Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

The explicit role of interfacial hydration during polyethylene glycol induced lipid fusion: a THz spectroscopic investigation

Sumana Pyne, Partha Pyne and Rajib Kumar Mitra*

Department of Chemical & Biological Sciences, S N Bose National Centre for Basic Sciences, Block JD, Sector III, Salt Lake, Kolkata 700106, INDIA

* Email: rajib@bose.res.in

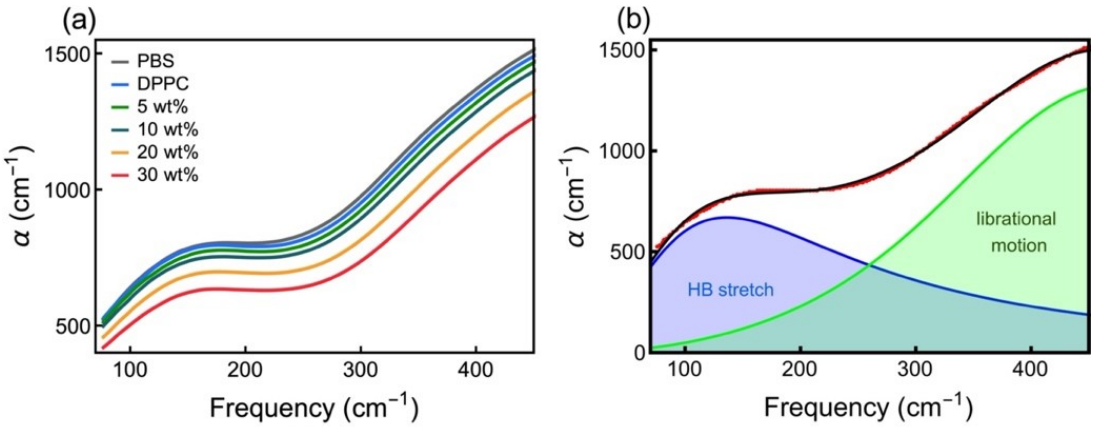

Figure S1: absorption coefficient as a function of frequency for DPPC liposomes with different concentration of PEG 4000. (b) Representative fitted profile for water. Red curve shows the raw data of water, black line shows the total fitted data. Blue curve indicated HB-stretch and green curve indicates libration motion of water molecule.

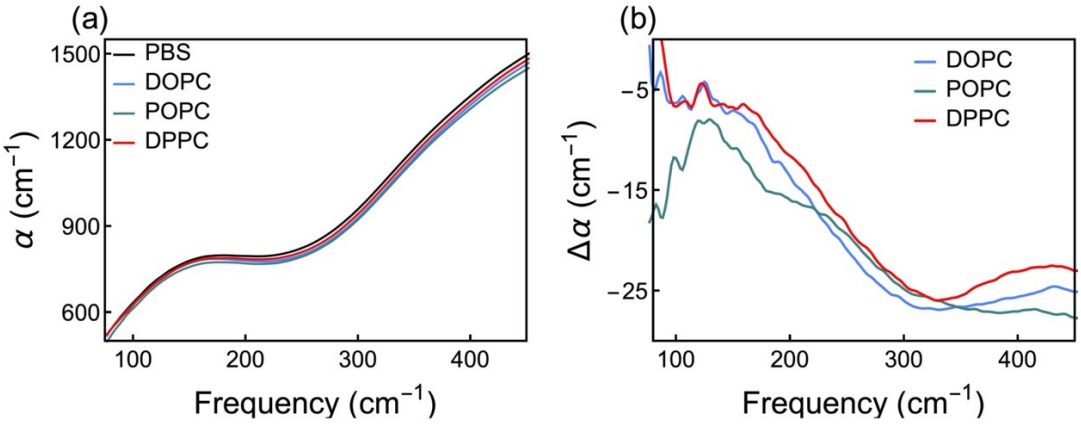

Figure S2: (a) absorption coefficient and (b) $\Delta\alpha$ as a function of frequency for three liposomes respectively.

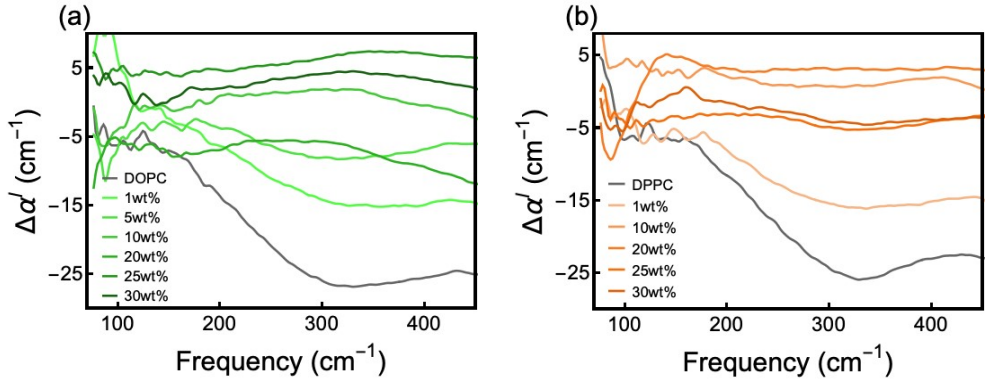

Figure S3: $\Delta\alpha$ as a function of frequency at different concentration of PEG 4000 for (a) DOPC and (b) DPPC liposomes.

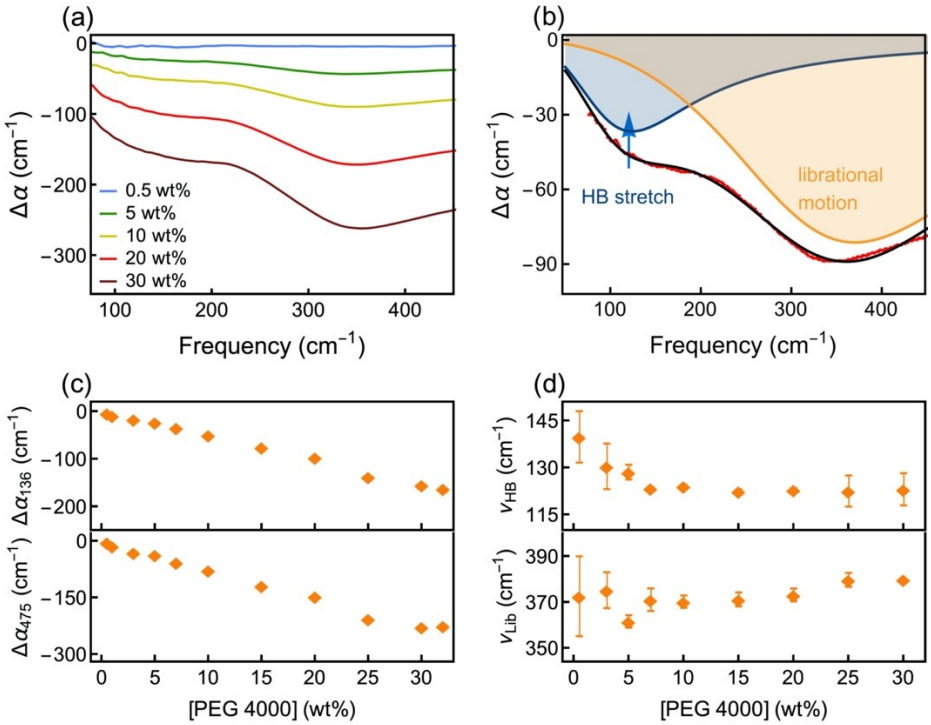

Figure S4: (a) Change in absorption coefficient ($\Delta\alpha_{PEG}(\nu) = \alpha_{PEGsolution}(\nu) - \alpha_{water}(\nu)$) at different concentration of PEG. (b) Representative fitting of $\Delta\alpha_{PEG}(\nu)$ profiles for PEG solution (10 wt%) using the damped harmonic oscillator model (equation 7). The red broken curve represents the raw data and the black solid line stands for the total fitting. The 1st peak with frequency ν_1 (blue line) represents the hydrogen bond stretching of water molecules, the 2nd peak with frequency ν_2 (brown line) presents the librational motion of water molecules. (c) $\Delta\alpha$ measured at 136 and 475 cm^{-1} respectively as a function of [PEG] for both HB-stretch and librational mode of water. (d) Peak frequency (HB stretch and librational mode) of water as a function of PEG 4000.

Table S1: Concentration of PEG 4000 at different state of lipids.

	LLS	**AS**	**FS**
DOPC	$0 \leq$ [PEG] ≤ 0.5	$1 \leq$ [PEG] ≤ 25	$25 \leq$ [PEG]
POPC	$0 \leq$ [PEG] ≤ 0.5	$1 \leq$ [PEG] ≤ 25	$25 \leq$ [PEG]
DPPC	$0 \leq$ [PEG] < 0.5	$0.5 \leq$ [PEG] ≤ 7	$10 \leq$ [PEG]

Table S2. Hydrodynamic diameter of liposomes (DOPC,POPC and DPPC) at different concentration of PEG 4000

DOPC		POPC		DPPC	
[PEG 4000] (wt%)	Hyd. Dia (um)	[PEG 4000] (wt%)	Hyd. Dia (um)	[PEG 4000] (wt%)	Hyd. Dia (um)
0	0.1	0	0.1	0	0.1
0.1	0.1	0.1	0.1	0.5	0.1
0.5	0.1	0.5	0.1	1	1.1
1	1.3	1	1.0	3	2.3
3	1.5	2	1.5	7	4.2
5	1.5	3	1.5	10	2.3
7	1.7	5	5.6	15	2.0
10	5.6	10	5.6	20	1.7
12	5.6	12	5.6	25	2.3
15	5.6	15	5.6	30	2.0
20	4.2	20	4.8	32	1.0
25	3.1	25	2.7		
30	2.3	30	2.3		
32	1.7	32	2.3		
35	1.7				

Table S3. Peak frequency both HB-stretch and librational motion for three liposomes. Data are fitted by using damped harmonic oscillator equation:

DOPC				POPC				DPPC			
PEG (wt%)	ν_{HB} (cm^{-1})	ν_{Lib} (cm^{-1})	**R^2**	**PEG (wt%)**	ν_{HB} (cm^{-1})	ν_{Lib} (cm^{-1})	**R^2**	**PEG (wt%)**	ν_{HB} (cm^{-1})	ν_{Lib} (cm^{-1})	**R^2**
0	96.5 ± 1	349.2 ± 2.8	0.999	0	107.4 ± 2.3	389.8 ± 10.7	0.999	0	104.3 ± 1.4	346.0 ± 3.5	0.996
0.5	100.4 ± 1.3	357.1 ± 2.9	0.999	0.5	114.3 ± 2	389.6 ± 19.1	0.999	0.5	105.6 ± 1.2	351.3 ± 3.3	0.996
3	80.6 ± 2.5	330.6 ± 2.8	0.997	3	119.8 ± 1	376.6 ± 6.3	0.997	1	121.3 ± 0.9	348.3 ± 3.9	0.998
5	89.2 ± 0.5	326.3 ± 3.2	0.995	5	113.7 ± 0.3	368.1 ± 5.9	0.999	3	105.8 ± 2.8	338.5 ± 2.6	0.996
7	136.3 ± 1.8	303.2 ± 5.5	0.975	7	166.1 ± 1.6	362.4 ± 4.5	0.997	5	130.2 ± 1.8	362.6 ± 11.8	0.978
10	125.7 ± 1.1	276.4 ± 0.8	0.822	10	119.5 ± 13	356.3 ± 4.9	0.999	7	97.8 ± 6.1	360.3 ± 19.5	0.969
15	100.6 ± 9.3	382.3 ± 4.8	0.998	15	161.7 ± 6.7	384.7 ± 7.6	0.999	10	137.3 ± 2.2	305.9 ± 0.4	0.942
20	161.6 ± 3.7	440.8 ± 6.8	0.988	20	129.9 ± 3.1	387.4 ± 7.6	0.999	15	129.8 ± 2.3	360.9 ± 27.5	0.900
25	144.4 ± 1.6	347.9 ± 4.6	0.997	25	123.5 ± 1.4	331.6 ± 10.8	0.996	25	117.4 ± 2.2	336.5 ± 4.9	0.651
30	138.9 ± 1.7	321.1 ± 3.7	0.981	30	123.1 ± 1.4	382.5 ± 17.7	0.963	30	91.5 ± 0.4	349.4 ± 4.2	0.990

Table S4. Peak frequency both HB-stretch and librational motion for PEG 4000. Data are fitted by using damped harmonic oscillator equation:

PEG (wt%)	ν_{HB} (cm^{-1})	ν_{Lib} (cm^{-1})
0.5	140.0 ± 8.2	372.8 ± 17.4
3	130.5 ± 7.3	375.4 ± 7.8
5	128.7 ± 2.4	361.8 ± 2.7
7	123.6 ± 0.3	371.3 ± 4.9
10	124.2 ± 0.4	370.4 ± 2.7
15	122.6 ± 0.5	371.4 ± 3
20	123.1 ± 0.5	373.3 ± 2.8
25	122.7 ± 5	379.9 ± 3.1
30	123.2 ± 5.1	380.1 ± 0.2

Table S5. Amplitude and relative amplitude of both HB-stretch and librational motion for three liposomes after performing PCA. Data are fitted by using damped harmonic oscillator equation:

	DOPC			**POPC**			**DPPC**		
	A_{HB}	A_{Lib}	A_{HB}/A_{Li}	A_{HB}	A_{Lib}	A_{HB}/A_{Lib}	A_{HB}	A_{Lib}	A_{HB}/A_{Lib}
Pristine Liposome	-940.7	-141247.4	0.007	-7317.3	-187880.4	0.039	-883.4	-117993.5	0.007
LLS	-679.9	-126642.1	0.005	-10783.5	-181601.6	0.059	-1134.1	-100539.7	0.011
AS	-1629.6	-143177.0	0.011	-27689.6	-240607.0	0.115	-3425.8	-140100.0	0.024
FS	-2715.5	-48590.2	0.056	-8766.6	-27505.5	0.319	-1116.5	-26224.4	0.043