



Fig. 1 Walden plot of NaClO_4 aq. electrolyte.

Fig. S1 (ESI†) summarizes the viscosity and the ionic conductivity at each NaClO_4 concentration. The viscosity was higher with increasing NaClO_4 salt concentration, but the ionic conductivity showed a maximum value at 7 m NaClO_4 aq. solution. The 17 m NaClO_4 aq. solution had a viscosity of 7.8 mPa s and an ionic conductivity of 108 mS cm^{-1} . The viscosity of the NaClO_4 aq. electrolyte was comparable to that of the non-aqueous electrolyte (6.8 mPa s, 1 M NaClO_4 in PC), but the ionic conductivity was much higher than that of the non-aqueous electrolyte (6.5 mS cm^{-1}).¹ These results suggested that the ionic conductivity of the NaClO_4 aq. electrolyte was not impaired even at a high salt concentration. Fig. 1 shows the Walden plot of the NaClO_4 aq. solution, and that of KCl aq. solution as an ideal solution. Here, Walden's rule is “ $\Lambda \times \eta = \text{const.}$ ” (Λ : molar conductivity; η : viscosity). For 1 m NaClO_4 aq. solution, it was close to the straight line of the KCl aq. solution, and it was again close to the straight line of KCl aq. solution at 17 m NaClO_4 aq. solution. Although NaClO_4 was completely dissociated in 1 m NaClO_4 aq. solution, ion pairs between the Na^+ ions and ClO_4^- ions were formed in concentrated NaClO_4 aq. solution, as shown by the Raman and EPSR results described later. Nevertheless, no significant decrease in ionic conductivity was observed in the concentrated region, suggesting the specific ion-transport mechanism, such as ion hopping mechanism, between vicinal Na^+ ions in the orderly solution structure over a long range. Similar behavior was also reported in concentrated LiTFSA aq. solution² and LiFSA in dinitrile electrolytes.³

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References

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