Synthesis of deuterated SB3-18

Preparation of *N*-(($^2H_{37}$-octadecyl)-*N,N*-dimethylamine

The preparation method for the production of this compound was adapted by Hazell *et al.*[1] from a process published by Menger *et al*.[2] Deuterated Bromooctadecane (0.5 g) was dissolved in ethanol, 2 mL and dimethylamine solution (5.6 M in ethanol), 2.4 ml, was added dropwise under N_2. This was then heated to 75 °C for 2 hours and allowed to cool. The solution was then dried under reduced pressure and NaOH, 1M 30mL, and hexane, 3 x 30ml, added to the resulting white solid. The phases were then separated, and the organic phase dried over $MgSO_4$. The resulting solution was then dried under reduced pressure to give 0.3154g (70 %) of *N*-(($^2H_{37}$-octadecyl)-*N,N*-dimethylamine. ^{1}H NMR (250Hz, $CDCl_3$) δ 2.21 (s, 6H, -CH_3), as reported by Hazell *et al.*[1]

Preparation of [2] 3-(dimethyl(octadecyl)ammonio)propane-1-sulfonate

Again this synthetic route was taken from Hazell *et al.*[1] who have modified it from Qu *et al.*[3] The product above, *N*-(($^2H_{37}$-octadecyl)-*N,N*-dimethylamine, (0.25g) was dissolved in acetone, (2.5 mL) and added dropwise to a solution of 1,3 propanesulfonate, (0.44 g), in acetone, (4 mL). This was heated to reflux for 18 hours and then allowed to cool prior to filtration of the white solid. This was then washed with acetone and recrystallized in an acetone/methanol mix prior to drying under high vacuum. 0.09g, (27 %) of 3-(dimethyl($^2H_{37}$-octadecyl)ammonio)propane-1-sulfonate was produced. ^{1}H NMR (500Hz, $CDCl_3$) δ3.72 (t, 2H, CH_2), δ3.14 (s, 6H, CH_3), δ 2.70 (t, 2H, CH_2), δ2.24 (m, 2H, CH_2), solvent peak at δ 2.17, acetone and δ 1.79, water

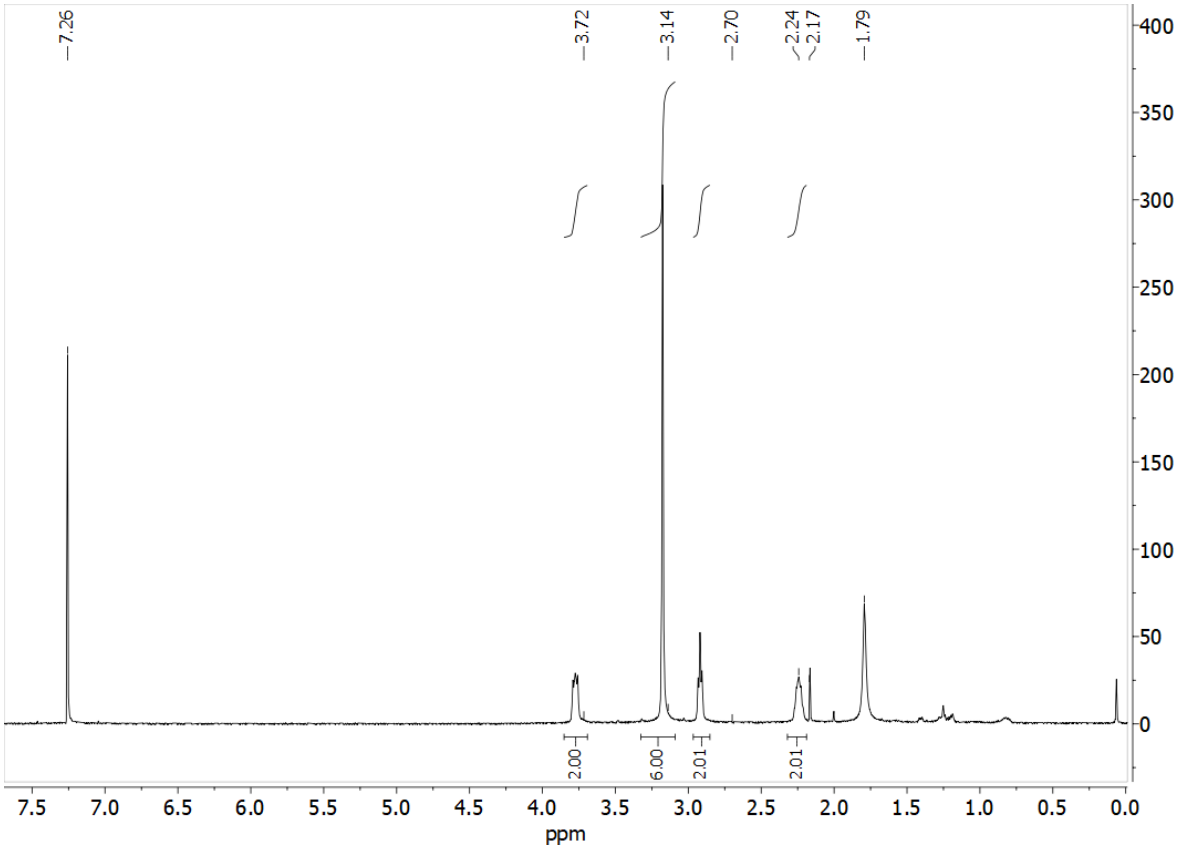

Figure 1: Proton NMR for deuterated SB3-18: 3-[dimethyl(($^2H_{37}$)-octadecyl)ammonio]propane-1-sulfonate

Pressure-Area isotherms for SB3-18: DMPC mixtures

Table 1: Physical parameters derived from pressure-area isotherms for mixtures of DMPC and SB3-18, error in areas is 5% from systematic errors in calibration and sample preparation. Errors in collapse point and compressional modulus were calculated from maximum and minimum values of repeats

Sample	Collapse Point mNm^{-1}	Collapse Area $Å^2$	Limiting area $Å^2$	Compression modulus $mN\ m^{-1}$
DMPC	45±1	45	77	115±4
3:1	44 ±3	39	70	100 ±3
1:1	43 ±2	37	66	93±3
1:3	41±5	33	61	78 ±1
SB3-18	37 ±2	35	69	57±4

Table 2: Excess APM and ΔG_{excess} values calculated from pressure-area isotherm data. [4]

Sample	$15mNm^{-1}$		$35mNm^{-1}$	
	Excess APM, $Å^2$/molecule	ΔG_{excess}, $kJmol^{-1}$	Excess APM, $Å^2$/molecule	ΔG_{excess}, $kJmol^{-1}$
DMPC	-	-	-	-
3:1	0	0	-1.35	-0.28
1:1	-3.6	-0.32	-0.5	-0.11
1:3	-4.1	-0.37	-1.45	-0.31
SB3-18	-	-	-	-

Peak positions from XRR data

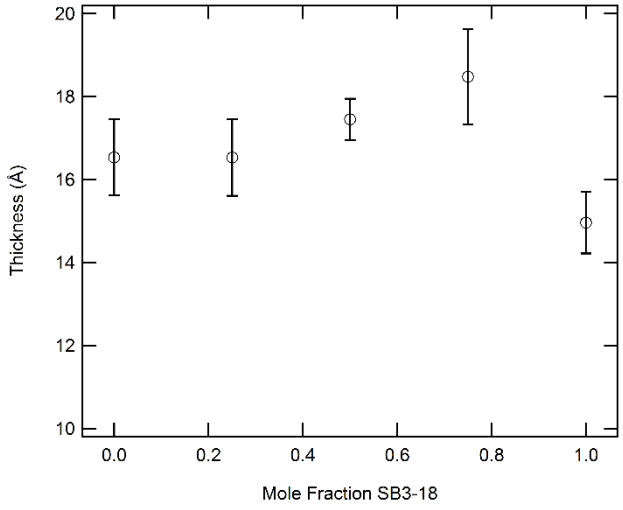

Figure 2: Thickness of the monolayers at 15 mNm^{-1}, extracted from the data in Fig. 4 in the main paper, errors are from determined variations in the minima.

Fitted Reflectivity Data

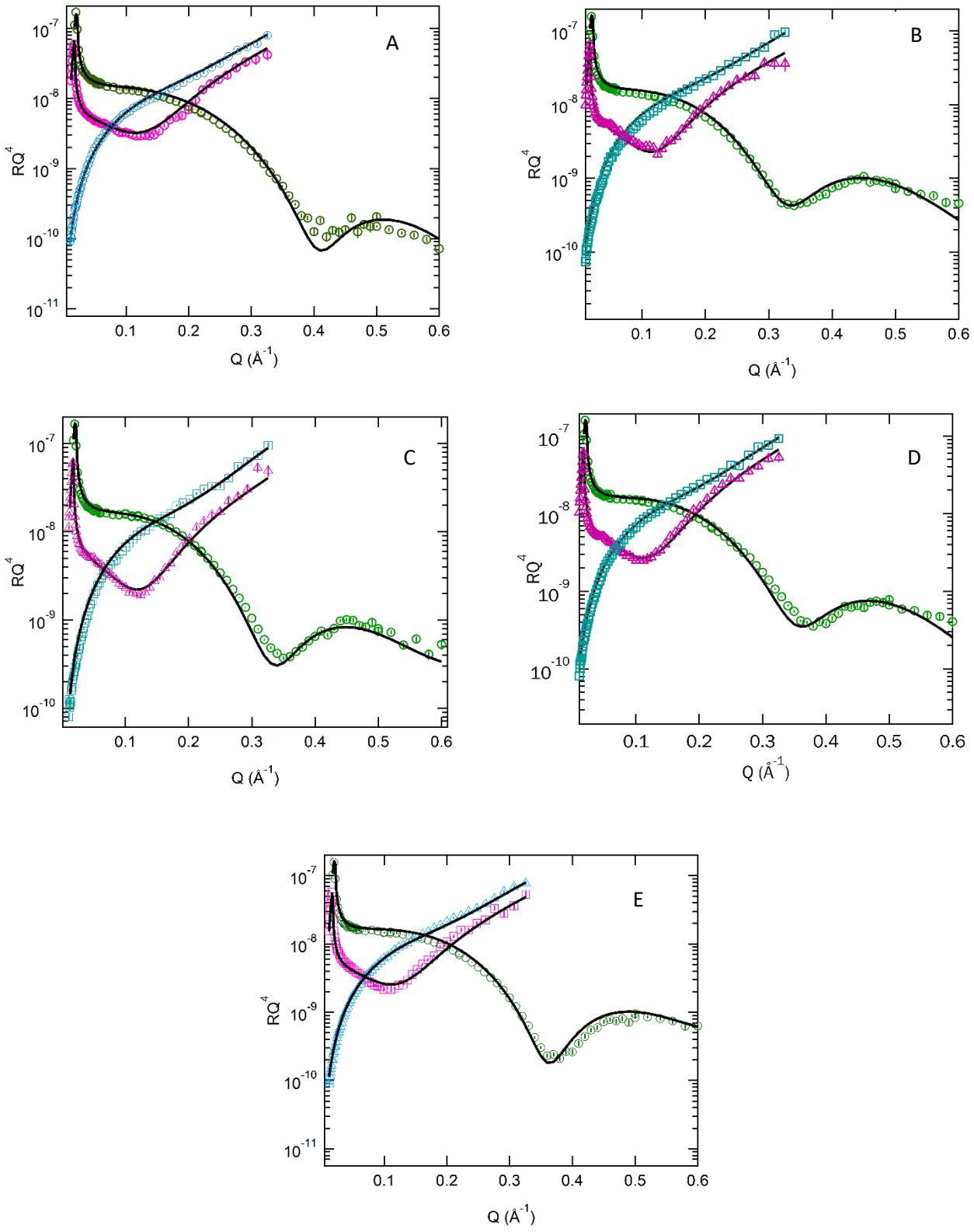

Figure 3*:* Fitted co-refined reflectivity data for monolayers at 15 mNm-1, green= XRR data, Blue: NR data for deuterated compounds on D2O, Pink: NR data for deuterated compounds on ACMW a: SB3-18, B: 1:3 DMPC: SB3-18, C: 1:1 DMPC:SB3-18, D: 3:1 DMPC: SB3-18, E: DMPC

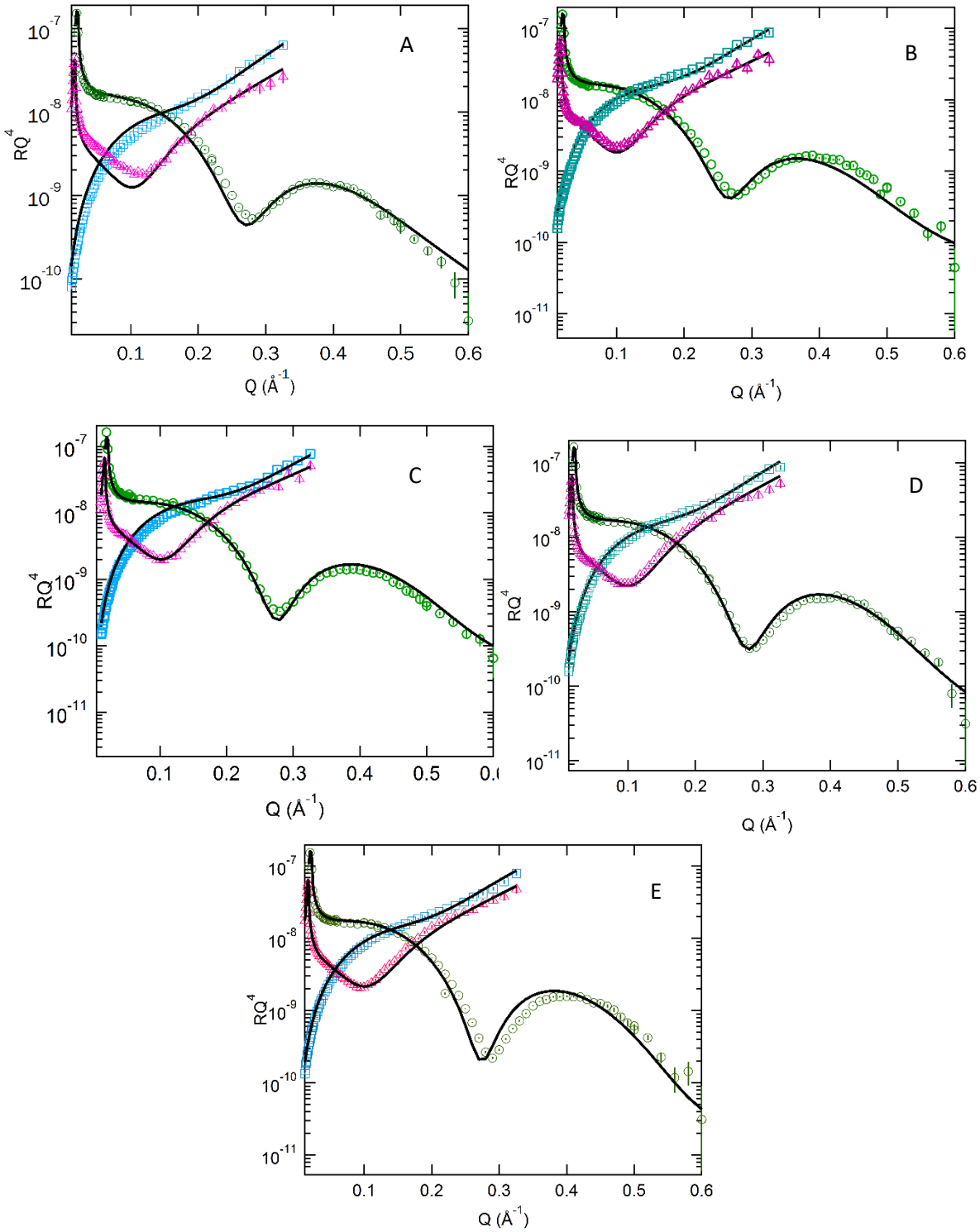

Figure 4: Fitted co-refined reflectivity data for monolayers at 35 mNm^{-1}, green= XRR data, Blue: NR data for deuterated compounds on D_2O, Pink: NR data for deuterated compounds on ACMW a: SB3-18, B: 1:3 DMPC: SB3-18, C: 1:1 DMPC:SB3-18, D: 3:1 DMPC: SB3-18, E: DMPC

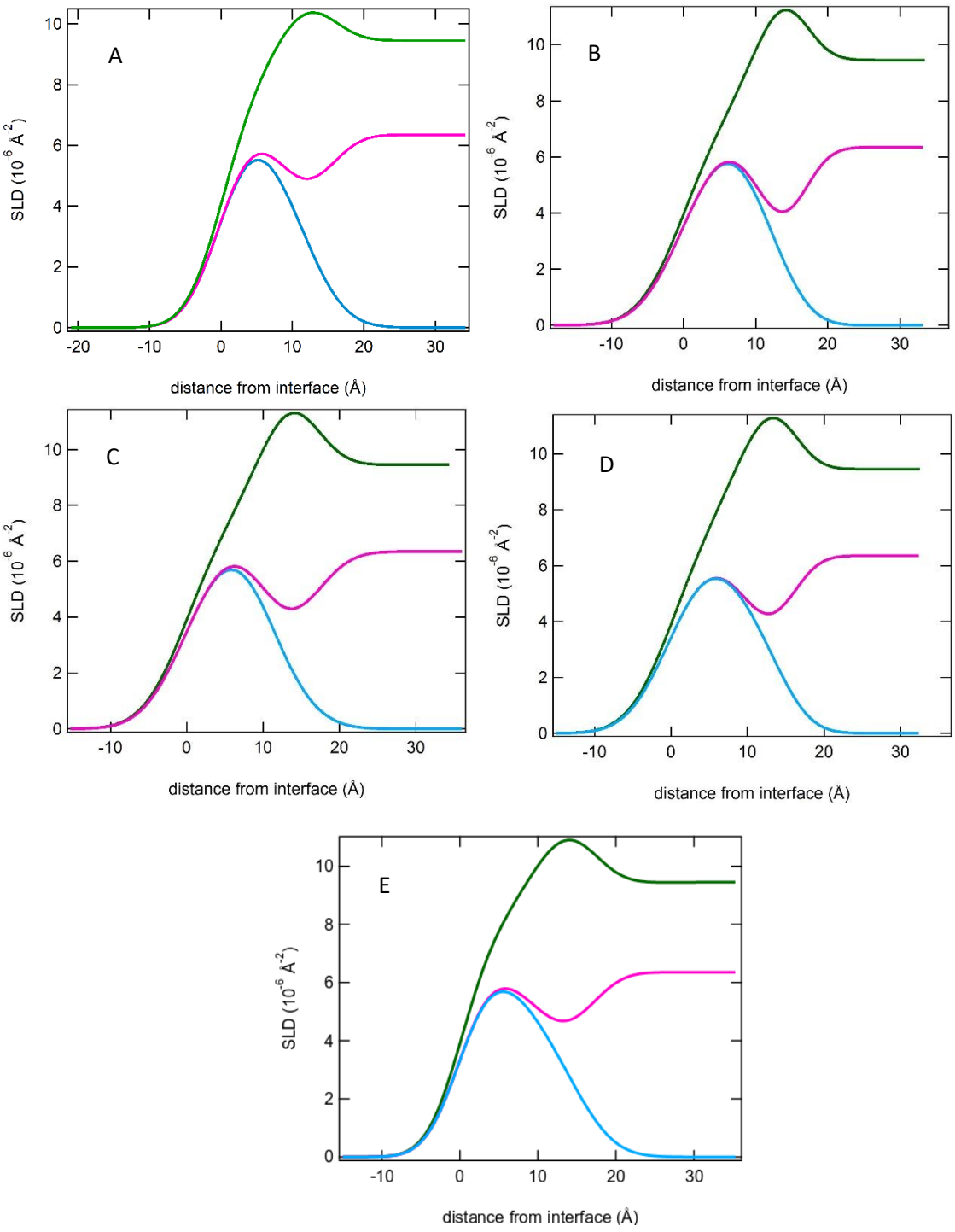

Figure 5: SLD profiles for the mixtures of DMPC and SB3-18 at 15mNm^{-1}, top left: SB3-18 top right 1:3, middle left 1:1 middle right 3:1, Bottom: DMPC, the values associated with this are reported in Table 3 in the main paper

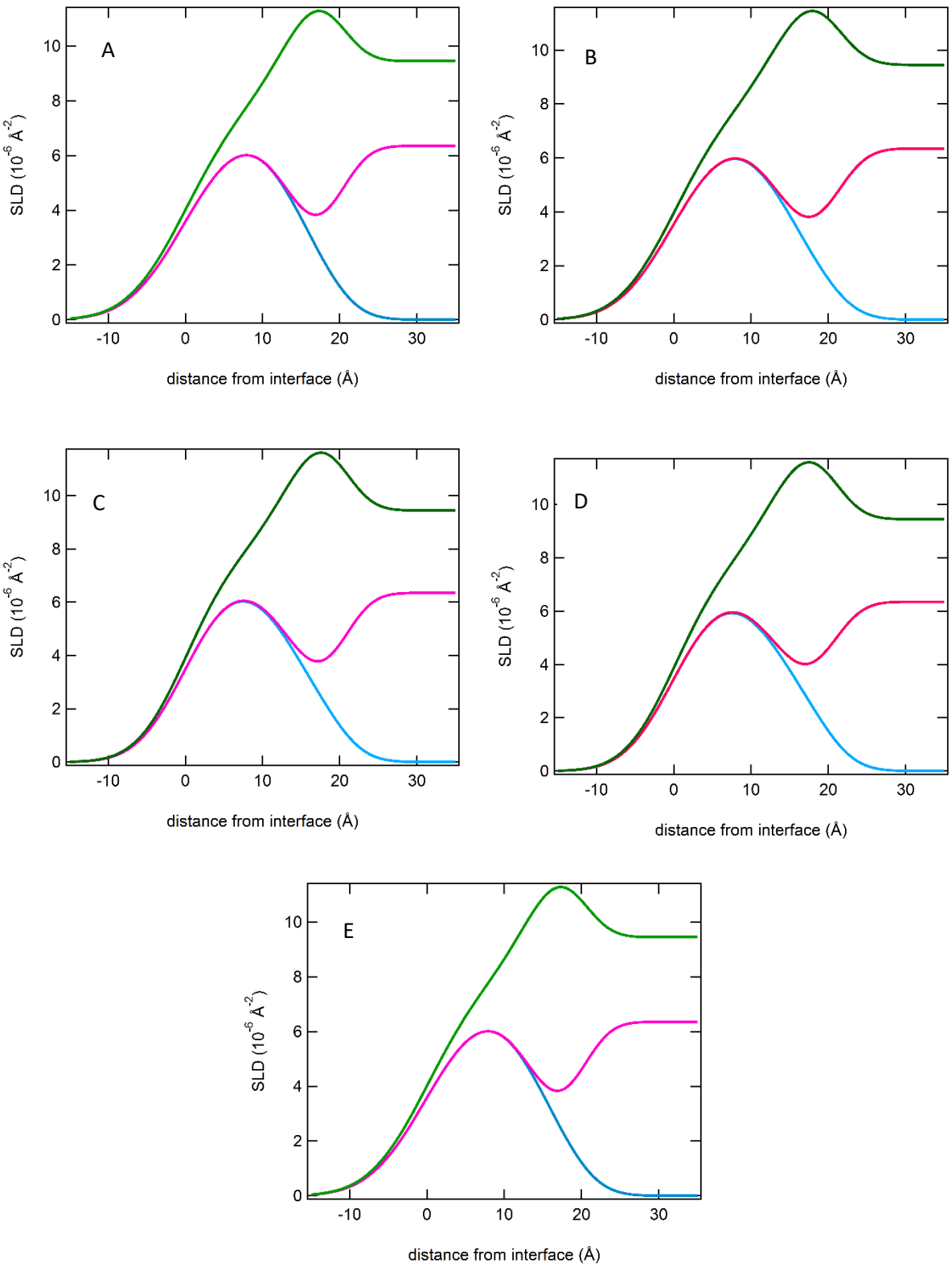

Figure 6: SLD profiles for the mixtures of DMPC and SB3-18 at 35mNm^{-1}, top left: SB3-18 top right 1:3, middle left 1:1 middle right 3:1, Bottom: DMPC, the values associated with this are reported in Table 4 in the main paper

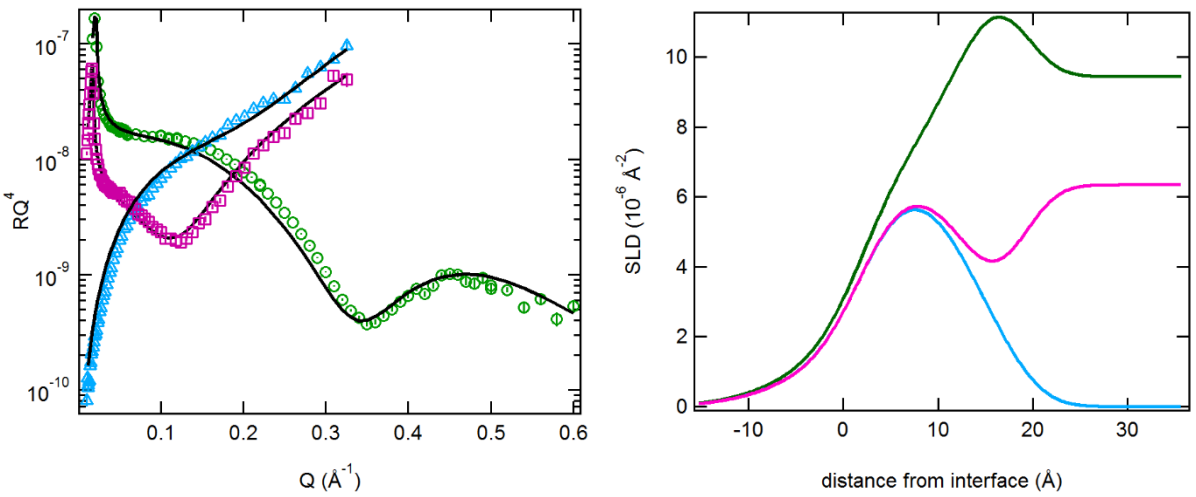

Figure 7: Three slab model fit to the 1:1 DMPC:sb3-18 mixture data at 15 mNm^{-1}. Left: Fitted co-refined reflectivity data. Right: SLD profile for this fit.

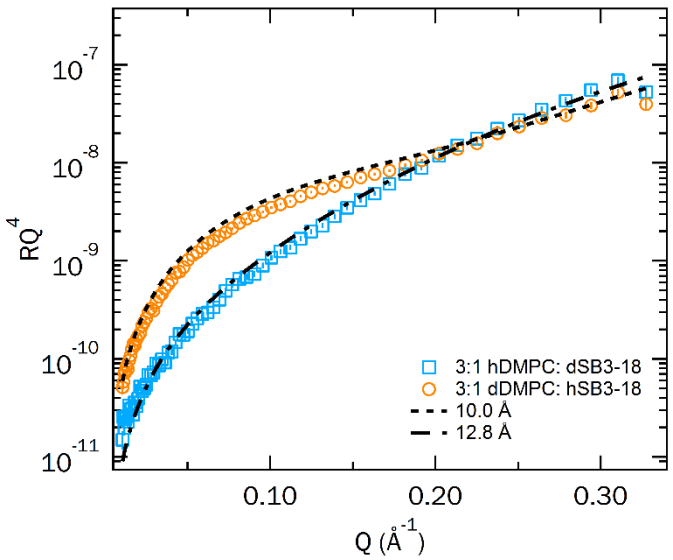

Figure 8: Models for the fitting of NR data from a monolayer consisting of a 3:1 mixture of DMPC and SB3-18. Dotted and dashed lines indicate the thickness of the two components at a tail tilt of 55.8°. Error bars on the NR data are shown but are within the symbol size.

Comparison of the area per molecule calculated from fitting reflectivity data and pressure-area isotherms

Table 3: Comparison of calculated APM, as shown in Equation 3 of the main body of the paper, and APM from Pressure-area isotherms, with the associated 5% systematic error.

Sample	Surface pressure	APM Theory, Å^2	APM Isotherm, Å^2	% Difference
DMPC	15mNm^{-1}	69.9	67.4	3.6%
DMPC	35mNm^{-1}	57.5	54.2	5.6%
3:1 DMPC:SB3-18	15mNm^{-1}	65.0	60.1	8.1%
3:1 DMPC:SB3-18	35mNm^{-1}	50.6	47.3	7.0%
1:1 DMPC:SB3-18	15mNm^{-1}	56.4	55.1	2.3%
1:1 DMPC:SB3-18	35mNm^{-1}	45.9	42.6	7.7%
1:3 DMPC:SB3-18	15mNm^{-1}	50.9	49.5	2.8%
1:3 DMPC:SB3-18	35mNm^{-1}	39.4	36.5	7.9%
SB3-18	15mNm^{-1}	50.0	47.0	6.3%
SB3-18	35mNm^{-1}	35.3	32.1	9.9%

Comparison of the parameter reported by Johnson *et al.*[5] and those we obtained while fitting the DMPC data

Table 4: Comparison of our current fit with the values from Johnson *et al.* for DMPC

DMPC Fit Comparison	**Johnson *et al.* (22°C, 10mNm^{-1})**	**Johnson *et al.* (22°C, 30mNm^{-1})**	**This work (22°C, 15mNm^{-1})**	**This work (22°C, 35mNm^{-1})**
Head SLD (neutron) / x10^{-6} Å^{-2}	1.75		1.9	
Headgroup Volume / Å^3	344		319	
Headgroup Thickness / Å	9.6±1.5	10.7±1.5	5.1±0.5	7.2±0.4
Headgroup Roughness / Å	not reported	not reported	5.3±0.8	5.0±0.8
Headgroup Solvation / %	70	57	11±8	20±7
Tail SLD (neutron) / x10^{-6} Å^{-2}	-0.41 / 6.65		-0.37 / 6.8	
Tail Volume / Å^3	800 / 711		782	
Tail Thickness / Å APM / V_M	11.4±1.5 87 / 991	15.8±1.5 61 / 964	11.2±1.0	13.6±0.8
Tail Roughness / Å	not reported	not reported	3.5±0.2	4.8±0.4
Tail Solvation / % (solvated with air)	30	20	0	0

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