used to predict the emulsifying properties of hydrocarbon surfactants.¹

“HLB value as the molecular weight percent of the water-loving portion of the surfactant divided by 5. Experience showed that if a surfactant has an HLB = 1, it is very oil-soluble, however a surfactant with an HLB = 15 is water-soluble. Surfactants with an HLB = 1-3 may be used to mix unlike oils, that water-in-oil emulsions can form with surfactants that have an HLB = 4-6, that one can compatibilize small particles in oil using surfactants with HLB = 7-9, that surfactants with HLB = 7-10 may be used to form self-emulsifying oils, that blends of surfactants in the range HLB = 8-16 can be used to make oil-in-water emulsions, that detergent solutions require surfactants with HLB = 13-15 and that surfactant blends with HLB = 13-18 may be used to solubilize oils (and form microemulsions) in water. It is also very useful to know that for making oil-in-water emulsions, the combination of the oil and the suitable HLB value changes from HLB = 6 for vegetable oils, HLB = 8-12 for silicone oils, HLB = 10 for petroleum oils and HLB = 14-15 for fatty acids and alcohols.”¹

For HLB calculations, the mass fractions of hydrophilic or lipophilic constituents are separately considered. HLB cannot be directly applied to silicone surfactants, because silicones have unique solubility parameters that differ significantly from hydrocarbons.² For example, the silicone portion of a siloxane surfactant will be hydrophobic, but may not be lipophilic.³ Siloxane surfactants are better described by the 3D HLB system that takes into account the oil solubility, water solubility and silicone

solubility. The 3D HLB scale is represented on triangular coordinates, whereas the original (2D) HLB scale is linear.³ The 3D HLB system predicts six different structure types: w/o, o/w, silicone-in-water, water-in-silicone, silicone-in-oil, and oil-in-silicone.²

References

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- (3) Somasundaran, P.; Mehta, S. C.; Purohit, P. Silicone emulsions. *Advances in Colloid and Interface Science* **2006**, *128*, 103–109. DOI: 10.1016/j.cis.2006.11.023.