

Electronic Supplementary Information (ESI)

**A New Solvent Polymeric Membrane Electrode incorporating
Poly(N-isopropylacrylamide) as a Polymer**

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All reagents were commercially available and used as such unless otherwise specified. Tetrahydrofuran (THF) was dried over sodium and distilled.

The composition of a potentiometric polymeric membrane incorporating poly(N-isopropylacrylamide) (PIPA) was 53.9 mg (28.0 wt%) of PIPA as a polymer, 132.0 mg (68.5 wt%) of 2-Nitrophenyl octyl ether (*o*-NPOE) as a membrane solvent, 4.8 mg (2.5 wt%) of 5,10,15,20-tetraphenyl porphyrin (**TPP**) as an ionophore, and 1.9 mg (1.0 wt%) of potassium tetrakis(4-chlorophenyl)borate (KTpClPB) as an anion excluder for the potentiometric cation-sensing membranes. The components were put into a 5 mL of sample glass tube and dissolved in ca. 3 mL of THF.

The composition of the thin poly(vinyl chloride) (PVC) liquid membrane for covering was 23.1 mg (28.7 wt%) of PVC as a polymer and 57.4 mg (71.3 wt%) of *o*-NPOE as a membrane solvent. A thin solvent PVC membrane was obtained by spontaneous evaporation of THF for a few days.

The PVC-PIPA-PVC potentiometric polymeric membrane was formed on the tip of the ISE body assembly with an electrode kit (DKK Co. Ltd., Tokyo) by a casting method: a thin solvent

PVC membrane was first casted on the tip of the electrode kit. Next, the potentiometric polymeric membrane incorporating PIPA was casted on a thin solvent PVC membrane. Finally, another thin solvent PVC membrane was casted on the potentiometric polymeric membrane incorporating PIPA. As a result, the PIPA potentiometric polymeric membrane was covered with thin solvent PVC membranes, obtaining the PVC-PIPA-PVC potentiometric polymeric membrane.

For comparison, the PIPA-free PVC potentiometric polymeric membrane was also prepared by same method. The composition of a potentiometric polymeric membrane was 53.9 mg (28.0 wt%) of PVC as a polymer, 132.0 mg (68.5 wt%) of *o*-NPOE as a membrane solvent, 4.8 mg (2.5 wt%) of **TPP** as an ionophore, and 1.9 mg (1.0 wt%) of KTpClPB as an anion excluder. The composition of a thin poly(vinyl chloride) (PVC) liquid membrane for covering was 23.1 mg (28.7 wt%) of PVC as a polymer and 57.4 mg (71.3 wt%) of *o*-NPOE as a membrane solvent.

The obtained PVC-PIPA-PVC and PIPA-free PVC potentiometric polymeric membrane-based ISEs were then conditioned in an aqueous 0.01 M AgNO₃ solution overnight. EMF measurements were performed on cells of type Ag–AgCl | 0.1 M AgNO₃ || membrane || sample solution | 0.1 M CH₃COOLi || 3.3 M KCl | AgCl–Ag using a pH/mV meter equipped with a double junction type Ag–AgCl reference electrode. The activity coefficients were calculated according to the Davies equation. EMF measurements of the PVC-PIPA-PVC and PIPA-free PVC potentiometric polymeric membrane-based ISEs were carried out in increasing AgNO₃ concentration at 25 and 40 °C. As shown in Fig. S1, the PVC-PIPA-PVC potentiometric polymeric membrane displayed near Nernstian responses at both 25 and 40 °C. The PIPA-free PVC potentiometric polymeric membrane-based ISE responded Ag⁺–activity changes with the slopes of 56.1 (for 25 °C) and 58.9 (for 40 °C) mV decade⁻¹ over the activity ranges from 10^{-4.5} (for 25 °C) and 10^{-5.0} (for 40 °C) to 10^{-4.5} M.

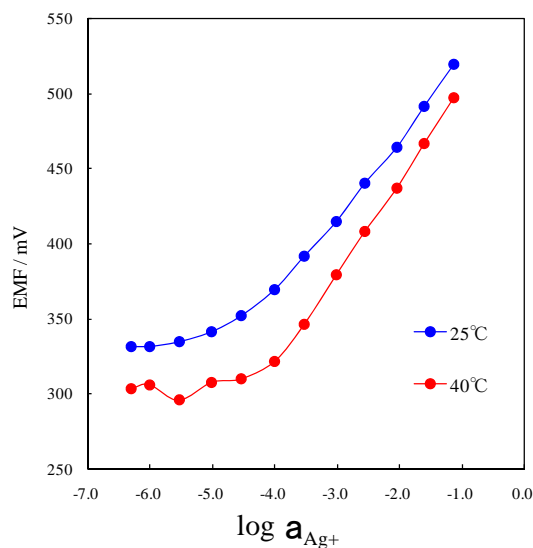


Fig. S1 EMF responses of the PVC-PIPA-PVC potentiometric polymer membrane-based ISE at 25 and 40 °C.

The selectivity coefficients were determined by the fixed interference method (FIM). Figure S2 illustrates the change of selectivity coefficients for Ag^+ of the PIPA-free PVC potentiometric polymer membrane-based ISE by heating from 25 and 40 °C.

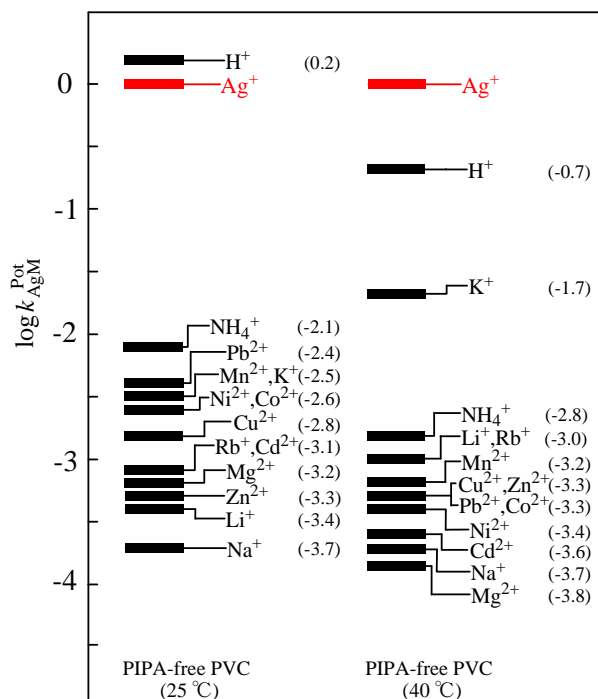


Fig. S2 Selectivity coefficients of the PIPA-free PVC potentiometric polymer membrane-based ISE at 25 and 40 °C.

Pulsed NMR measurements were carried out on JEOL JNM-MU-25 spectrometer operating at a frequency of 25 MHz. In all cases, one sheet of the above mentioned potentiometric polymeric membrane was arranged in a 10 mm ϕ NMR tube so that it took the pulse irradiation at the center. The free induction decay (FID) signals were recorded at probe temperatures 25 and 40°C. The spin-spin relaxation time T_2 values were estimated from a Hahn-Echo method (the 90°– τ –180° pulse sequence) with a pulse width (Pw1) of 2.2 μ s and a repetition time (Rep) of 4.0 s. Figure S3 shows the FID signal analyses of the PIPA-free PVC potentiometric polymeric membrane at 25 and 40°C. The proton spin-spin relaxation times T_2 and the fraction of each component were calculated by fitting the FID signal to the Weibull function.

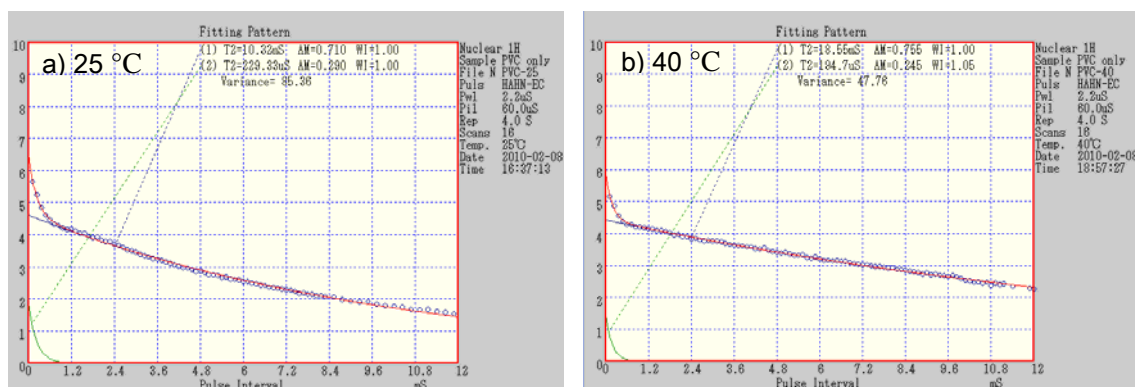


Fig. S3 FID signal changes of the PIPA-free PVC potentiometric polymeric membrane at (a) 25 and (b) 40 °C.