

**Supporting Information for:**

**From seawater to saline: novel lower critical solution temperature phase transition materials effectively control osmosis by mild temperature change**

**Experimental Procedures**

**Synthesis:** Thermosensitive solutes were synthesized by a previously described method with some modifications.<sup>8</sup> Tris(2-aminoethyl)amine (TAEA) (Aldrich, USA) (10.0 mL; 64.0 mmol) was dissolved in 400 mL of 1M NaHCO<sub>3</sub> in methanol. *n*-Butyric anhydride and isobutyric anhydride were slowly added to the solution at 0°C with vigorous stirring. After 1 hr stirring at 0°C, the solution was further stirred for 18 hr at ambient temperature. The pH of the reaction mixture was adjusted to about 11 with 1M NaOH, and the mixture was extracted with methylene chloride (×3). The organic extracts were dried with MgSO<sub>4</sub>, and evaporated under vacuum to produce the final product, acylated TAEA as a white solid. Val-TAEA was synthesized from valeroyl chloride and TAEA in methylene chloride solvent with pyridine by a similar method as described above. The <sup>1</sup>H-NMR spectra of acylated TAEA derivatives are shown in **Figure S1**.

**Characterization of thermosensitive solutes:** The LCST phase transitions of solutions containing thermosensitive solutes were measured by a UV-Vis spectrophotometer. By increasing the temperature, the transmittance at a wavelength of 600 nm was measured to determine the phase transition temperature. The phase transition temperature was defined at which the transmittance was below 5%.

**Analysis of osmotic flow:** The osmotic flow was measured using a handmade U-shaped glass tube. A semipermeable membrane (diameter: 3.3 cm) made from cellulose trifluoroacetate (Hydration Technology Innovation (HTI), USA) was placed in the middle of the tube and

each tube was filled with *n*Bu-TAEA solutions or NaCl solutions, respectively. The selective layer of the semipermeable membrane was faced toward the *n*Bu-TAEA solutions. The temperature was controlled by thermostat water bath. Osmotic water flux from NaCl solutions to *n*Bu-TAEA solutions was calculated from the volumetric change of each solution during 1 hr after 1 hr-stabilization at 21(±2)°C. (In the case of 1.8M and 2.2M *n*Bu-TAEA, the flux at 18(±2)°C was measured instead.) The reversal of osmotic flow was similarly calculated using the volumetric change at 55(±2)°C. The graphic interchange format (GIF) file (**Figure S3**) was made from the osmosis between 0.50M NaCl and 1.8M *n*Bu-TAEA.

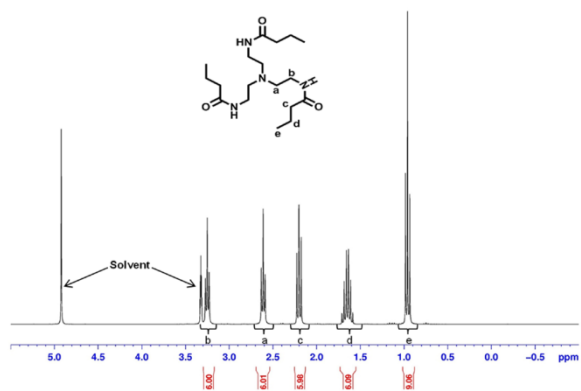
The remaining *n*Bu-TAEA concentrations in the H<sub>2</sub>O-rich phase after phase separation were measured using HPLC. The penetration of NaCl and solute molecules through the semipermeable membrane was determined by using an inductively coupled plasma emission spectrometer and HPLC, respectively. The permeation percentage of solute A (%P<sub>A</sub>) was calculated by an equation:

$$\%P = \frac{C_A' \times V}{C_A \times v} \times 100$$

where C<sub>A</sub> is the initial concentration of A solution, v is the volume of permeated water, C<sub>A</sub>' is the concentration of A on the other side of the membrane after the osmosis, and V is the volume of the solution of the other side of the membrane. The permeation percentage is shown in **Table S2**.

**Figure S1**  $^1\text{H-NMR}$  spectra of (a) *n*Bu-TAEA, (b) *i*Bu-TAEA, (c) Val-TAEA in  $\text{D}_2\text{O}$ .

**Figure S1a**



**Figure S1b**

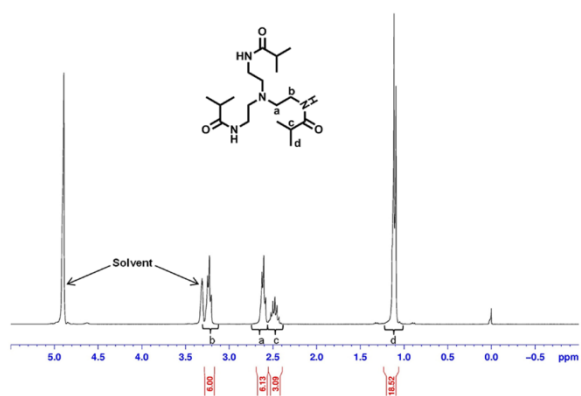
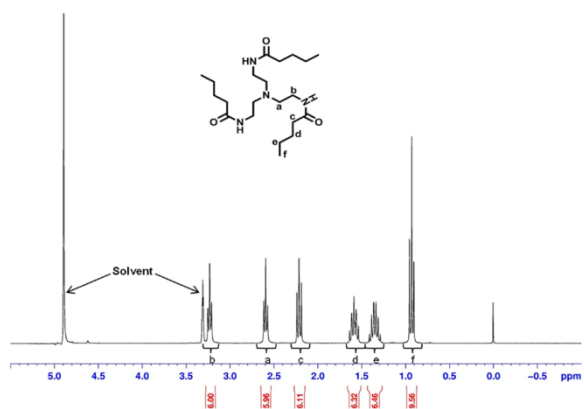


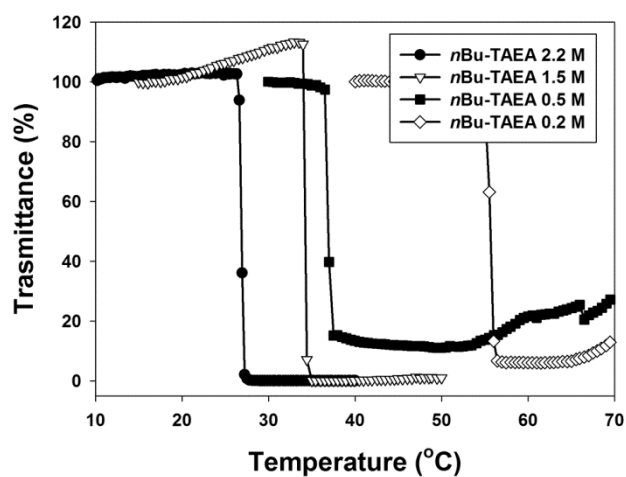
Figure S1c



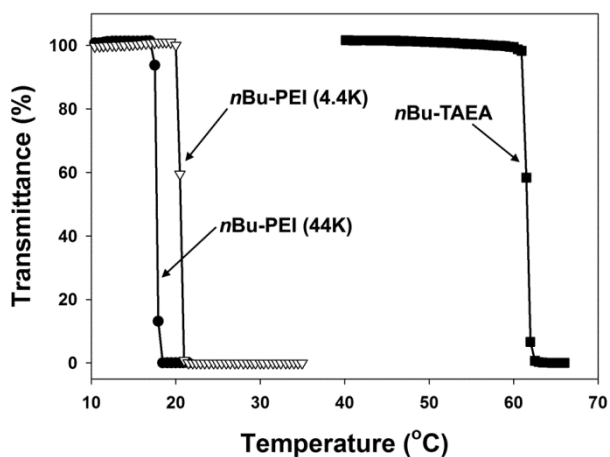
**Figure S2** (a) Concentration-phase transition temperature relationship of *n*Bu-TAEA.<sup>a</sup>

<sup>a</sup>The molarity was calculated on the basis of the density at 25°C. (b) Molecular weight-phase transition temperature relationship of thermosensitive solutes. The phase transition was measured at the same mass concentration of 70 g/L.

**Figure S2a**

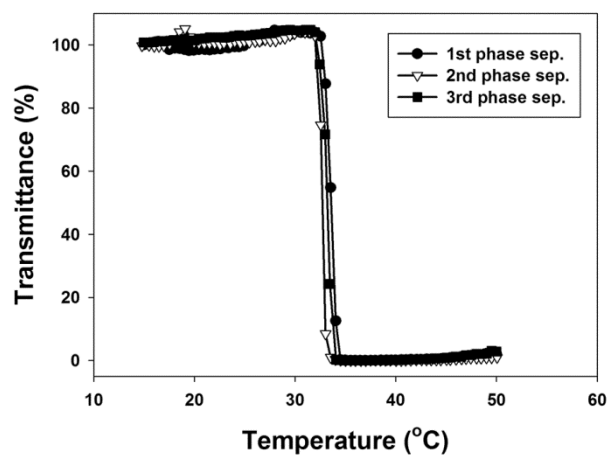


**Figure S2b**

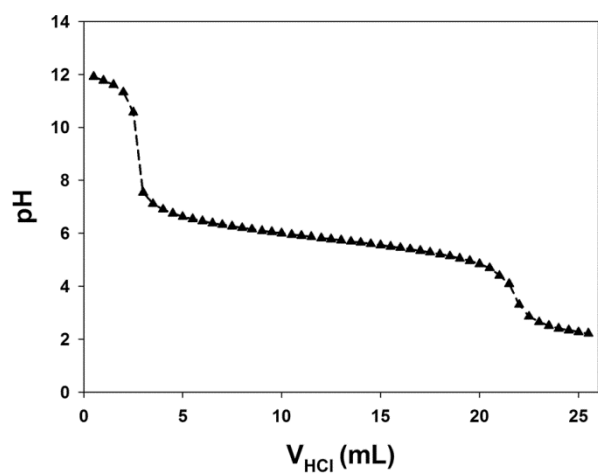


**Figure S3** Graphic interchange format (GIF) animation of temperature controlled osmosis based on *n*Bu-TAEA. The GIF file was made from 27 photos during the osmosis for 13 hrs.

**Figure S4** Reproducibility of the phase transition of *n*Bu-TAEA at the concentration of 1.5M.



**Figure S5** Titration profile *n*Bu-TAEA at the concentration of 0.1M.





**Table S1.** Solubility and phase transition temperature of *N*-acyl TAEA derivatives.

N-acyl TAEA derivatives	Molecular weight	Diffusion coefficient ( $D/10^{-9} \text{ m}^2\text{s}^{-1}$ ) <sup>a</sup>	Solubility (mol/L) <sup>b</sup>	Phase transition temperature (°C) <sup>c</sup>	
				at 0.20M	at the max. concentration
<i>n</i> Bu-TAEA	356.5	0.29	2.2	54	23
<i>i</i> Bu-TAEA	356.5	0.31	0.28	39	33
Val-TAEA	398.6	0.26	0.074 <sup>d</sup>	-	17

<sup>a</sup>The diffusion coefficient was calculated by using Stokes-Einstein equation assuming that *N*-acyl derivatives have spherical shape.

<sup>b</sup>The molarity was calculated on the basis of the density at 25°C.

<sup>c</sup>The phase transition temperature is corresponding to 1.0% decrease of the transmittance at 600 nm.

<sup>d</sup>The solubility of Val-TAEA was measured in the water:ethanol (10:1) cosolvent.

**Table S2.** Permeation/rejection percentage of NaCl and *n*Bu-TAEA through the semipermeable membrane.

Permeated solute	Initial concentration (mol/L) <sup>a</sup>	Transferred concentration (mol/L) <sup>a</sup>	Permeation [rejection] (%)
NaCl	0.30	0.0048 <sup>b</sup>	1.6 [98.4]
<i>n</i> Bu-TAEA	1.5	0.024 ( $\pm 0.0035$ ) <sup>c</sup>	1.6 [98.4] ( $\pm 0.22$ )

<sup>a</sup>The molarity was calculated on the basis of the density at 25°C. <sup>b</sup>The NaCl concentration was measured by inductively coupled plasma emission spectrometer. <sup>c</sup>The concentration of *n*Bu-TAEA was measured by HPLC.