Electronic Supplementary Material (ESI) for Soft Matter.

± ± Migration of phospholipid vesicles in response to OH^- stimuli

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Supporting Information:

S1: Response of DOPC vesicles to the micro-injection of NaOH solution

Video S1: Micro-injection of 10 mM NaOH solution

This movie shows the real time observation of the migration of DOPC vesicles induced by a micro-injection of 10 mM NaOH solution with 5 hPa. The tip of a micro-pipette is labeled with a green arrow head. Elapsed time since the start of the injection is shown at the upper left of this movie. The scale bar shows 30 μm.

S2: Response of DOPC vesicles to the micro-injection of NaCl solution

Video S2: Micro-injection of 10 mM NaCl solution

This movie shows the response of DOPC vesicles subjected to a micro-injection of 10 mM NaCl solution with 5 hPa. Elapsed time since the start of the injection is shown at the upper left of this movie. The scale bar shows 30 μm.

S3: Examination of Marangoni convection in vesicle membrane

Video S3: Motion of small domains on a DOPC/DPPC (6/4) vesicle in its migration

This movie shows the migration of a phase separated binary vesicle induced by an injection of 10 mM NaOH with 5 hPa. The binary vesicle was composed of DOPC and DPPC with a mixing ratio of DOPC/DPPC=6/4. The experiment was performed at room temperature, where the binary vesicle shows the phase separation into a liquid phase rich in DOPC (bright region in the movie) and a solid phase rich in DPPC (dark domains in the movie). Elapsed time since the start of the injection is shown at the upper left of this movie. The scale bar shows 20 μm.

S4: The effect of the OH^- stimuli on the domain dynamics

It is well known that in the high pH region OH^- ions hydrolyze the glycerol group in the phosphatidylcholine.[1-4] This hydrolysis might affect the domain dynamics. The amount of the lyso-PC produced by the hydrolysis reaction is given by

$$[\mathrm{LPC}] = [\mathrm{PC}]_0 \{1 - \exp(-k_1 C_{\mathrm{OH}} t)\}\ , \qquad \text{(S1)}$$

where $[PC]_0$ is the concentration of PC lipids before the micro-injection, k_1 is the rate constant of the hydrolysis reaction having 10^{-1}–10^{-3} $M^{-1}s^{-1}$,[5] C_{OH} is the concentration of OH^- at the membrane surface, and t is the time. When we micro-inject 10 mM NaOH solution (pH 12), the lyso-PC concentration at the tip of the pipette (the vesicle stay at the tip for ~ 10 s at most) is about 10^{-2} – $10^{-4}[PC]_0$, which does not affect the phase behavior significantly. In fact domains survive after the vesicle reaches the tip as shown in Video S4. When the vesicle reaches the tip, the direct asymmetric pH stimulus induces convection in the membrane due to the localized steep pH gradient. It should be noted that this convection is not the uni-directional flow. When the vesicle is released from the tip, the convection disappears and domains resume the Brownian motion.

Video S4: Motion of small domains on a DOPC/DPPC (6/4) vesicle after reaching the tip of a micro-pipette

The experimental condition is same as that of video S3. Elapsed time since the start of the injection is shown at the upper left of this video. The scale bar shows 30 μm. The tip of the micro-pipette is shown by a yellow arrowhead.

S5: Response of DOPC vesicle and polystyrene colloid mixture subjected to OH^- stimuli

Video S5: Micro-injecion of 10 mM NaCl to DOPC vesicle and polystyrene colloid mixture

We demonstrate the difference in migration mechanism between the vesicles and the polystyrene particles by using a mixed sample. When we micro-injected 10 mM NaCl solution to the vesicle and the colloid located at ~ 30 μm apart from the tip, the colloid migrated toward the tip, whereas the vesicle went away slowly following the injection flow. This difference originates from the difference in the driving mechanism. The vesicles are driven by the surface tension gradient caused by the hydrolysis of PC lipids due to OH^- ions, whereas colloids are driven by the diffusiophoresis mechanism. The micro-injection was performed with 15 hpa of the injection pressure. The scale bar in the video shows 30 μm.

S6: Contact angle measurement

Here we describe notes for the measurement of the contact angle on supported lipid bilayer. For the contact angle measurement, we prepared the well cleaning glass substrate, where water droplets show complete wetting (contact angle $\varphi \sim 0$), and then formed the supported bilayer on it using the standard vesicle fusion technique.[6-9] Since we cannot control the humidity of the sample, the surface state of the membrane is different for every measurement, which might be responsible for the large error shown in Fig. 11. To minimize the error of contact angle, we included a standard sample (pure water) in the

measurements within the same day and normalized the data using the contact angle of the pure water. As an example we show time dependence of the contact angle for pure water and 100 mM NaOH solution droplet in Fig. S1. For both samples obtained contact angle decreases rapidly during first 10 sec and then gradually approaches to the equilibrium value. Here we adopted the contact angle at t = 30 sec. The obtained pH dependence of the contact angle of NaOH solution on the supported lipid bilayer is shown in Fig. 11. We fitted the pH dependence with a linear function and obtained $\varphi = -7.13(\pm 1.35)C_{\infty}^{\mathrm{OH}} + 0.78(\pm 0.05)$.

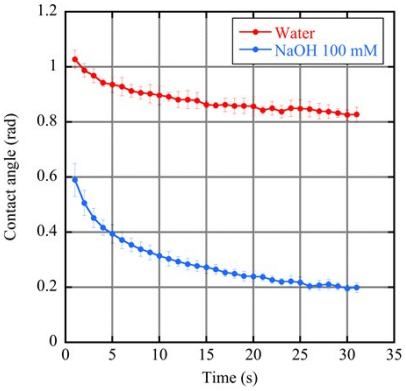

Fig. S1 Time dependence of contact angles for pure water and 100 mM NaOH solution on the SLB.

Another important point is lipid transfer from SLB to water phase.[10] When we drop a water droplet on the SLB, lipids in upper monolayer might transfer from SLB to water droplet as shown in Fig. S2. Then to evaluate the gradient of the surface tension, $\partial\gamma_{\mathrm{lg}} / \partial C_{\infty}^{\mathrm{OH}}$, (eqn. (22) in the text)

$$\frac{\partial\gamma}{\partial C_{\infty}^{\mathrm{OH}}} = -\frac{\partial\gamma_{\mathrm{lg}}}{\partial C_{\infty}^{\mathrm{OH}}}\cos\varphi + \gamma_{\mathrm{lg}}\sin\varphi\frac{\partial\varphi}{\partial C_{\infty}^{\mathrm{OH}}}, \qquad \text{(S2)}$$

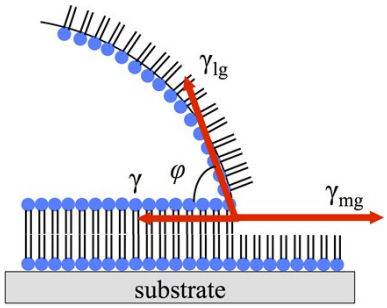

Fig. S2 Schematic representation of contact angle measurement.

we have to measure the surface tension between water phase including lipids and air as a function of C_{∞}^{OH}. We measured the surface tension of DOPC LUV suspension as a function of NaOH concentration using pendant droplet method (DM-501, Kyowa Interface Science) as shown in Fig. S3. The measured surface tension, γ_{lg}, is independent of the pH and has the same value of pure water of 73 mN/m. Then the gradient of the surface tension is given by (eqn. (23) in the text)

$$\frac{\partial\gamma}{\partial C_{\infty}^{\mathrm{OH}}} = \gamma_{\mathrm{lg}}\sin\varphi\frac{\partial\varphi}{\partial C_{\infty}^{\mathrm{OH}}}. \qquad \text{(S3)}$$

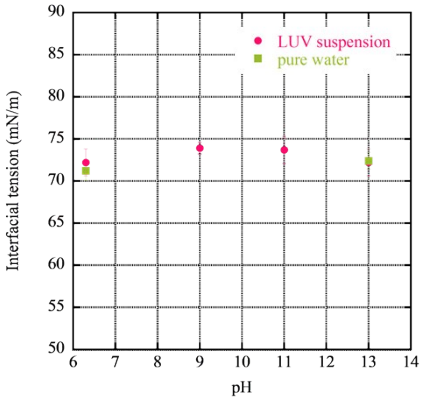

Fig. S3 pH dependence of surface tension for LUV suspension and pure water.

S7: Migration velocity calculated from ion binding model

Ion binding between OH^- and phospholipid head group is another candidate to explain the observed decrease of the contact angle (Fig. 11). The ion binding equilibria between the head group of phospholipid and OH^- are given by

$-PO^- + H^+ \Leftrightarrow -PO^- - H^+$ (A)

(A^-) (AH)

$-N^+(CH_3)_3 + OH^- \Leftrightarrow -N^+(CH_3)_3 - OH^-$ (B)

(B^+) (BOH)

These equilibria are governed by the dissociation constants[11]

$$K_A = \frac{a_{AH}}{a_{A^-} a_{H^+}} = 10^{2.58} \quad \text{(S4)}$$

$$K_B = \frac{a_{BOH}}{a_{B^+} a_{OH^-}} = 10^{8.31} \quad \text{(S5)}$$

In this case the surface tension of the membrane, γ, is expressed by the sum of each component contribution[12],

$$\gamma = \gamma^0_{A^-}\left(\frac{1}{1+K_A a_{H^+}}\right) + \gamma^0_{AH}\left(\frac{K_A a_{H^+}}{1+K_A a_{H^+}}\right) + \gamma^0_{B^+}\left(\frac{1}{1+K_B a_{OH^-}}\right) + \gamma^0_{BOH}\left(\frac{K_B a_{OH^-}}{1+K_B a_{OH^-}}\right), \quad \text{(S6)}$$

where $\gamma^0_{A^-}$, γ^0_{AH}, $\gamma^0_{B^+}$, and γ^0_{BOH} are the specific interfacial energy density of the membrane components, and a_{H^+}, and a_{OH^-} are the surface concentrations of hydrogen and hydroxyl ions, respectively, and a_{AH}, a_{A^-}, a_{BOH}, and a_{B^+} are the surface concentrations of the membrane components. The estimated concentration gradient of the surface tension at high pH region (pH 10 ~ 13) using eq. (S6) gives completely different migration velocity profile as shown in Fig. S4. Then at present we consider that the hydrolysis of phospholipids is responsible for the observed migration.

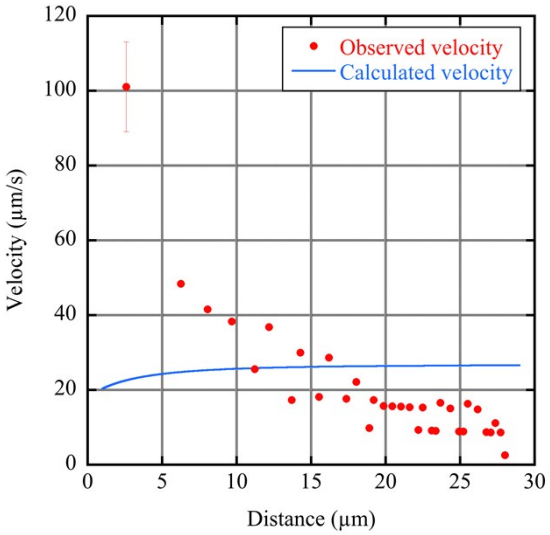

Fig. S4. Migration velocity obtained by ion binding model.

S8: Comparison of contact angles on DOPC membrane between NaOH and NaCl solutions.

The migration of vesicles is observed for micro-injection of NaOH solution, whereas NaCl solution does not drive the vesicles. According to the surface tension gradient model, this difference attributes to the effect of OH^- on the surface tension of DOPC membrane. Figure S5 shows concentration dependence of contact angles of NaCl and NaOH solution droplets on supported DOPC bilayer. The contact angle on DOPC membrane decreases with increase of NaOH concentration, whereas it is independent of NaCl concentration. Thus OH^- ions are responsible for the observed migration.

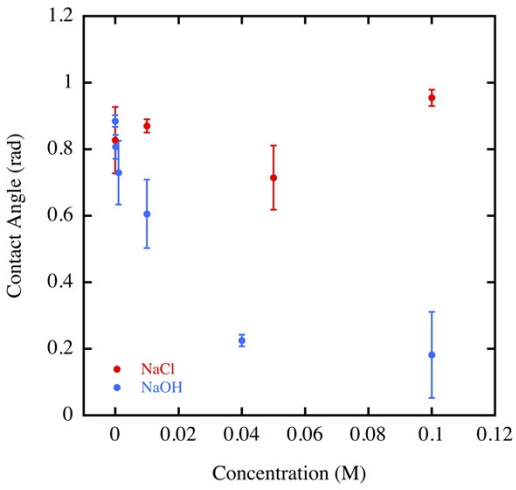

Fig. S5 Concentration dependence of contact angles of NaCl and NaOH solution droplets on supported lipid (DOPC) bilayer.

S9: Migration of a DOPC vesicle with an important excess area coupled with its deformation

Video S6: Migrating vesicle with shape deformation

This movie shows the response of a vesicle with an invaginated tube subjected to a micro-injection of 10 mM NaOH with 15 hPa. Elapsed time since the start of the injection is shown at the upper left of this movie. The scale bar shows 20 μm.

S10: Pulling force acting on a vesicle induced by a micro-injection of NaOH solution

Pulling force acting on the center of the vesicle induced by micro-injection of 10 mM NaOH calculated by eqn. (14) and (15) in the main text is shown Fig. S6. The force acting on the vesicle increases exponentially as the vesicle approaches the tip and reaches 5 pN at the distance of 10 μm.

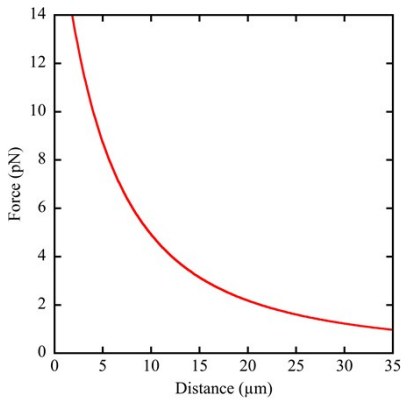

Fig. S6 Pulling force acting on a vesicle with the radii of 10 μm calculated using eqn. (14) and (15) in the main text. The concentration of injected NaOH solution is 10 mM.

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