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Dependence of cobaltocenium diffusion in ionic liquids on the alkyl chain length of 1-alkyl-3-methylimidazolium cations

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I. Quality of the ILs evaluated by UV-Vis spectroscopy and the AgNO₃ test

UV-Vis spectroscopy measurements were carried out to qualitatively investigate the purity of each ionic liquid (IL) based on the method in the previous literature.^{S1} Fig. S1 shows UV-Vis spectra of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([C_nmim][Tf₂N]). Although the higher absorbance appeared in the range from 350 to 550 nm for [C₁₀mim][Tf₂N], no significant peaks were observed for others in the region between 400 and 800 nm.

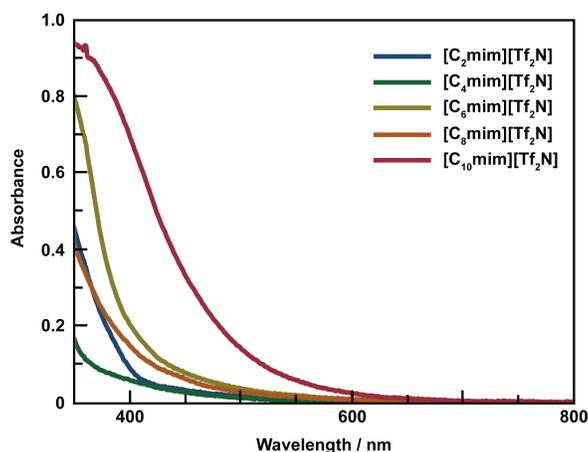


Fig. S1 UV-Vis spectra of each [C_nmim][Tf₂N].

In general, it is known that the viscosity values of the ILs are influenced by dissolved impurities. Halide impurities were qualitatively investigated by the AgNO₃ test for hydrophobic ILs.^{S2} In this test, individual [C_nmim][Tf₂N] ILs were thoroughly washed with ultrapure water (Milli-Q, 18.2 MΩ cm). Then, diluted AgNO₃ was added into the washed water. No silver salts (e.g., AgCl) were found in the solution. These results indicate that the purity of [C_nmim][Tf₂N] is sufficiently high for the electrochemical measurements of cobaltocenium (Cc⁺).

II. Temperature dependence of the viscosities and the densities obtained in this study

Fig. S2 shows the temperature dependence of the viscosities of the ILs. Viscosity of each $[C_n\text{mim}][\text{Tf}_2\text{N}]$ decreased with an increase in the alkyl chain length of $[C_n\text{mim}]^+$, which was analogous to the tendency found in the literature.^{S3} The relationship between viscosity and temperature was described by the VFT equation. As indicated in Table S1, the best-fit parameters of the VFT equation for viscosity of each $[C_n\text{mim}][\text{Tf}_2\text{N}]$ ($n = 2, 4, 6, \text{ or } 8$) were similar to those reported in the literature.^{S3}

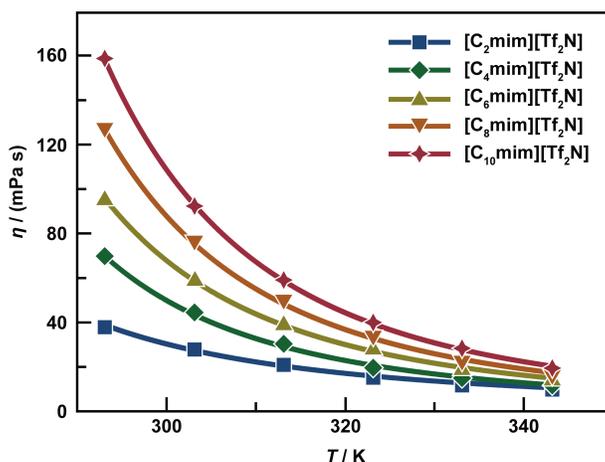


Fig. S2 Plots of η vs. T over the range 293.15–343.15 K for $[C_n\text{mim}][\text{Tf}_2\text{N}]$.

Table S1 The best-fit parameters for viscosity of $[C_n\text{mim}][\text{Tf}_2\text{N}]$.

| IL | η_0 (/ 10^{-1} mPa s) | B (/ 10^2 K) | T_0 (/K) | Reference |
|---|---------------------------------|---------------------|---------------|-----------|
| $[C_1\text{mim}][\text{Tf}_2\text{N}]$ | 2.9 ± 0.6 | 5.87 ± 0.57 | 178 ± 7 | [S3] |
| $[C_2\text{mim}][\text{Tf}_2\text{N}]$ | 5.3 | 4.77 | 182 | This work |
| $[C_2\text{mim}][\text{Tf}_2\text{N}]$ | 4.0 ± 1.3 | 5.09 ± 0.81 | 182 ± 10 | [S3] |
| $[C_4\text{mim}][\text{Tf}_2\text{N}]$ | 2.1 | 6.47 | 182 | This work |
| $[C_4\text{mim}][\text{Tf}_2\text{N}]$ | 2.5 ± 0.2 | 6.25 ± 0.22 | 180 ± 2 | [S3] |
| $[C_6\text{mim}][\text{Tf}_2\text{N}]$ | 1.5 | 7.81 | 172 | This work |
| $[C_6\text{mim}][\text{Tf}_2\text{N}]$ | 1.6 ± 0.2 | 7.57 ± 0.39 | 173 ± 3 | [S3] |
| $[C_8\text{mim}][\text{Tf}_2\text{N}]$ | 1.3 | 8.48 | 171 | This work |
| $[C_8\text{mim}][\text{Tf}_2\text{N}]$ | 1.5 ± 0.2 | 8.02 ± 0.30 | 173 ± 2 | [S3] |
| $[C_{10}\text{mim}][\text{Tf}_2\text{N}]$ | 1.0 | 9.42 | 165 | This work |

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Figs. S3 shows the temperature dependence of the densities of the ILs. The intercepts decreased with the increase in the alkyl chain length of $[C_n\text{mim}]^+$. The relationship between density and temperature is known to obey the following equation:

$$\rho = b - aT \quad (\text{S1})$$

where ρ is the density (g cm^{-3}), T is the temperature in Kelvin (K), and a and b are the constants. Table S2 shows the best linear-fitting parameters for the lines made by the least squares method in Fig. S3. The estimated values of the parameters were almost the same as the values reported in the previous literature.^{S3}

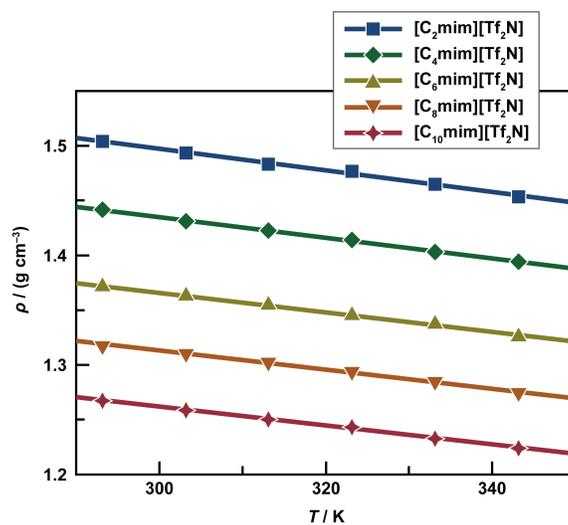


Fig. S3 Plots of ρ vs. T over the range 293.15–343.15 K for $[C_n\text{mim}][\text{Tf}_2\text{N}]$.

Electronic supplementary information**Table S2** Density equation parameters of $[C_n\text{mim}][\text{Tf}_2\text{N}]$.

| IL | a (/ 10^{-3} g cm $^{-3}$ K $^{-1}$) | b (/g cm $^{-3}$) | Correlation coefficient | Reference |
|--|--|-------------------------|----------------------------|-----------|
| $[\text{C}_2\text{mim}][\text{Tf}_2\text{N}]$ | 0.984 | 1.79 | 0.999 | This work |
| $[\text{C}_2\text{mim}][\text{Tf}_2\text{N}]$ | 1.00 | 1.82 | 1.000 | [S3] |
| $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ | 0.941 | 1.71 | 0.999 | This work |
| $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ | 0.94 | 1.72 | 0.999 | [S3] |
| $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ | 0.888 | 1.63 | 0.999 | This work |
| $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ | 1.02 | 1.67 | 0.998 | [S3] |
| $[\text{C}_8\text{mim}][\text{Tf}_2\text{N}]$ | 0.875 | 1.57 | 0.999 | This work |
| $[\text{C}_8\text{mim}][\text{Tf}_2\text{N}]$ | 1.00 | 1.62 | 1.000 | [S3] |
| $[\text{C}_{10}\text{mim}][\text{Tf}_2\text{N}]$ | 0.861 | 1.52 | 0.999 | This work |

These results suggest that the viscosities and the densities of the ILs are not affected in the presence of the trace amount of impurities. Therefore, we can conclude that the analysis of the diffusion of Cc^+ in the ILs was properly performed.

III. Dependence of viscosity on the number of methylenes in the alkyl chain of $[C_n\text{mim}]^+$

Fig. S4 indicates the effect of the number of methylenes in the alkyl chain of $[C_n\text{mim}]^+$ on viscosity of $[C_n\text{mim}][\text{Tf}_2\text{N}]$ over the temperature range from 293.15 to 343.15 K. Except for $[C_1\text{mim}][\text{Tf}_2\text{N}]$, the viscosity value was dependent upon the number of methylenes. The dependency on the number of methylenes ($n = 2, 4, 6, 8, \text{ or } 10$) for the viscosity was fitted linearly or exponentially. The correlation coefficients for each fitting method are tabulated in Table S3. Over the range 293.15–343.15 K, the both fitting methods allow us to understand a function of the number of methylenes. However, the exponential curve is more appropriate at the higher temperature range (≥ 333.15 K).

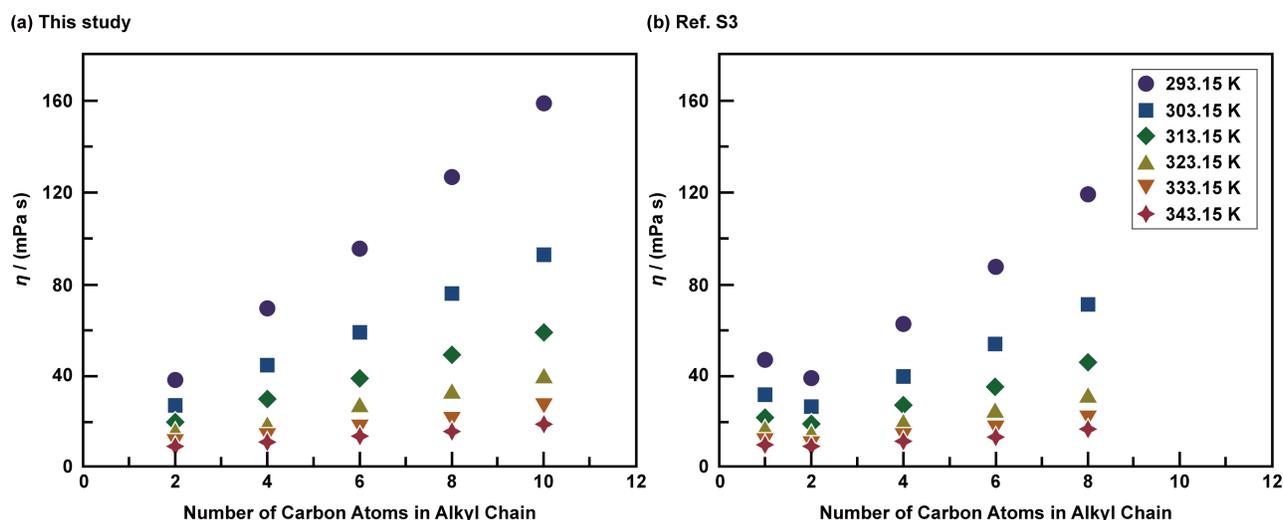


Fig. S4 The influence of the number of methylenes in the alkyl chain of $[C_n\text{mim}]^+$ on the viscosity values estimated in (a) this study and (b) ref. S3.

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Table S3 The correlation coefficients for the viscosity values of $[C_n\text{mim}][\text{Tf}_2\text{N}]$ ($n = 2, 4, 6, 8, \text{ or } 10$ for the values estimated in this study and $n = 2, 4, 6, \text{ or } 8$ for the values estimated in ref. S3) fitted by either the linear line or the exponential curve.

| T (/K) | Correlation coefficient for the linear line | Correlation coefficient for the exponential curve | Reference |
|-------------|--|--|-----------|
| 293.15 | 0.999 | 0.980 | This work |
| 293.15 | 0.997 | 0.994 | [S3] |
| 303.15 | 1.000 | 0.985 | This work |
| 303.15 | 0.998 | 0.996 | [S3] |
| 313.15 | 1.000 | 0.988 | This work |
| 313.15 | 0.998 | 0.997 | [S3] |
| 323.15 | 0.993 | 0.991 | This work |
| 323.15 | 0.998 | 0.998 | [S3] |
| 333.15 | 0.988 | 0.998 | This work |
| 333.15 | 0.997 | 0.999 | [S3] |
| 343.15 | 0.994 | 0.999 | This work |
| 343.15 | 0.996 | 1.000 | [S3] |

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IV. Estimation of the activation energies of viscosity

It is known that the viscosities of ILs obey the VFT equation, Eq. (3),^{S3,S4} whereas it can be approximated to the following Arrhenius equation:

$$\eta = \eta_0 \exp[E_{\text{app},\eta}/(RT)] \quad (\text{S2})$$

where η is the viscosity of the medium (mPa s), η_0 (mPa s) is the constant, $E_{\text{app},\eta}$ is the apparent activation energy of viscosity (kJ mol^{-1}), R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and T is the temperature in Kelvin (K).

In this study, the activation energy of viscosity ($E_{a,\eta}$) was defined as the following equation:

$$E_{a,\eta} = R d(\ln \eta)/d(1/T) \quad (\text{S3})$$

When the Arrhenius equation is used for the estimation of the activation energy, $E_{a,\eta}$ equals to $E_{\text{app},\eta}$. $E_{\text{app},\eta}$ can be estimated by Eq. (S2). Plots of $\log \eta$ vs. $1/T$ in Fig. S5 show a linear relationship. The slopes of the lines obtained by means of the least squares method were used to estimate $E_{\text{app},\eta}$. The same procedure for the estimation of $E_{\text{app},\eta}$ was described in the literature.^{S5} It was reported that the estimated value of $E_{\text{app},\eta}$ is not rigorous but its value can be utilized to estimate the magnitude of $E_{a,\eta}$.

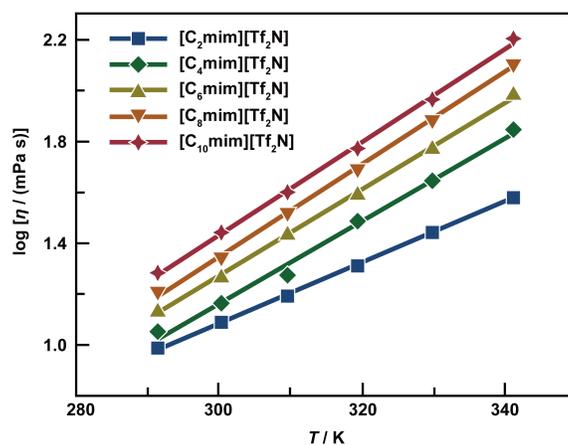


Fig. S5 Plots of $\log \eta$ vs. T over the range 293.15–343.15 K for $[\text{C}_n\text{mim}][\text{Tf}_2\text{N}]$.

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For the rigorous estimation of $E_{a,\eta}$, the right side of Eq. (S3) should be calculated using the VFT equation. In this case, the Eq. (S3) is modified as the following equation:

$$E_{a,\eta} = BR/[1 - (T_0/T)]^2 \quad (\text{S4})$$

Eq. (S4) indicates that $E_{a,\eta}$ is dependent on the temperature, in contrast with $E_{\text{app},\eta}$. Therefore, $E_{a,\eta}$ gives the rate of change in the viscosity at a particular temperature. This estimation procedure for the $E_{a,\eta}$ was also reported in the literature.^{S6}

V. Temperature effect on $D\eta/T$

Fig. S6 shows the plots of $D\eta/T$ vs. T . The fitting curve for each $[C_n\text{mim}][\text{Tf}_2\text{N}]$ was drawn using Eq. (10) with the best-fit parameters. $D\eta/T$ is expected to be the constant when $\theta\alpha$ in Eq. (6) is assumed to be a constant. However, as described in Fig. S6, the value of $D\eta/T$ was dependent on the temperature. Therefore, it is concluded that the value of $\theta\alpha$ is influenced by the temperature.

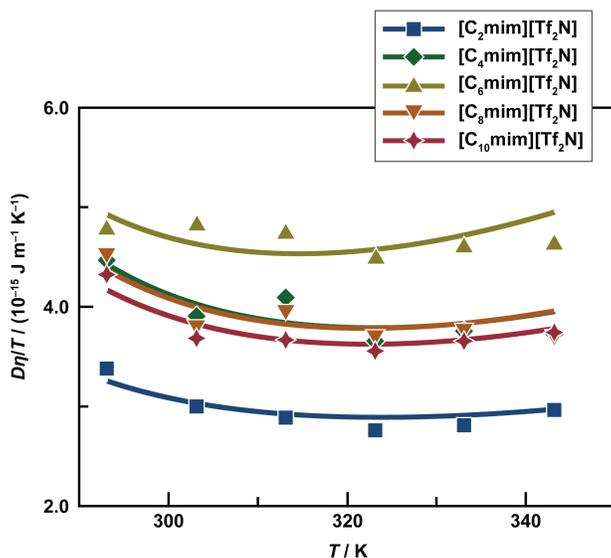


Fig. S6 Plots of $D\eta/T$ vs. T over the range 293.15–343.15 K for $[C_n\text{mim}][\text{Tf}_2\text{N}]$.

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VI. The effect of the alkyl chain of $[C_n\text{mim}]^+$ on the plots of D vs. $T/(\theta\pi\eta\alpha)$

Fig. S7 shows the plots of D vs. $T/(\theta\pi\eta\alpha)^{-1}$ for Cc^+ in each $[C_n\text{mim}][\text{Tf}_2\text{N}]$. The result was the same as Fig. 9: straight lines passing through the origin were obtained, and the Boltzmann constant was almost equal to the slope estimated for each plot. Consequently, the high validity of the application to Eq. (6) was clarified.

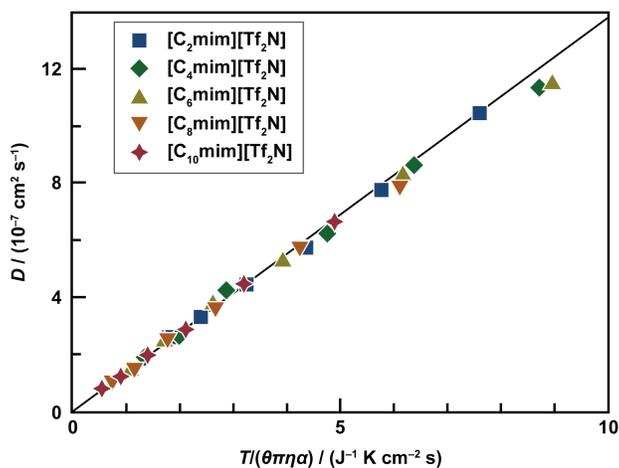


Fig. S7 Plots of D vs. $T/(\theta\pi\eta\alpha)^{-1}$ estimated over the range of 293.15–343.15 K for Cc^+ in each $[C_n\text{mim}][\text{Tf}_2\text{N}]$.

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