

Electronic Supplementary Information

Thermodynamics of ionic liquid evaporation under vacuum

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I. Decomposition temperature of OdMI-TFSI in air

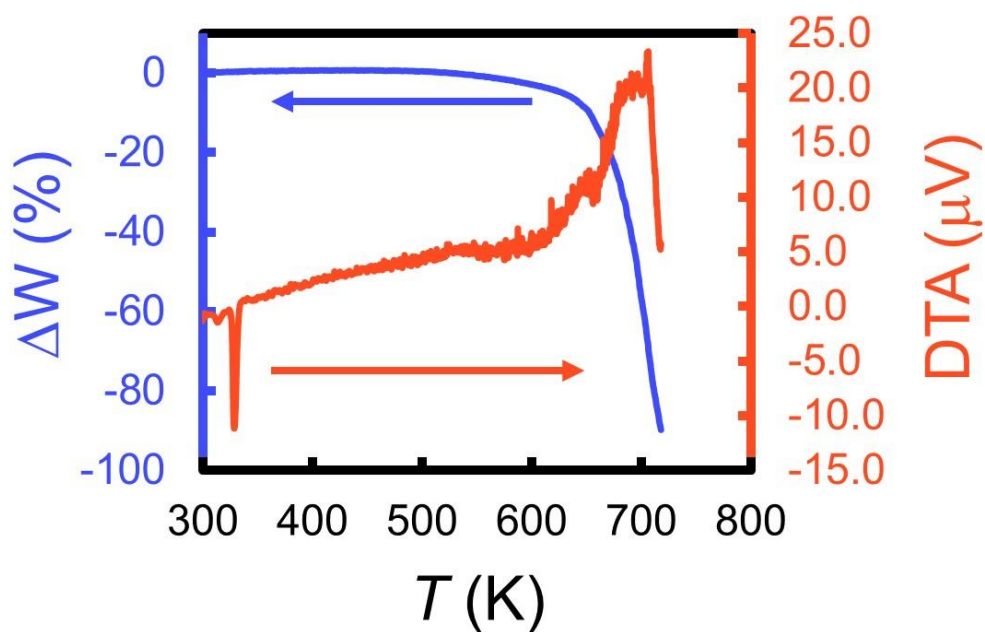


Fig. S1 TG/DTA results of OdMI-TFSI in air. The decomposition temperature of OdMI-TFSI was not available in the other literature. The weight loss and exothermic onset temperature (562 K) was determined as the decomposition temperature of the IL. This value is listed in Table 1 of the main article. The endothermic peak around 320 K is due to the melting of OdMI-TFSI.

II. Determination of coagulation factor α

According to the Hertz-Knudsen-Langmuir equation, the evaporation rate of liquid is expressed as:

$$r = \alpha p \sqrt{\frac{M}{2\pi RT}} \quad (\text{S1})$$

where r is the evaporation rate, α is the coagulation factor ($0 < \alpha \leq 1$), p is the saturation vapour pressure, M is the molecular mass, R is the gas constant, and T is the absolute temperature. The coagulation factor means the hampering degree of evaporation by residual gas molecules. Under ultra-high vacuum, α may be regarded as 1; however, under low vacuum level or in air, α takes the value lower than 1, which causes the error of the saturation vapour pressure. Since the coagulation factor is an apparatus constant, we preliminarily determined the value.

According to the Clausius-Clapeyron equation, the external pressure and the boiling temperature are correlated as:

$$\ln \frac{p_2}{p_1} = - \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (\text{S2})$$

where T_1 and T_2 are boiling points under the external pressures of p_1 and p_2 , and ΔH is the evaporation enthalpy. Once the boiling point in air (1.01325×10^5 Pa) and the evaporation enthalpy are obtained, the boiling point under given external pressure can be calculated.

We selected eicosane ($\text{C}_{20}\text{H}_{42}$) as the standard compound with known boiling point in air (617.415 K) and evaporation enthalpy ($101.8 \text{ kJ}\cdot\text{mol}^{-1}$). Using these data and equation (S2), the boiling points of eicosane under given external pressures can be calculated (334.1, 389.2, 411.6, 536.1 K under 5×10^{-3} , 9×10^{-1} , 5×10^1 , and 5×10^3 Pa, respectively).

Next, we measured the TG data of eicosane under the above external pressures. The evaporation rates were then calculated from the following equation:

$$r = - \frac{1}{U} \cdot \frac{d\Delta W}{dt} = - \frac{1}{U} \cdot \frac{d\Delta W}{dT} \cdot \frac{dT}{dt} \quad (\text{S3})$$

Here, U is the cross section area of the sample cell ($1.40 \times 10^{-5} \text{ m}^2$), ΔW is the weight loss, and t is the time. The dT/dt corresponds to the heating rate ($2 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$). By applying the molecular weight of eicosane (282.5), the external pressure, and the evaporation rate and the estimated boiling point under the external pressure to equation (S1), α values could be obtained as summarized in Fig. S2 and Table S1.

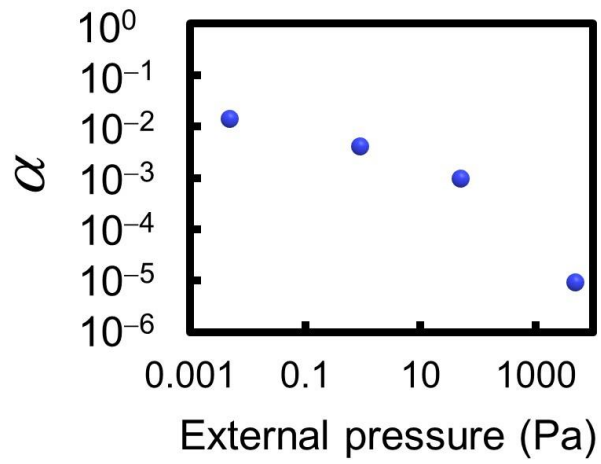


Fig. S2 The obtained coagulation factor versus the external pressure. The value asymptotically approach with 1 as the vacuum level increases.

Table S1 The coagulation factors. Note that these values are apparatus constants of our setup.

External pressure [Pa]	Coagulation factor
5×10^{-3}	1.39×10^{-2}
9×10^{-1}	3.96×10^{-3}
5×10^1	9.49×10^{-4}
5×10^3	9.28×10^{-6}

III. TG measurement of the vaporized EMI-TFSI

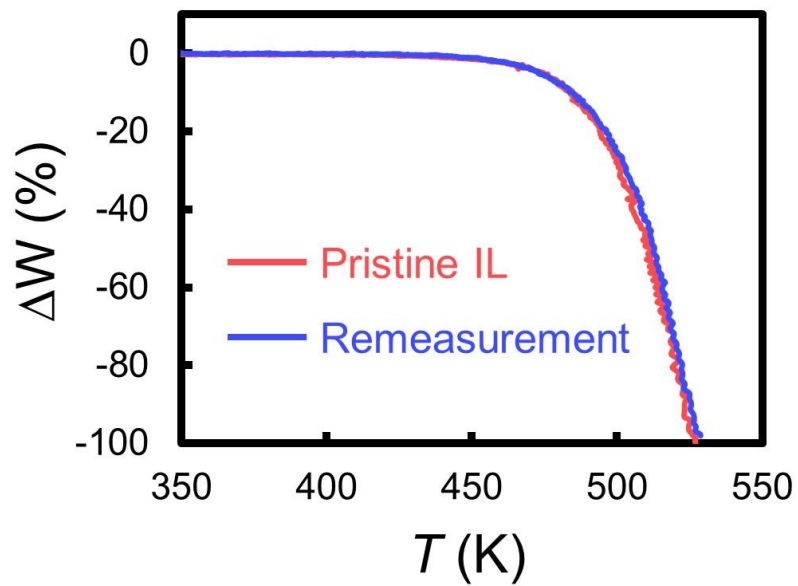


Fig. S3 Comparison of the TG data of pristine EMI-TFSI and once vaporized EMI-TFSI under 5×10^{-3} Pa. The remeasurement was performed after collecting the deposited EMI-TFSI inside of the glass tube of the TG setup.

IV. Saturation vapour pressures of EMI-TFSI under various pressures

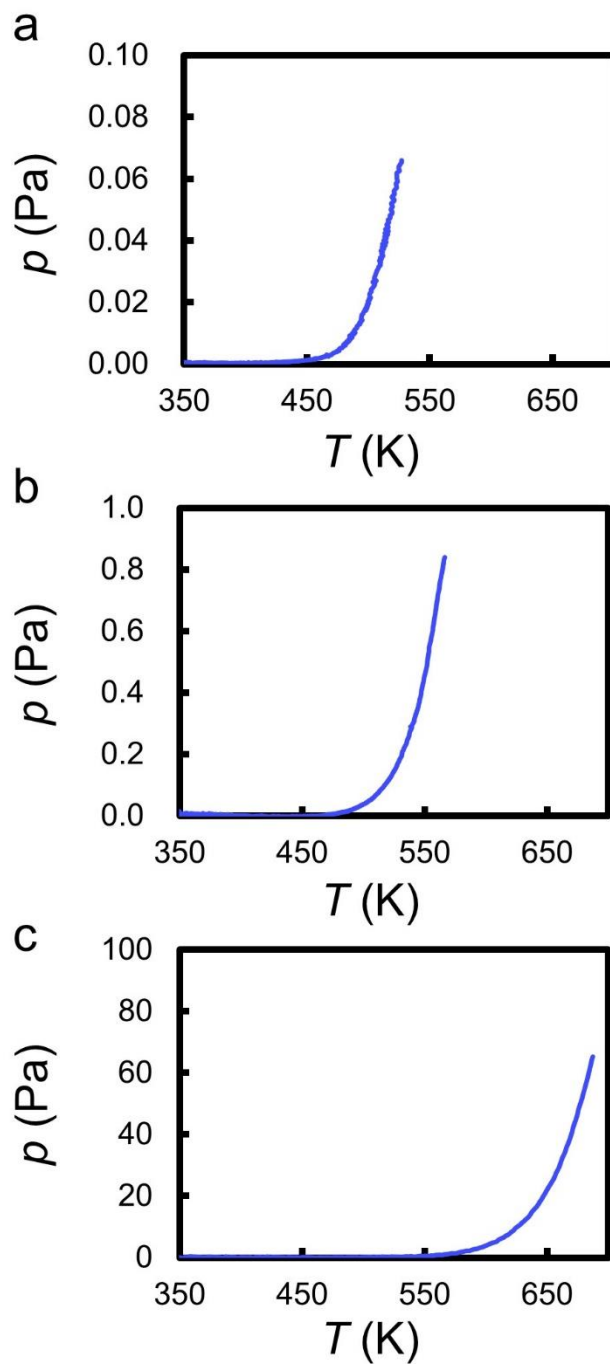


Fig. S4 Saturation vapour pressure versus temperature obtained from the TG data and the Hertz-Knudsen-Langmuir equation under (a) 5×10^{-3} , (b) 5×10^1 , and (c) 5×10^3 Pa, respectively.

V. Deriving the empirical equation (5) displayed in the main article

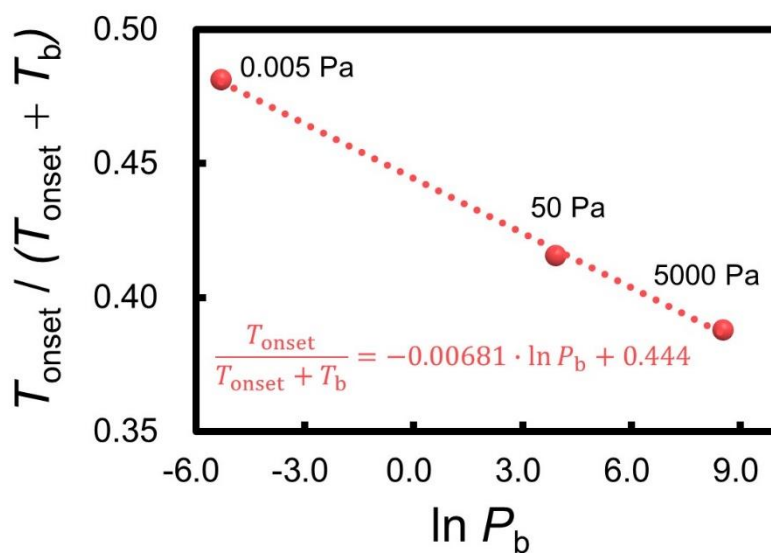


Fig. S5 $T_{\text{onset}} / (T_{\text{onset}} + T_b)$ vs. $\ln P_b$ plot. T_{onset} is the experimentally determined evaporation onset temperature of EMI-TFSI under each external pressure, T_b is the estimated boiling point under each external pressure from the Clausius-Clapeyron plots, and P_b is the external pressure. This equation could be applied to predict the evaporation onset temperatures of the other tested ILs (BMI-TFSI, HMI-TFSI, OdMI-TFSI, P13-TFSI, and Li-TFSI) within the error of about 4.6% as listed in Table 3 of the main article.

VI. Clausius-Clapeyron plots of the tested ILs

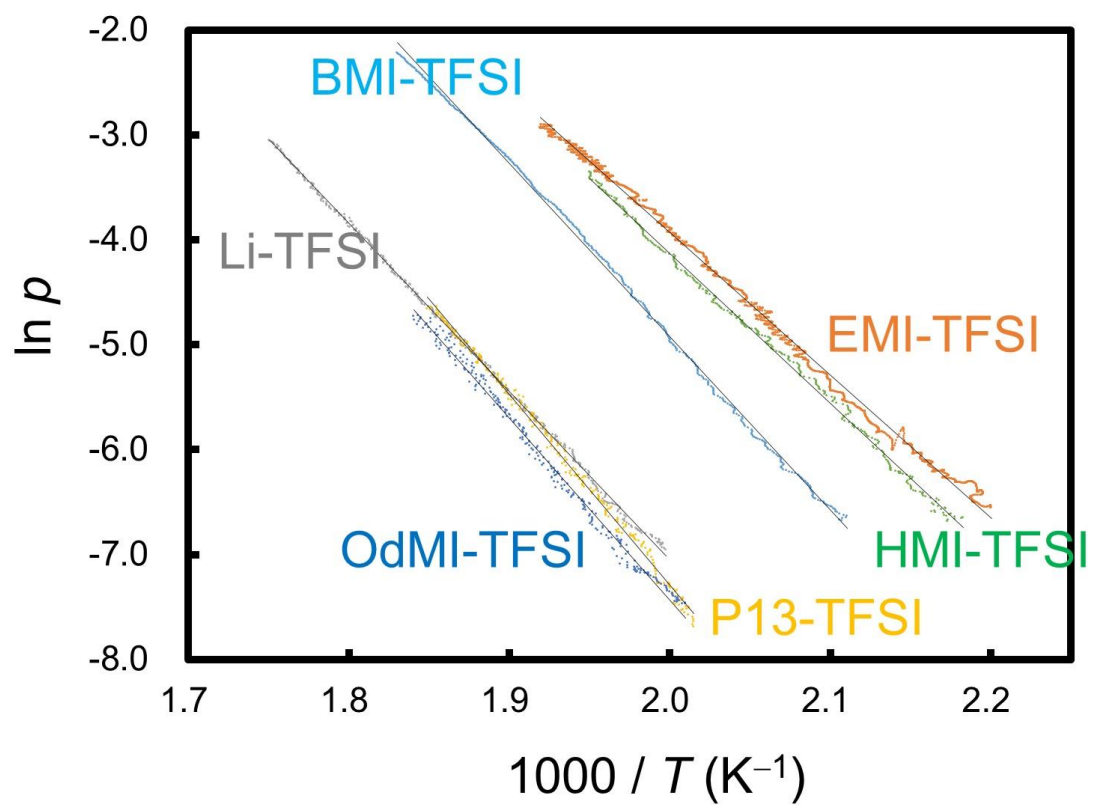


Fig. S6 Clausius-Clapeyron plots of ILs. The enthalpy and the constant C values are summarized in the main article.