

Amino acid ionic liquid-based facilitated transport membranes for CO₂ separation

Shohei Kasahara, Eiji Kamio, Toru Ishigami and Hideto Matsuyama

*Center for Membrane and Film Technology,
Department of Chemical Science and Engineering, Kobe University,
1-1 Rokkodai-cho, Nada-ku, Kobe, Hyogo 657-8501, Japan.
Fax: +81-78-803-6180; Tel: +81-78-803-6180;
E-mail: matuyama@kobe-u.ac.jp*

SUPPLEMENTARY INFORMATION

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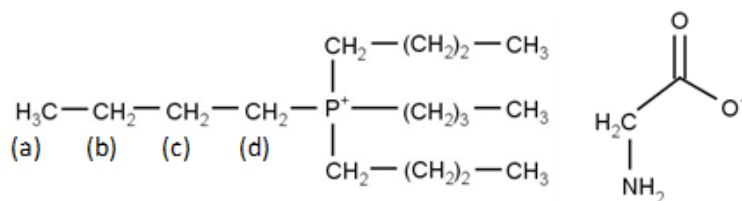
(1) Materials and general procedures for membrane preparation

Tetrabutylphosphonium hydroxide (40 wt% in water), 1-Ethyl-3-methylimidazolium hydroxide (10 wt% in water) and 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($\geq 98\%$) were purchased from Sigma-Aldrich Co. Glycine (99.8%) and DL-2,3-Diaminopropionic acid hydrochloride ($>98.0\%$) were purchased from Tokyo Chemical Industry Co. Methanol (99.8%) was purchased from Wako Pure Chemical Industry Ltd. Acetonitrile (99.90%) was purchased from Sigma-Aldrich Co. They were used as received. Poly(vinyl alcohol)-poly(acrylic acid) copolymer (PVA/PAA copolymer) was supplied from Kyodo Yakuin Co. Ltd. The CO₂ and N₂ gases of 99.9% purity were used for the gas permeation tests. A hydrophilic PTFE microporous membrane was purchased from Sumitomo Electric industries, Ltd. It has an average pore size of 0.2 μm and a film thickness of 37.5 μm . It was used as a support of the facilitated transport membrane with DL-2,3-Diaminopropionic acid as a CO₂ carrier (DAPA-FTM) membranes prepared in this study. On the other hand, a hydrophilic PTFE membrane filter with 0.1 μm of an average pore size and 37.5 μm of film thickness was used as a support of the amino acid ionic liquid-based facilitated transport membranes and [Emim][Tf₂N]-based supported ionic liquid membrane.

Tetrabutylphosphonium glycine ([P(C₄)₄][Gly]) and 1-ethyl-3-methylimidazolium glycine ([Emim][Gly]) were synthesized according to literature procedures.⁹ The structures of the resulting [P(C₄)₄][Gly] and [Emim][Gly] were confirmed by ¹H NMR spectroscopy (Bruker Advance 500, Bruker BioSpin) and FT-IR (ALPHA FT-IR Spectrometer, Bruker Optics) measurements. ¹H-NMR data of [Emim][Gly] and FT-IR data of [P(C₄)₄][Gly] were almost consistent with those published in the literatures.^{9,10} The resulted ¹H-NMR results and IR spectra are shown below.

[P(C₄)₄][Gly]

¹H-NMR (DMSO, δ /ppm relative to TMS): δ = 0.92 (t, 12H, J = 7.1; a), 1.37-1.50 (m, 16H; b,c), 2.08 (s, 1H; DMSO), 2.16-2.22 (m, 8H; d), 2.50-2.51 (m, 1H, acetonitrile), 2.64 (s, 2H; N-CH₂-CO₂), 3.16 (s, 3H; methanol), 3.39 ppm (broad; water)



[Emim][Gly]

¹H-NMR (DMSO, δ/ppm relative to TMS): δ = 1.41 (t, 3H, J = 7.4; a), 2.51 (s, 0H; DMSO), 2.73 (s, 2H; N-CH₂-CO₂), 3.20 (broad; water), 3.87 (s, 3H; b), 4.22 (q, 2H, J = 11.2; c), 7.75 (s, 1H; d), 7.84 (s, 1H; e), 9.68 (s, 1H; f)

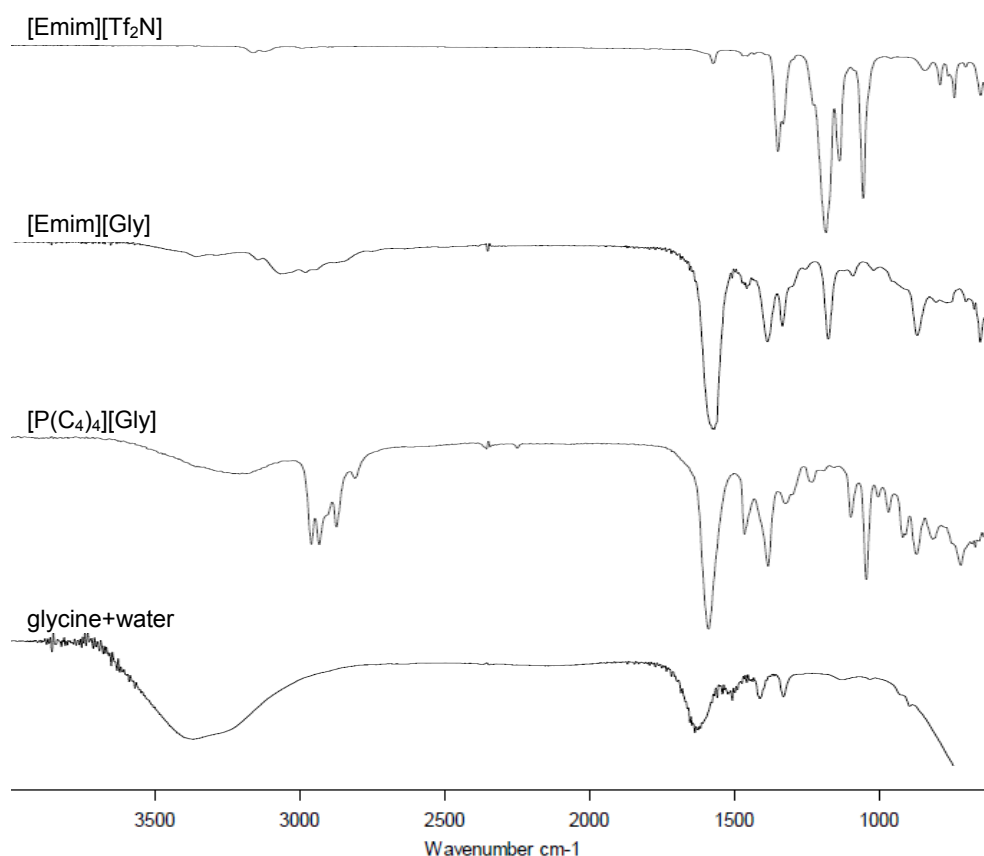
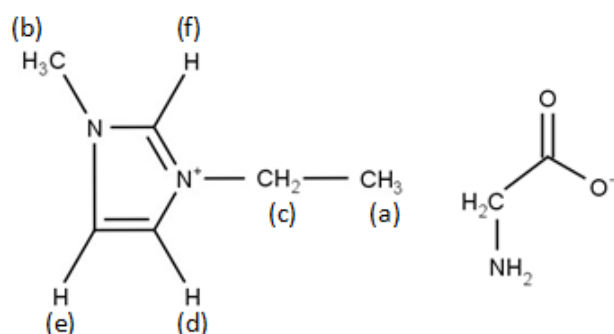


Fig. S1 FT-IR spectra of [Emim][Tf₂N], [Emim][Gly], [P(C₄)₄][Gly] and glycine aqueous solution.

The details of preparation method of amino acid ionic liquid-based facilitated transport membranes and the supported ionic liquid membrane of [Emim][Tf₂N] was as follows. A hydrophilic PTFE microporous membrane was immersed into the ionic liquid ([P(C₄)₄][Gly], [Emim][Gly] or

[Emim][Tf₂N]) and whole of them were decompressed for 1,800 s in order to completely replace air in the PTFE membrane to ionic liquid. The ionic liquid impregnated PTFE membrane was taken out and wiped an excess ionic liquid on the surface.

The details of preparation method of the facilitated transport membrane with _{DL}-2,3-Diaminopropionic acid as a CO₂ carrier (DAPA-FTM) was as follows. PVA/PAA copolymer, DAPA and CsOH were dissolved in water by stirring the solution for 24 h at 298 K. The molar ratio of CsOH to DAPA was adjusted to 2 so that two amine groups in DAPA might be converted to deprotonated amine groups. The prepared solution was centrifuged at 5,000 rpm at room temperature for 1,800 s to remove small bubbles, which might cause membrane instability. Then the solution was cast onto a hydrophilic microporous PTFE membrane using an applicator with a gap setting of 500 μm. The cast membrane was dried at 298 K overnight. The concentrations of copolymer and DAPA in the dried membrane were 52.0 and 24.0 wt.%, respectively. Finally, the coated layer was crosslinked by heat treatment for 2 h at 393 K for crystallization.

(2) General procedures for gas permeability testing

The schematic diagram of the experimental apparatus is shown in Fig. S2. The gas transport properties of the membrane were measured by using a flat-type permeation cell (Fig. S3) that was placed in a thermostat oven (YAMATO Scientific Co. Ltd., Japan) adjusted at a desired temperature. The permeation cell (GTR TEC Co., Japan) was made of stainless steel with an effective permeation area of 2.88 cm².

A model feed gas was prepared by mixing CO₂, N₂ and/or Steam. The flow rates of CO₂ and N₂ were controlled by mass flow controllers (Hemmi Slide Rule Co. Ltd., Japan), and the water flow rate was adjusted by a reciprocating metering pump (Nihon Seimitsu Kagaku Co. Ltd., Japan). The total flow rate of the feed gas was adjusted to 1.49×10^{-4} mol/s at 298 K, 101.3 kPa. The feed gas was pre-heated by a coiled heat exchanger and introduced into the cell. The feed side pressure was kept constant at atmospheric pressure.

Helium was supplied to the permeate side of the cell as a sweep gas through a coiled heat exchanger at the flow rate of 2.98×10^{-5} mol/s at 298 K, 101.3 kPa. The pressure in the sweep side was also kept constant at almost atmospheric pressure.

Water vapor in the streams from both the feed and permeate sides of the permeation cell was removed by condensers, and the flow rates of the dried streams were measured by soap-film flow meters (HORIBA STEC Ltd., Japan). The dried sweep gas was sent to a gas chromatograph (Shimadzu GC-8A, column: activated carbon, 1 m) to determine the composition of permeate. Each test was performed more than 5 h, the differences between the successively observed CO₂ and N₂ peak areas by GC became less than 1%, which suggested that the steady state was established. An example of time course of permeabilities of CO₂ and N₂ was shown in Fig. S4.

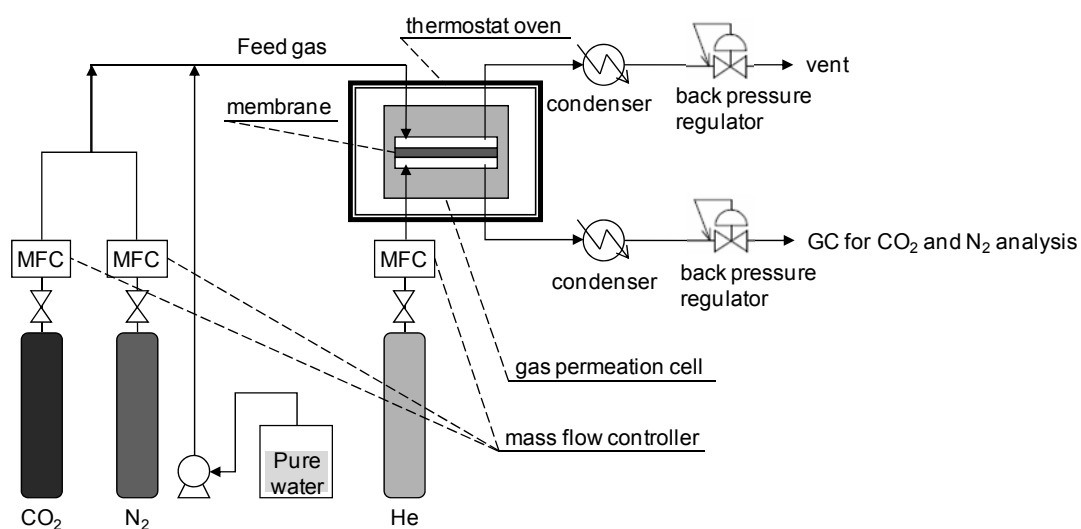


Fig. S2 Schematic diagram of the apparatus for gas permeation test

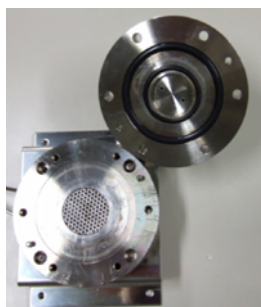


Fig. S3 Stainless steel flat-type permeation cell

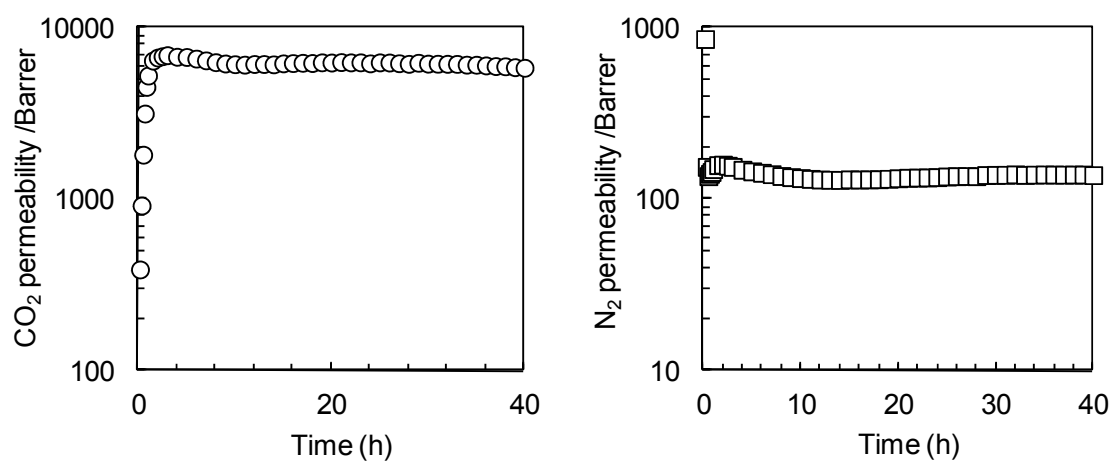


Fig. S4 Time course of (a) CO_2 and (b) N_2 permeability through [P(C₄)₄][Gly]-FTM ($T = 373.15$ K, $\text{CO}_2 = 10$ mol%, $\text{N}_2 = 90$ mol%, without moisture, $P_F = P_S = 101.3$ kPa)

(3) Measurement of water content of $[\text{P}(\text{C}_4)_4][\text{Gly}]$ and $[\text{Emim}][\text{Tf}_2\text{N}]$

Water content of $[\text{P}(\text{C}_4)_4][\text{Gly}]$ and $[\text{Emim}][\text{Tf}_2\text{N}]$ at 373 K under humid condition were measured by using a thermogravimetry-differential thermal analyzer with a humidity generator (TG-DTA/HUM, Rigaku Co., Japan). A desired amount of sample was set in the cell and dry nitrogen was fed initially. The temperature of the cell was heated to 423 K at 0.0167 K/s and kept constant for 10 h to remove water remained in each ionic liquid. Subsequently, the cell temperature was dropped to 373 K at 0.033 K/min and kept constant for 1 h to reach a steady state. After 1 h, humid gas of 2.5% relative humidity (RH) was introduced into the cell. The condition in the cell was kept for 5.5 h. The weight of the sample was continuously monitored. The water content in the ionic liquid at the condition was calculated from the weight difference to the dried ionic liquid at 423 K. Then, to measure the water contents in the different conditions, the RH was changed to 5.0%, 10.0% and 20.0% in order. Every measurement was performed for 5.5 h.

The raw data of the measurement of $[\text{P}(\text{C}_4)_4][\text{Gly}]$, $[\text{Emim}][\text{Gly}]$ and $[\text{Emim}][\text{Tf}_2\text{N}]$ are shown in Figs. S5, S6 and S7, respectively.

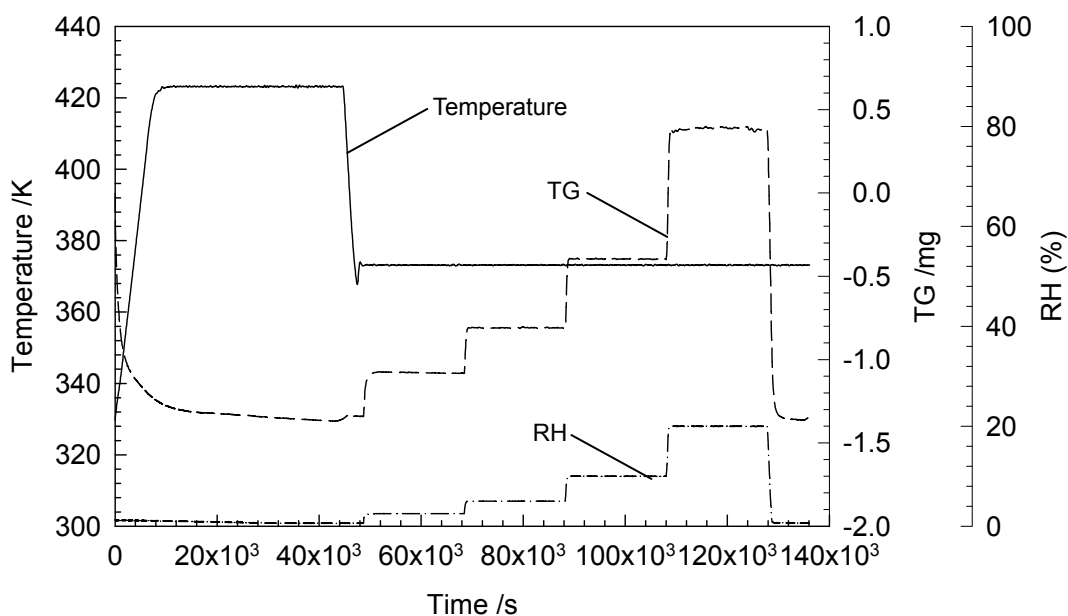


Fig. S5 Relationship among temperature, RH and TG of $[\text{P}(\text{C}_4)_4][\text{Gly}]$.

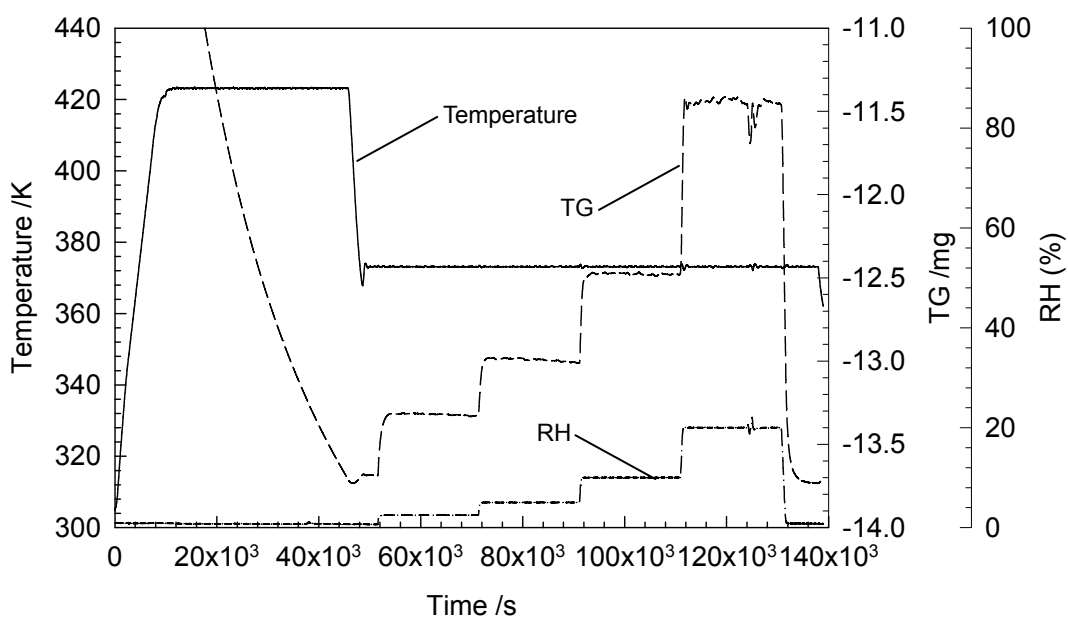


Fig. S6 Relationship among temperature, RH and TG of [Emim][Gly].

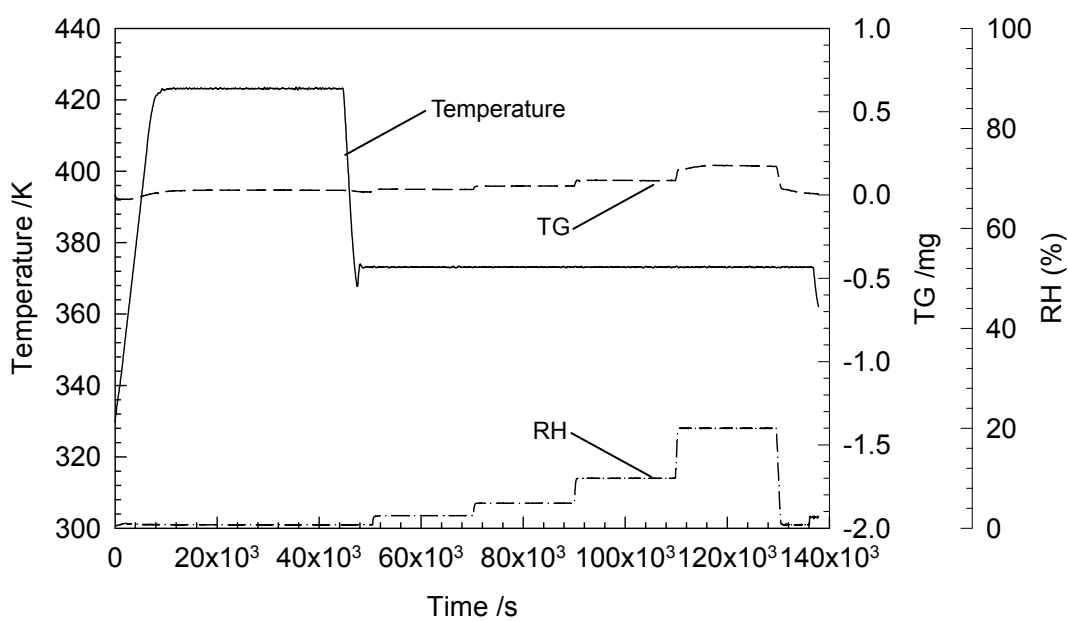


Fig. S7 Relationship among temperature, RH and TG of [Emim][Tf₂N].