

Supporting Information

Raft-like Mixtures of Sphingomyelin and Cholesterol Investigated by Solid-State ^2H NMR Spectroscopy

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Table 1. ^2H NMR spectral assignments and $\Delta\nu_Q$ splittings for PSM- d_{31} , at various temperatures

	carbon		$\Delta\nu_Q/\text{kHz}^a$									
peak	<i>i</i>	$T/^\circ\text{C}$	15	20	25	30	36	38	40	45	50	55
A	3		117.0	116.8	114.3	105.5	90.9	68.0	72.3	70.6	69.3	67.3
B	3								65.7	67.1	65.2	63.9
C	2,4-6									63.2	55.8	57.9
D	7-9								63.7	59.3		53.2
E	10							55.1	56.8	52.8	51.2	47.2
F	11								54.4		48.8	45.2
G	12								51.6	46.3	42.8	39.5
H	2							43.8	48.0	42.2	39.4	36.5
I	13								38.9	37.7	37.3	
J	14							36.6	31.3	34.3	31.4	28.7
K	15		32.8	31.8	27.6	25.6	35.0	7.4	6.2	27.5	25.0	22.9
L	16						13.6			5.3	4.8	4.4

^a Quadrupolar splitting corresponding to $\theta = 0^\circ$ bilayer orientation.

Table 2. ^2H NMR spectral assignments and $\Delta\nu_Q$ splittings for PSM- d_{31} in binary mixture with cholesterol $X_C = 0.15$ at various temperatures

	carbon		$\Delta\nu_Q/\text{kHz}^a$							
peak	<i>i</i>	$T/^\circ\text{C}$	20	25	30	35	40	45	50	55
A	2-5		102.3	95.3	93.2	83.9	81.0	79.8	77.2	72.9
B	6-9							76.5	74.8	
C	10,11					64.2	62.2	59.9	58.4	56.7
D	12,13								51.5	47.6
E	14,15							51.9	45.3	40.8
F	16		21.9	21.0	19.3	14.7	11.6	9.3	8.2	7.4

^a Quadrupolar splitting corresponding to $\theta = 0^\circ$ bilayer orientation.

Table 3. ^2H NMR spectral assignments and $\Delta\nu_Q$ splittings for PSM- d_{31} in binary mixture with cholesterol $X_C = 0.2$ at various temperatures

	carbon		$\Delta\nu_Q/\text{kHz}^a$							
peak	<i>i</i>	$T/^\circ\text{C}$	20	25	30	35	40	45	50	60
A	2-9		114.5	110.1	107.7	99.7	84.8	79.6	76.9	70.6
B	10-13		97.7	96.1	93.3	89.2				
C	14		81.3	78.1	74.9	67.5	61.2	58.7	56.6	53.1
D	15								40.5	42.2
E	16		18.4	17.4	15.7	13.5	11.0	8.3	6.8	4.9

^a Quadrupolar splitting corresponding to $\theta = 0^\circ$ bilayer orientation.

Table 4. ^2H NMR spectral assignments and $\Delta\nu_Q$ splittings for PSM- d_{31} in binary mixture with cholesterol $X_C = 0.25$ at various temperatures

	carbon		$\Delta\nu_Q/\text{kHz}^a$							
peak	<i>i</i>	$T/^\circ\text{C}$	20	25	30	35	40	45	50	60
A	2-7		114.3	113.1	110.1	106.7	101.2	93.4	89.0	84.0
B	8-12		99.3	97.8	95.7	93.3	91.0	85.1	81.8	
C	13,14		79.9	77.5	75.2	70.2	66.2	63.1	61.8	59.4
D	15								51.3	45.3
E	16		20.2	19.2	17.8	16.2	14.1	12.2	10.7	9.2

^a Quadrupolar splitting corresponding to $\theta = 0^\circ$ bilayer orientation.

Table 5. ^2H NMR spectral assignments and $\Delta\nu_Q$ splittings for PSM- d_{31} in binary mixture with cholesterol $X_C = 0.33$ at various temperatures

	carbon		$\Delta\nu_Q/\text{kHz}^a$								
peak	<i>i</i>	$T/^\circ\text{C}$	20	25	30	35	38	40	45	50	60
A	2-6		113.2	111.7	109.7	107.4	105.7	104.8	99.7	97.4	91.0
B	7-10		100.4	98.9	97.3	94.6	92.4	91.2	87.9	85.8	80.2
C	11,12				87.1	84.1	82.1	80.3	75.9	73.2	66.7
D	13		76.1	74.0	71.0	68.1	66.6	65.6	64.1	62.9	58.8
E	14,15								60.5	57.5	52.2
F	16		19.8	19.0	17.8	16.9	15.3	14.8	13.5	13.2	10.2

^a Quadrupolar splitting corresponding to $\theta = 0^\circ$ bilayer orientation.

Table 6. ^2H NMR spectral assignments and $\Delta\nu_Q$ splittings for POPC- d_{31} at various temperatures

	carbon		$\Delta\nu_Q/\text{kHz}^a$				
peak	<i>i</i>	$T/^\circ\text{C}$	15	20	30	45	55
A	2-5		55.3	54.5	50.7	47.5	44.2
B	6-8					44.1	40.4
C	9		50.1	50.6	44.7	40.2	36.1
D	10		47.9	47.8	41.9	37.2	33.4
E	11		42.5	42.8	37.4	32.6	29.1
F	12		39.0	38.9	33.7	29.2	25.8
G	13		33.2	33.3	28.6	24.7	21.5
H	14		27.9	28.1	24.1	20.6	17.8
I	15		21.0	21.0	17.9	15.3	13.2
J		16	6.2	6.3	5.3	4.4	3.7

^a Quadrupolar splitting corresponding to $\theta = 0^\circ$ bilayer orientation.**Table 7.** ^2H NMR spectral assignments and $\Delta\nu_Q$ splittings for POPC- d_{31} in binary mixture with cholesterol $X_C = 0.2$ at various temperatures

	carbon		$\Delta\nu_Q/\text{kHz}^a$					
peak	<i>i</i>	$T/^\circ\text{C}$	15	20	30	40	45	60
A	2-7		77.5	75.1	67.7	61.6	59.2	53.7
B	8-10		65.9	63.5	60.4	54.3	53.7	48.2
C	11					49.4	47.0	40.3
D	12			58.0	50.0	44.6	42.1	36.0
E	13		53.1	50.0	42.7	37.8	36.0	30.5
F	14		44.6	41.5	35.4	31.7	29.3	25.0
G	15		33.0	31.1	26.2	22.6	21.4	18.3
H	16		9.8	9.2	7.3	6.7	6.1	4.9

^a Quadrupolar splitting corresponding to $\theta = 0^\circ$ bilayer orientation.

Table 8. ^2H NMR spectral assignments and $\Delta\nu_Q$ splittings for POPC- d_{31} in binary mixture with cholesterol $X_C = 0.33$ at various temperatures

	carbon		$\Delta\nu_Q/\text{kHz}^a$									
peak	<i>i</i>	$T/^\circ\text{C}$	15	20	25	30	35	38	40	45	50	60
A	2-5		106.1	103.3	99.5	96.0	92.4	87.4	85.0	80.3	74.7	66.5
B	6-8		100.5	97.3	93.2	89.5	85.7	80.7	78.3	76.0	71.0	
C	9										67.3	58.3
D	10,11		94.9	92	87.7	82.5	79.0	74.2	71.9	66.8	61.7	
E	12		90.0	86.7	82.2	77.8	73.8	68.2	66.2	60.8	55.4	47.9
F	13		81.4	78.0	73.6	69.5	65.5	60.0	57.4	52.6	47.4	40.4
G	14		68.9	65.8	61.7	58.0	54.4	49.7	47.5	43.2	39.0	32.8
H	15		52.7	49.9	46.4	43.3	40.4	36.7	34.9	31.6	28.3	23.8
I	16		14.3	13.5	12.5	11.6	10.8	9.8	9.4	8.5	7.6	6.2

^a Quadrupolar splitting corresponding to $\theta = 0^\circ$ bilayer orientation.

Table 9. ^2H NMR spectral assignments and $\Delta\nu_Q$ splittings for PSM- d_{31} /POPC 1:1 at various temperatures

	carbon		$\Delta\nu_Q/\text{kHz}^a$									
peak	<i>i</i>	$T/^\circ\text{C}$	15	20	25	30	35	37	40	45	50	55
A	3		73.9	71.7	74.1	72.3	70.5	70.2	69.7	68.2	66.7	65.9
B	3				67.9	65.7	63.2	62.4	61.7	63.7	62.0	61.3
C	4-7									60.2	57.5	56.2
D	2,8,9					63.0	60.0	59.2	58.1	55.7	52.9	51.6
E	10		58.9	57.6	61.4	55.6	52.7	52.0	52.1	50.5	49.34	48.8
F	11										47.5	46.2
G	12		47.8	44.6	55.4	49.6	46.2	43.1	50.5	48.1	45.2	43.8
H	2				49.8	45.5	42.21	41.3	40.5	42.0	39.3	37.9
I	13		37.5	35.8	39.6	37.0	37.1	37.1	37.2	38.1	35.8	34.4
J	14				33.0	29.5	33.7	32.8	32.1	30.2	28.0	26.9
K	15						26.9	26.2	25.6	24.0	22.0	21.2
L	16		7.3	6.7	6.1	5.4	5.0	4.9	4.7	4.5	4.1	4.0

^a Quadrupolar splitting corresponding to $\theta = 0^\circ$ bilayer orientation.

Table 10. ^2H NMR spectral assignments and $\Delta\nu_Q$ splittings for EYSM/POPC- d_{31} 1:1 at various temperatures

	carbon		$\Delta\nu_Q/\text{kHz}^a$								
peak	<i>i</i>	$T/^\circ\text{C}$	15	20	25	30	35	40	45	50	60
A	2-5		56.8	55.2	54.5	52.9	51.0	48.8	47.3	45.6	43.4
B	6-8										39.6
C	9			51.2	49.0	49.3	47.3	44.5	42.6	40.7	36.4
D	10					47.4	44.9			37.6	33.5
E	11					41.9	39.6	37.2	35.0	33.1	29.3
F	12			41.3	39.6	37.6	35.6	33.3	31.5	29.4	25.8
G	13			35.2	34.3	32.0	30.1	28.1	26.3	24.6	21.4
H	14		32.0	29.6	28	26.6	24.9	23.4	21.5	20.2	17.5
I	15		23.0	21.8	20.7	19.5	18.2	17.1	16.0	15.0	13.0
J	16		6.7	6.1	5.7	5.4	5.0	4.8	4.4	4.1	3.7

^a Quadrupolar splitting corresponding to $\theta = 0^\circ$ bilayer orientation.

Table 11. ^2H NMR spectral assignments and $\Delta\nu_Q$ splittings for PSM- d_{31} /POPC 1:1 with cholesterol $X_C = 0.33$ at various temperatures

	carbon		$\Delta\nu_Q/\text{kHz}^a$									
Peak	<i>i</i>	$T/^\circ\text{C}$	15	20	25	30	35	38	40	45	50	60
A	3-9		111.0	109.1	106.6	103.2	99.9	97.5	95.2	91.6	87.2	79.5
B	10-13		99.7	95.8	91.9	89.1	86.9	84.2	84.4	81.4	78.8	
C	14		89.0	85.0	81.4	76.5	71.9	69.5	68.2	63.5	58.6	52.0
E	2		73.4	70.4	66.2	62.3	63.2	62	61.4	60.0		
F	15						59.0	55.3	53.7	50.8	47.1	40.2
G	16		18.6	17.3	15.9	14.4	13.4	12.4	12.0	10.9	10.0	8.3

^a Quadrupolar splitting corresponding to $\theta = 0^\circ$ bilayer orientation.

Table 12. ^2H NMR spectral assignments and $\Delta\nu_Q$ splittings for EYSM/POPC- d_{31} 1:1 with cholesterol $X_C = 0.33$ at various temperatures

	carbon		$\Delta\nu_Q/\text{kHz}^a$									
Peak	<i>i</i>	$T/^\circ\text{C}$	15	20	25	30	35	38	40	45	50	60
A	3-6		109.1	106.3	103.8	100.7	97.2	92.3	89.9	85.7	80.6	71.4
B	7-9				98.7	94.1	89.9	85.5	83.4	79.2	75.1	

C	10,11				93.4	89	85.1	80.1	77.4	72	67.9	60.0
D	12,2		93.6	90.76	86.8	82.8	78.8	74.0	71.5	66.9	62.7	54.6
E	13		83.6	81.1	77.4	73.2	69.2	64.2	61.8	57.6	53.6	45.7
F	14		70.4	68.2	64.4	60.5	57.0	52.7	50.7	46.9	43.4	36.8
G	15		52.5	50.3	47.4	44.3	41.4	38.1	36.5	33.7	30.9	26.0
H	16		13.8	13.2	12.4	11.5	10.8	9.9	9.5	8.7	7.9	6.6

^a Quadrupolar splitting corresponding to $\theta = 0^\circ$ bilayer orientation.

Table 13. Summary of structural results for PSM- d_{31} and POPC- d_{31} components in binary mixtures with cholesterol

	$T/^\circ\text{C}$	$D_C/\text{\AA}^a$	$\langle A \rangle/\text{\AA}^2{}^b$	$\alpha_{\parallel}/10^{-3}\text{ K}^{-1}{}^c$	$\alpha_{\perp}/10^{-3}\text{ K}^{-1}{}^d$	$L_C^*/\text{\AA}^e$	$L_C/\text{\AA}^f$
PSM- d_{31} $X_C=0$	20	19.8	21.9	-0.3	0.9	16.4	18.4
	30	19.1	23.0	-8.8	11.9	15.8	17.7
	45	15.7	28.5	-4.0	6.5	12.8	14.3
	55	14.9	30.4	-0.1	0.5	12.3	13.6
$X_C=0.15$	20	18.9	23.0	-1.6	2.9	16.6	19.0
	30	18.3	24.1	-5.3	6.5	16.1	18.4
	45	17.2	26.0	-1.8	2.9	14.2	16.0
	55	16.6	27.3	-7.0	7.9	13.9	15.5
$X_C=0.20$	20	19.7	22.0	-1.0	2.0	16.7	18.9
	30	19.3	22.8	-4.8	6.2	16.4	18.5
	45	17.2	26.0	-6.2	7.6	15.0	17.0
	60	16.4	27.8	-0.6	1.4	14.3	16.0
$X_C=0.33$	20	19.6	22.1	-0.6	1.7	16.3	18.6
	30	19.4	22.7	-1.4	2.7	16.0	18.2
	45	18.7	23.9	-2.7	3.8	15.4	17.5
	60	18.1	25.1	-1.9	3.2	14.8	16.9
POPC- d_{31} $X_C=$	20	14.7	29.5	-2.5	3.7	12.1	13.6
	30	14.3	30.8			11.6	13.0
	45	13.9	32.2			11.1	12.4
	55	13.4	33.7			10.6	11.9

$X_c = 0.20$	20	16.8	25.9	-3.5	4.6	13.8	15.5
	30	16.1	27.3			13.3	14.8
	45	15.3	29.3			12.5	14.0
	60	14.7	31.1			11.9	13.3
$X_c = 0.33$	20	19.0	22.9	-2.0	3.1	15.7	17.7
	30	18.5	23.8	-3.6	4.8	15.2	17.1
	45	17.3	25.9	-5.4	6.5	14.1	15.8
	60	16.0	28.4	-4.0	5.3	13.1	14.7

^a hydrocarbon thickness of one acyl chain (Eq. 10), ^b average cross-sectional chain area (eq. 9), ^c isobaric thermal expansion coefficient parallel to the membrane normal (eq. 18), ^d isobaric thermal expansion coefficient perpendicular to the membrane normal (Eq 19), ^e average chain length C3 to C15 (eq. 7), ^f estimated average chain length C2 to C16 (eq. 8).