Electronic Supplementary Material (ESI) for Soft Matter.

Insight into Formation and Permeability of Ionic Liquid Unilamellar Vesicles by Molecular Dynamic Simulation

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S1. Details of non-bond parameters of cation and anion.

The structure of cation and head/tail region division was shown in figure S1, and atom charge and LJ parameters were shown in Table S1.

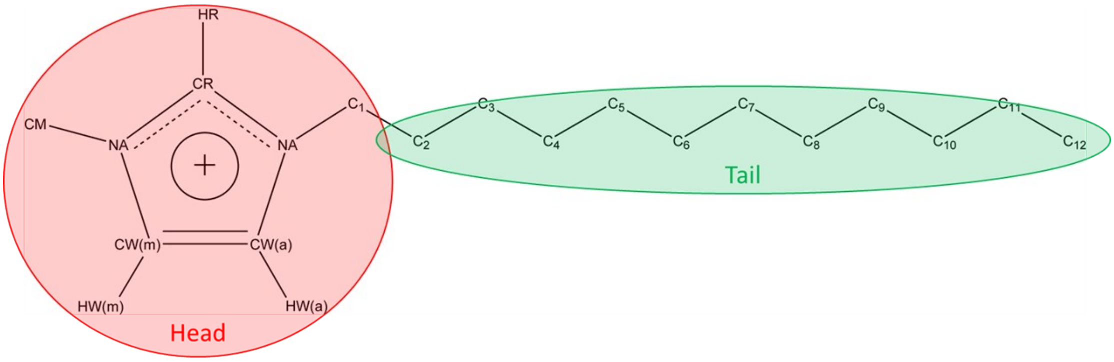

Figure S1. Schematic structures of cation and head/tail region division.

Table S1. Atom charges and Van der Waals Parameters of cation.

	q	ε_i $(kJ\ mol^{-1})$	σ_i (Å)
NA(a)	0.239	0.2931	3.5722
CR	-0.155	0.2774	3.5812
NA(m)	0.261	0.2931	3.5722
CW(a)	-0.241	0.2774	3.5812
CW(m)	-0.19	0.2774	3.5812
CM	0.153	0.8672	3.7479
C1	-0.002	0.4105	4.0704
C2	0.143	0.4105	4.0704
C3	0.023	0.4105	4.0704
C4	-0.023	0.4105	4.0704
C5	0.025	0.4105	4.0704
C6	0.005	0.4105	4.0704
C7	-0.03	0.4105	4.0704
C8	0.072	0.4105	4.0704
C9	-0.083	0.4105	4.0704
C10	0.023	0.4105	4.0704
C11	0.108	0.4105	4.0704
C12	-0.094	0.8672	3.7479
H5	0.256	0.1184	2.3734
H4(a)	0.269	0.1184	2.3734
H4(m)	0.241	0.1184	2.3734

The structure of anion was shown in figure S2, and atom charge and LJ parameters were shown in Table S2

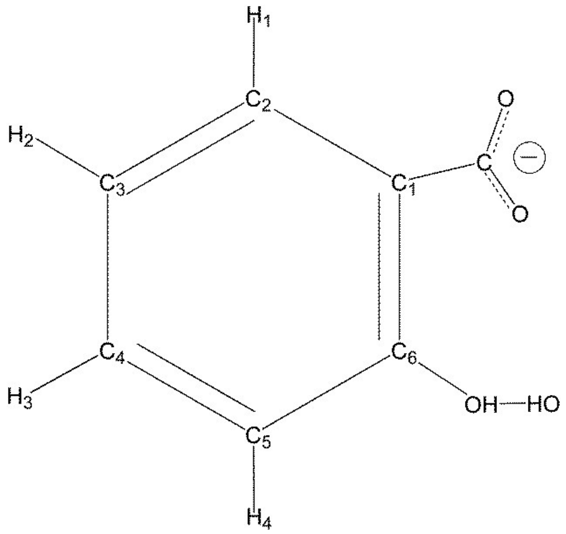

Figure S2. Schematic structures of anion.

Table S2. Atom charges and Van der Waals Parameters of anion.

	q	ε_i $(kJ\ mol^{-1})$	σ_i (Å)
O	-0.768	1.7250	2.6259
C	0.752	0.2774	3.5812
C1	-0.157	0.2774	3.5812
C2	-0.146	0.2774	3.5812
C3	-0.205	0.2774	3.5812
C4	-0.088	0.2774	3.5812
C5	-0.319	0.2774	3.5812
C6	0.334	0.2774	3.5812
H1	0.123	0.1184	2.3734
H2	0.135	0.1184	2.3734
H3	0.122	0.1184	2.3734
H4	0.150	0.1184	2.3734
OH	-0.594	0.8496	2.9548
HO	0.429	0.0000	0.0000

S2. Vesicle information at different temperatures.

The average radius of the vesicle (r_{av}) is defined as the average distance from the mass center of vesicle to the IL. Because ionic liquids and water contact each other in the interface, the vesicle size information was computed by analyzed the radial density distribution (RDD) function. The position where half of the maximum distribution of the cation head group is regard as the interface, and the position where half of the bulk distribution of water is also regard as the interface, so the both results are shown in the Table S3 (the values in parentheses were computed based on water RDD).

Table S3. Vesicle information at different temperatures. The average radius of vesicle (r_{av}), interior water volume, vesicle diameter (calculated by the interface based on cation head group, the values in parentheses based on water), vesicle volume.

T (K)	r_{av} (nm)	interior water volume (nm^3)	vesicle diameter (nm)	vesicle volume (nm^3)
300	3.216 ± 0.007	32.21 ± 0.02	9.227 (9.072)	411.374
310	3.227 ± 0.009	32.36 ± 0.03	9.279 (9.085)	418.247
320	3.241 ± 0.010	32.85 ± 0.03	9.31 (9.104)	422.513
330	3.250 ± 0.010	33.14 ± 0.07	9.334 (9.132)	425.842
340	3.269 ± 0.010	33.90 ± 0.10	9.348 (9.148)	427.654
350	3.284 ± 0.011	34.97 ± 0.06	9.385 (9.171)	432.806
360	3.303 ± 0.011	36.27 ± 0.11	9.424 (9.200)	438.299
370	3.326 ± 0.014	37.21 ± 0.52	9.495 (9.217)	448.170

S3. Energy profile of interaction between cations and anions.

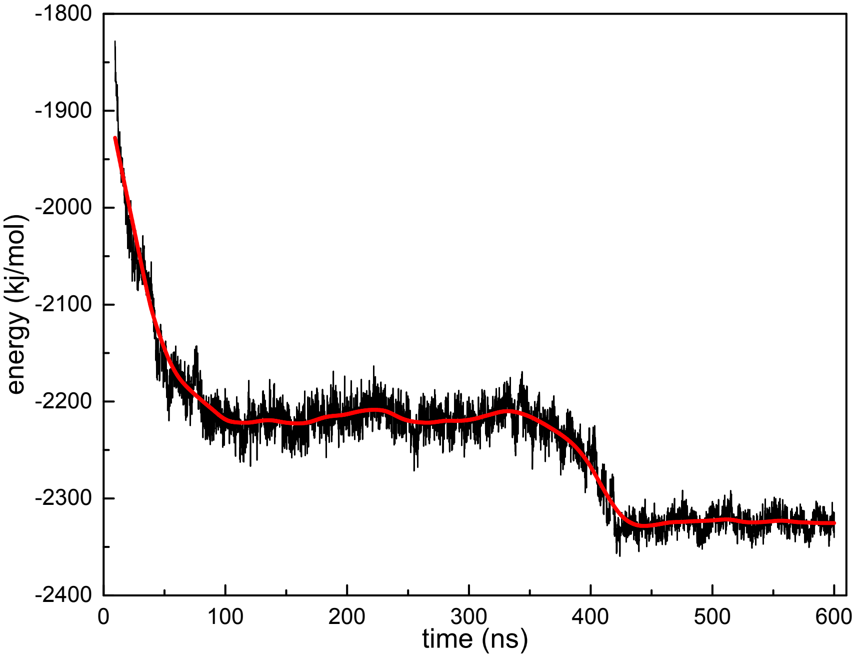

Figure S3. Interaction energy between cation and anion along the whole simulation duration in the vesicle forming process. A cutoff of 1.6 nm was set for both LJ and electrostatic interactions energy calculation.

S4. Theoretical prediction model of water molecules diffusing through the vesicle membrane.

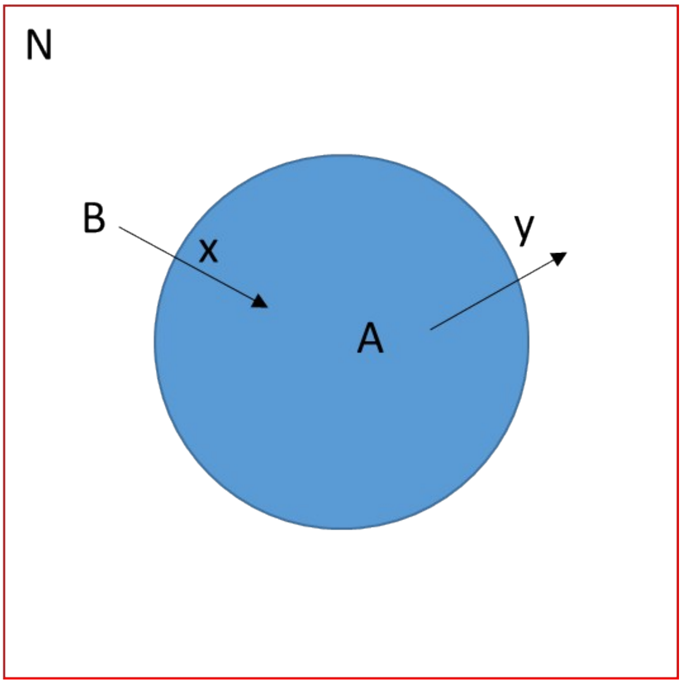

Figure S4. Schematic of simplified model for prediction of vesicle water exchange correlation function.

The system has N water molecules, including A water molecules inside the vesicle and B water molecules outside the vesicle. The entry rate x is defined as the ratio of water molecules entering the vesicle per unit time to water molecules outside the vesicle, while the escape rate y is defined as the ratio of water molecules get out from the vesicle per unit time to water molecules inside the vesicle. As shown in eq 1..

$$x = \frac{\Delta water_{in}}{\Delta t} \div (N - A), \qquad y = \frac{\Delta water_{out}}{\Delta t} \div A \tag{1}$$

When the system is stable, $\Delta water_{in}$ = $\Delta water_{out}$, which is considered as the exchanged water. And x and y are in the follow relationship,

$$Ay = (N - A)x \tag{2}$$

A_0 is the number of water molecules inside the vesicle at 0. At time t, some water of A_0 escaped to the outside, which is B(t), the remaining water is the A(t), so the distribution of A_0 is as follow,

$$A_0 = A(t) + B(t) \tag{3}$$

From time from *t* to *t+Δt*, the change of A is described as follow,

$$A\left(t+\Delta t\right)-A\left(t\right)=\left[-A\left(t\right)y+B\left(t\right)x\right]\Delta t \tag{4}$$

Then

$$\frac{dA\left(t\right)}{dt}=\left[-A\left(t\right)y+B\left(t\right)x\right] \tag{5}$$

Eliminate the B(t) by A_0-A(t), the differential equation for the change of the vesicle water are shown,

$$\frac{dA\left(t\right)}{dt}+\left(x+y\right)A\left(t\right)=A_0 x \tag{6}$$

The equation can be solved, and the general solution is eq(x),

$$A\left(t\right)=ce^{-(x+y)t}+\frac{A_0^2}{N} \tag{7}$$

Bring the value A(t) = A_0 at time 0, we got the parameter c

$$t=0, A\left(t\right)=A_0 \Rightarrow c=A_0-\frac{A_0^2}{N} \tag{8}$$

Therefore, $A\left(t\right)=A_0 e^{-\frac{t}{T_0}}+\frac{A_0^2}{N}\left(1-e^{-\frac{t}{T_0}}\right), T_0=\frac{1}{x+y}=\frac{A}{Nx}$ 9

Considered the average water molecules (A) in simulations instead the theoretical stability water molecules (A_0), the time correlation function of C(t) could be descripted as follow,

$$C\left(t\right)=e^{-\frac{t}{T_0}}+\frac{A}{N}\left(1-e^{-\frac{t}{T_0}}\right) \tag{10}$$