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Title: An empirical relation between the limiting ionic molar conductivities and self-diffusion coefficients of pure solvents

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ABSTRACT

The limiting ionic molar conductivity (λ_{∞}) of an electrolyte solution depends on the self-diffusion coefficient (D_s) of the pure solvent when the temperature (T) changes. To study the D_s -dependence of λ_{∞} , we proposed a new empirical relation $\lambda_{\infty} \propto (D_s/T)^t$, with a parameter t . The relation is applied to the λ_{∞} and D_s of alkali, tetra-alkyl ammonium, and halogen ions in water or methanol. All ions except for tetra-alkyl ammonium ions in water exhibit excellent linear relationships in their $\lambda_{\infty} \propto (D_s/T)^t$ plots, with t in the range from 0.88–1.26. This is the first report showing an affirmative linear correlation between λ_{∞} and D_s .

1. Introduction

The limiting molar conductivity λ_{∞} ($\text{S m}^2 \text{mol}^{-1}$) of an ion is a physical quantity often used in the fields of electrochemistry and solution chemistry; it is a measure of the performance of electrolyte solutions [1]. The relationship between the limiting molar conductivity and viscosity η_s (Pa s) of pure solvents has attracted much attention [2]. This is probably because of unusual behavior in the ionic-radius dependence or temperature dependence of the Walden product $\lambda_{\infty}\eta_s$, which is a component of the famous empirical formula, the Walden rule [1]. For example, according to a simple hydrodynamic model [2], the limiting molar conductivity in an electrolyte solution is inversely proportional to the viscosity η_s and the hydrodynamic radius r of an ion:

$$(1) \quad \lambda_{\infty} = |z|^2 e F / (6\pi \eta_s r),$$

where z is the electric charge of the ion, e is the elementary charge, and F is the Faraday constant. If

the radius r in Eq. (1) is independent of the solution temperature, we expect that the product $\lambda_{\infty}\eta_s$ should also not depend on the temperature. However, the Walden product of ions, such as K^+ , Cl^- , and NO_3^- , in water decreases with increasing temperature [1]. As a result, based on the model, the temperature dependence of the Walden product led to the development of several theoretical expressions between λ_{∞} and η_s [3], although the hydrodynamic model failed to explain the temperature dependence of the Walden product.

To our knowledge, no study on the empirical and theoretical relations between λ_{∞} and the self-diffusion coefficient D_s ($m^2 s^{-1}$) of a pure solvent has been previously reported. This may be because for pure solvents, the number of temperature-dependent experiments on self-diffusion coefficient is less than that on viscosity [4, 5]. The purpose of this paper is to propose a new empirical relation between λ_{∞} and D_s and apply the relation to representative monovalent ions (alkali, tetra-alkyl ammonium, and halogen ions) in water or methanol to better understand the ionic transfer behaviors in electrolyte solutions and encourage the development of theoretical expressions between λ_{∞} and D_s .

If an empirical relation between λ_{∞} and D_s (to be proposed later) holds for various electrolyte solutions, the relation can be employed for the following: if the limiting molar conductivity of an ion in an electrolyte solution is known for a given temperature, we can calculate the self-diffusion coefficient of a pure solvent in the solution at that temperature, and vice versa. The empirical relation between λ_{∞} and D_s should also be valid for theoretically calculated values of λ_{∞} and D_s . Therefore, the experimental relation between λ_{∞} and D_s can be used to assess an approximate relation between λ_{∞} and D_s , as calculated by a method such as a molecular dynamics (MD) simulation [6, 7]. In the

next paper, we will assess the approximate relation between λ_{∞} and D_s in acetonitrile, as estimated by MD simulation.

In Section 2, we derive a new empirical relation between λ_{∞} and D_s using two existing relations between λ_{∞} and η_s and between D_s and η_s . Section 3 outlines the experimental values of λ_{∞} for selected alkali cations (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+), tetra-alkyl ammonium cations (R_4N^+ , where $\text{R} = \text{Me}$, Et , or Pr), and halogen anions (Cl^- , Br^- , I^-) in ordinary water and for these ions except for Rb^+ and Cs^+ in methanol, together with the experimental values of λ_{∞} for Na^+ and K^+ in heavy water, D_2O , as cited from other papers. Moreover, we will introduce the experimental values of D_s , measured by other researchers, for the three solvents. These experimental values will be used to determine the values of parameters in the empirical relation between λ_{∞} and D_s . Section 4 shows an assessment of the proposed empirical relation based on the experimental data introduced in the Section 3. In general, the experimental relation between λ_{∞} and D_s is found to exhibit excellent linearity.

2. Theory

The empirical relation between λ_{∞} and D_s was constructed by combining two existing empirical relations between λ_{∞} and η_s , and between D_s and η_s . The former relation is a revised Walden product [1] between λ_{∞} and η_s , which is defined as:

$$(2) \quad \lambda_{\infty}(\eta_s)^b = a .$$

The symbols a ($\text{S m}^2 \text{ mol}^{-1}$) and b are parameters determined by fitting this equation to experimental values of λ_{∞} and η_s . Note that the viscosity η_s in Eq. (2) is divided by 1 Pa s and that the term inside

the parentheses in Eq. (2) is dimensionless. The exponent b represents the deviation from the Walden product $\lambda_{\infty}\eta_s$. Equation (2) has been previously used to study the effects of adding sucrose, glycerol, and mannitol to aqueous solutions [1]. The latter relation between D_s and η_s is a revised Stokes-Einstein relation, given by

$$(3) \quad D_s/T = c/(\eta_s)^d,$$

where c ($\text{m}^2 \text{s}^{-1} \text{K}^{-1}$) and d are parameters and T (K) is temperature. The two parameters are determined by matching Eq. (3) to experimental values of D_s and η_s . For the same reason as in Eq. (2), the term inside the parentheses on the right hand side of Eq. (3) is dimensionless. The exponent d in Eq. (3) indicates the deviation from the Stokes-Einstein relation [2], defined by $D_s = kT/(6\pi\eta_s r_s)$, where k is the Boltzmann constant and r_s is the Stokes radius of a solvent molecule. Equation (3) has been previously applied [8] to examine the linear relationships between the self-diffusion coefficients and viscosities of many molecules such as water, alcohols, and hydrocarbons.

Substituting Eq. (3) for η_s in Eq. (2) yields the following new empirical relations, with parameters q and t , between λ_{∞} and D_s :

$$(4a) \quad \lambda_{\infty} = q(D_s/T)^t,$$

$$(4b) \quad \ln(\lambda_{\infty}) = \ln(q) + t \ln(D_s/T),$$

where $t = b/d$ and $q = a/c^t$. The experimental values of λ_{∞} and D_s can be conveniently fitted into Eq. (4b) when we determine the values of parameters q and t . Using Eq. (4b), we investigated the linear correlations between λ_{∞} and D_s for selected alkali cations (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+), tetra-alkyl ammonium cations (Me_4N^+ , Et_4N^+ , Pr_4N^+), and halogen anions (Cl^- , Br^- , I^-) in ordinary water and

for these ions except for Rb^+ and Cs^+ in methanol along with Na^+ and K^+ in D_2O .

3. Materials and methods

For an electrolyte solution containing ordinary water as a solvent, measurements of λ_∞ have been previously conducted for Li^+ , Na^+ , K^+ , Cl^- at 5°C, 15°C, 25°C, 35°C, 45°C, 55 °C, and 100°C and for Rb^+ , Cs^+ , Br^- , I^- at 5°C, 15°C, 25°C, 35°C, 45°C, and 55 °C [1]. The measurements were reported to three from five significant figures, and the experimental errors of λ_∞ were less than 0.9%. For the R_4N^+ tetra-alkyl ammonium cations, λ_∞ has been previously measured at five temperatures (5°C, 10°C, 15°C, 20°C, and 25°C) [9]. The experimental values were reported to four significant figures and the errors were less than 0.9%.

Seven experimental values of D_s for ordinary water were taken from Mills' paper [10]; their measurement temperatures were 1°C, 4°C, 5°C, 15°C, 25°C, 35°C, and 45°C, and the self-diffusion coefficients were reported to four significant figures and the experimental errors were approximately 0.2%. To obtain the self-diffusion coefficients of ordinary water corresponding to λ_∞ of R_4N^+ at 10°C and 20°C, we compared a quadratic polynomial, $D_s = f_1(T/K)^2 + f_2(T/K) + f_3$, with an Arrhenius-type function, $\ln(D_s) = g_1/T + g_2$, where the coefficients f_1, f_2 , and f_3 (g_1 and g_2) were determined by fitting the above seven experimental self-diffusion coefficients into the quadratic polynomial (the Arrhenius-type function). For the quadratic polynomial, fitting of the seven experimental D_s values into the quadratic polynomial resulted in $f_1 = 3.484 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$, $f_2 = -1.512 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, and $f_3 = 1.641 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$. The largest and smallest deviations from the quadratic polynomial were 0.8%

(4°C) and 0.1% (25°C), respectively, and the average deviation was 0.4%. For the Arrhenius-type function, we obtained $g_1 = -2.257 \times 10^3$ K, and $g_2 = -12.34$. The largest and smallest deviations from the Arrhenius-type function were found to be 2.4% (15°C) and 0.3% (5°C), respectively, and the average deviation was 1.3%. By comparing the fitting errors of the quadratic polynomial with those of the Arrhenius-type function, we used the self-diffusion coefficients of ordinary water at 10°C and 20°C, as calculated using the quadratic polynomial. Finally, we obtained values of $1.530 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 10°C and $2.026 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 20°C for ordinary water. The errors of these values are considered to be approximately equal to those of the experimental values. We also used two experimental values of D_s for ordinary water at 55°C and 100°C [11], whose errors were about 1%.

For Na^+ and K^+ in heavy water, D_2O , these λ_∞ values were calculated with empirical equations in Refs. [12] and [13], respectively, at 5°C, 15°C, 25°C, 40°C, 45°C, and 55°C. These errors are probably less than 1%. We used the D_s values in Ref. [10] at 5°C, 25°C, and 45°C with an error of about 0.2%, and in Ref. [14] at 15°C, 40°C, and 55°C with an error of about 2%.

For the λ_∞ values of ions in methanol, the experimental values of four cations (Na^+ , K^+ , Me_4N^+ , Pr_4N^+) and three anions (Cl^- , Br^- , I^-) were taken from Ref. [15]. The values of λ_∞ for these seven ions were measured at -15°C, -5°C, 5°C, 15°C, and 25°C [15]. The values were reported to four significant figures and the experimental errors were about 0.1%.

For Li^+ in methanol, we calculated the limiting molar conductivities of Li^+ , $\lambda_\infty(\text{Li}^+)$, using the limiting molar conductivities of LiI , $\lambda_\infty(\text{LiI})$, at 0°C, 25°C, 35°C, 47.4°C, and 56.9°C, as taken from Ref. [16]. These values were reported to two or three significant figures and had an experimental error

of about 1%. We also used values for Γ , $\lambda_{\infty}(\Gamma)$, measured at -15°C to 25°C , as taken from Ref. [15].

The calculations were based on the law of independent migration of ions [17]. This law is expressed by $\Lambda_{\infty}(\alpha\beta) = \lambda_{\infty}(\alpha^{+}) + \lambda_{\infty}(\beta^{-})$ in the case of monovalent ions α^{+} and β^{-} . We interpolated and extrapolated $\lambda_{\infty}(\Gamma)$ at the five temperatures from 0°C to 56.9°C [16] with the five experimental values of $\lambda_{\infty}(\Gamma)$ from -15°C to 25°C [15] and an Arrhenius-type function, $\ln(\lambda_{\infty}) = h_1/T + h_2$. This function has often been used [18] to predict temperature dependency of λ_{∞} for various ions. The coefficients h_1 and h_2 were determined by fitting the five experimental $\lambda_{\infty}(\Gamma)$ from -15°C to 25°C [15] into the function, yielding $h_1 = -1162 \text{ K}$ and $h_2 = -1.175$. The largest and smallest deviations of the experimental $\lambda_{\infty}(\Gamma)$ values at -15°C , -5°C , 5°C , 15°C , and 25°C from the Arrhenius-type function were 0.11% (5°C) and 0.02% (-5°C), respectively, and the average deviation was 0.06%. Because the Arrhenius-type function reproduces the values of experimental $\lambda_{\infty}(\Gamma)$ well, we used this function to calculate the five $\lambda_{\infty}(\Gamma)$ values from 0°C to 56.9°C . The values of $\lambda_{\infty}(\Gamma)/10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ obtained using the function were: 43.92 (0°C), 62.74 (25°C), 71.19 (35°C), 82.37 (47.4°C), and 91.42 (56.9°C).

By subtracting $\lambda_{\infty}(\Gamma)$ from $\Lambda_{\infty}(\text{LiI})$ at the five temperatures from 0°C to 56.9°C , five limiting molar conductivities $\lambda_{\infty}(\text{Li}^{+})/10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ were obtained: 26.1 (0°C), 41.3 (25°C), 47.8 (35°C), 57.6 (47.4°C), and 63.6 (56.9°C). The errors of the $\lambda_{\infty}(\text{Li}^{+})$ values were approximately 2%.

For Et_4N^{+} in methanol, limiting molar conductivities, $\lambda_{\infty}(\text{Et}_4\text{N}^{+})$, were obtained in the same way as determined for $\lambda_{\infty}(\text{Li}^{+})$ in methanol. We used the limiting molar conductivities of Et_4NBr , $\Lambda_{\infty}(\text{Et}_4\text{NBr})$, measured at 4°C , 10°C , 25°C , 35°C , and 45°C to five or six significant figures and with an experimental error of about 0.1% [19], together with Br^{-} values, $\lambda_{\infty}(\text{Br}^{-})$, from -15°C to 25°C

[15]. We interpolated and extrapolated the $\lambda_{\infty}(\text{Br}^-)$ values at the five temperatures from 4°C to 45°C [19] with the five experimental values of $\lambda_{\infty}(\text{Br}^-)$ measured at -15°C to 25°C [15] and an Arrhenius-type function, $\ln(\lambda_{\infty}) = h_3/T + h_4$. The coefficients h_3 and h_4 were determined by fitting the five experimental $\lambda_{\infty}(\text{Br}^-)$ values from -15°C to 25°C [15] into the function to obtain $h_3 = -1181$ K and $h_4 = -1.215$. The largest and smallest deviations from the Arrhenius-type function were 0.14% (5°C) and 0.04% (15°C), respectively. The average deviation was 0.07%. We used the function to calculate the five $\lambda_{\infty}(\text{Br}^-)$ values from 4°C to 45°C because the Arrhenius-type function reproduced the values of experimental $\lambda_{\infty}(\text{Br}^-)$ well. The values of $\lambda_{\infty}(\text{Br}^-)/10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ obtained using the function were 41.88 (4°C), 45.83 (10°C), 56.53 (25°C), 64.29 (35°C), and 72.51 (45°C). Subtracting $\lambda_{\infty}(\text{Br}^-)$ from $\Lambda_{\infty}(\text{Et}_4\text{NBr})$ at the five temperatures from 4°C to 45°C yielded five limiting molar conductivities $\lambda_{\infty}(\text{Et}_4\text{N}^+)/10^{-4} \text{ S m}^2 \text{ mol}^{-1}$: 45.97 (4°C), 49.08 (10°C), 60.50 (25°C), 68.26 (35°C), and 77.05 (45°C). The errors of the $\lambda_{\infty}(\text{Et}_4\text{N}^+)$ values were approximately 0.2%.

For the self-diffusion coefficients of methanol, we used two data sets: five experimental values of D_s measured at -86°C, -72°C, -60°C, -33°C, and 19°C to three significant figures and with an experimental error of about 5% [20], and five experimental values of D_s measured at 5°C, 10°C, 25°C, 40°C, and 55°C to three significant figures and with an experimental error of about 0.8% [21]. Using these data, we calculated the self-diffusion coefficients of pure methanol at nine temperatures (-15°C, -5°C, 0°C, 4°C, 15°C, 35°C, 45°C, 47.4°C, and 56.9°C), corresponding to the λ_{∞} values of the nine ions. Therefore, we compared the quadratic polynomial, $D_s = f_4(T/K)^2 + f_5(T/K) + f_6$, with the Arrhenius-type function, $\ln(D_s) = g_3/T + g_4$, in a manner similar to calculating the self-diffusion

coefficients of water at 10°C and 20°C. The coefficients f_4, f_5 , and f_6 (g_3 and g_4) were determined by fitting experimental self-diffusion coefficients from the above two data sets into the quadratic polynomial (Arrhenius-type function). For the quadratic polynomial, we obtained $f_4 = 1.713 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$, $f_5 = -6.260 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, and $f_6 = 5.894 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. The largest and smallest deviations from the quadratic polynomial were 23.8% (−86°C) and 0.1% (55°C), respectively, and the average deviation was 5.4%. We also obtained $g_3 = -1426 \text{ K}$ and $g_4 = -15.05$, for which the largest and smallest deviations from the Arrhenius-type function were 3.6% (5°C) and 0.08% (−60°C), respectively, and the average deviation was 1.5%. Thus, we calculated the self-diffusion coefficients of methanol at nine temperatures from −15°C to 56.9°C using the Arrhenius-type function; this function reproduces the experimental values of the self-diffusion coefficients of methanol better than those reproduced by the quadratic polynomial. The values of $D_s/10^{-9} \text{ m}^2 \text{ s}^{-1}$ obtained using the Arrhenius-type function were 1.17 (−15°C), 1.43 (−5°C), 1.58 (0°C), 1.70 (4°C), 2.07 (15°C), 2.86 (35°C), 3.30 (45°C), 3.42 (47.4°C), and 3.88 (56.9°C). The errors of the values were approximately 5%.

To assess the deviation from Eq. (4), we used the correlation coefficients (CCs) between $\ln(\lambda_\infty)$ and $\ln(D_s/T)$ and the average absolute deviations (AADs; %). The AAD is defined by

$$(5) \quad \text{AAD} = \frac{1}{N} \sum_{j=1}^N \left| \frac{\ln[\lambda_{\text{exptl},j}(i)] - \ln[\lambda_{\text{calc},j}(i)]}{\ln[\lambda_{\text{exptl},j}(i)]} \right| \times 100 \quad ,$$

where $\lambda_{\text{exptl},j}(i)$ is the experimental or calculated value of $\lambda_\infty(i)$ of an ion i , and $\lambda_{\text{calc},j}(i)$ is a value of $\lambda_\infty(i)$ of the ion obtained from Eq. (4) using parameters q and t . The symbol N is the number of data

points (NDP).

4. Results and discussion

As an example, Figure 1 shows the linear correlations between $\ln(\lambda_\infty)$ and $\ln(D_s/T)$ of Li^+ , Me_4N^+ , and Cl^- in ordinary water. Note that the error bars are not shown because their values were very small. For Li^+ , the fitting intercept $\ln(q)$ and slope t were found to be 20.9 and 1.04, respectively. The CC was 1.00, and the AAD of Li^+ was 0.34%, indicating that the linear correlation of Li^+ in ordinary water is excellent. The fitting parameters $\ln(q)$ and t for Me_4N^+ (the five open triangles in Fig. 1), were 15 and 0.8, respectively. The CC was 0.98, and the AAD of Me_4N^+ was 0.44%. This relatively poor CC is mainly ascribed to the fact that $\lambda_\infty(\text{Me}_4\text{N}^+)$ at 5°C (left-most open triangle in Fig. 1) is larger than the value expected from the other limiting molar conductivities at higher temperatures, as noted by Salamanca et al. [9]. These authors studied the limiting molar conductivities of R_4N^+ from $\text{R} = \text{Me}$ to $\text{R} = \text{Bu}$ in aqueous solutions at five temperatures (5°C, 10°C, 15°C, 20°C, and 25°C) and found the same trend in the limiting molar conductivity at 5°C for the other tetra-alkyl ammonium cations as for Me_4N^+ . However, the cause for their trends has not yet been elucidated. For $\ln(\lambda_\infty)$ and $\ln(D_s/T)$ of Cl^- (shown in Fig. 1), we found $\ln(q) = 19.4$ and $t = 0.95$. The CC and AAD were 1.00 and 0.07%, respectively. The linear correlation of Cl^- in ordinary water was observed to be very strong.

The results of linear correlations between $\ln(\lambda_\infty)$ and $\ln(D_s/T)$ for the 11 ions in ordinary water demonstrate the following characteristics (see Table 1). For all alkali and halogen ions, the CCs were

1.00 and their AADs were smaller than 0.34%; thus, the linear correlations between $\ln(\lambda_\infty)$ and $\ln(D_s/T)$ were found to be excellent. On the other hand, the CCs of the tetra-alkyl ammonium cations ranged from 0.95 to 0.98 and their AADs were larger than those of the alkali and halogen ions. The main reason for the poorer linear correlations of the three cations, as compared with those of the alkali and halogen ions, relates to the fact that their experimental values of λ_∞ at 5°C were larger than the values expected at higher temperatures, as noted above. As mentioned in Section 2, t is equal to b/d , where b and d represent the deviation from the Walden product and the Stokes-Einstein relation, respectively. When we compare t 's values in ordinary water, the value of d is a constant. Thus, the value of t is controlled with only the value of b in ordinary water. If the simple hydrodynamic model with $b = 1$ holds for all ions, then these ions have the same value of t ($= 1/d$). We can see from Table 1 that the t values range from 0.8 (Me_4N^+) to 1.04 (Li^+). The values of t for Li^+ and Na^+ were found to quite different from those of larger ions or structure-breaking ions such as Rb^+ and Cs^+ . This suggests that the large difference in t between smaller and larger ions is mainly attributed to the difference in an ion-solvent interaction or hydration [22, 23] between their ions. However, a relation between t and hydration has not been fully clarified [3, 22].

Table 1 also shows the linear correlations between $\ln(\lambda_\infty)$ and $\ln(D_s/T)$ for Na^+ and K^+ in D_2O . The $\ln(q)$ and t values for Na^+ and K^+ in D_2O are roughly the same as those for Na^+ and K^+ in ordinary water, respectively. For example, $\ln(q) = 20.7$ and $t = 1.02$ for Na^+ in D_2O , whereas $\ln(q) = 20.2$ and $t = 1.00$ for Na^+ in ordinary water. Judging from only the results of Na^+ and K^+ in ordinary water and D_2O , we expect that the effect of deuterium on the linear correlations between $\ln(\lambda_\infty)$ and $\ln(D_s/T)$ is

also small for the other ions.

Next, we consider the linear correlations between $\ln(\lambda_\infty)$ and $\ln(D_s/T)$ for the nine ions (alkali, tetra-alkyl ammonium, and halogen ions) in methanol. Figure 2 shows the linear correlations between $\ln(\lambda_\infty)$ and $\ln(D_s/T)$ of Li^+ , Me_4N^+ , and Cl^- in methanol. Note that the error bars of $\ln(\lambda_\infty)$ are not shown in this figure because their values were very small. The error bars of $\ln(D_s/T)$ in Fig. 2 are equal to an error of $\pm 5\%$. For Li^+ in methanol, the parameters determined were $\ln(q) = 26.7$ and $t = 1.26$, and the CC and AAD were 1.00 and 0.22%, respectively. The parameters for Li^+ were much different from those of Li^+ in water: $\ln(q) = 20.9$ and $t = 1.04$. For Me_4N^+ , the values $\ln(q) = 20.4$ and $t = 0.99$ were also different from those of Me_4N^+ in water: $\ln(q) = 15$ and $t = 0.8$. The linearity between $\ln(\lambda_\infty)$ and $\ln(D_s/T)$ of Me_4N^+ in methanol was very strong: the CC was 1.00 and the AAD was 0.19%. Within the temperature range studied, the abnormal behaviors that appeared in the λ_∞ of R_4N^+ in water were not observed [15] for the λ_∞ of R_4N^+ in methanol. The empirical relation between $\ln(\lambda_\infty)$ and $\ln(D_s/T)$ of Cl^- in methanol was also very good, with a CC of 1.00 and AAD of 0.18. The parameters $\ln(q)$ and t were 22 and 1.06, respectively, and these values were also different from those of Cl^- in water.

The results of fitting Eq. (4b) to the experimental values for λ_∞ and D_s of all ions in methanol are shown in Table 2. All the ions exhibited excellent linear correlations between $\ln(\lambda_\infty)$ and $\ln(D_s/T)$; the CCs for all ions were 1.00 and their AADs varied from 0.07% (Et_4N^+) to 0.22% (Li^+) (although their AADs were about three to six times larger than those of K^+ , Cl^- , Br^- , and I^- in water). The intercepts $\ln(q)$ changed from 19.7 for Et_4N^+ to 26.7 for Li^+ . The intercept $\ln(q)$ for all ions in methanol was

found to be larger than that of the corresponding ions in water. The smallest value of exponent t was 0.97 for Et_4N^+ and its largest value was 1.26 for Li^+ . Except for Me_4N^+ and Et_4N^+ , the exponent t of all ions was greater than unity. The exponent t of all ions was greater than that of the corresponding ion in water. Thus, we conclude that $\ln(q)$ and t depend on the combination of ion and solvent. The orders of t 's values in methanol are $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ within alkali ions and $\text{Cl}^- > \text{Br}^- > \text{I}^-$ within halogen ions. This suggests that linear correlations between λ_∞ and D_s in methanol are also influenced by ion-solvent interactions, as seen in water. The effects of such interactions on λ_∞ are complicated and not fully elucidated theoretically [3]. For example, Hubbard and Onsager (HO) theory cannot explain the magnitudes of $\lambda_\infty \eta_s$ for ions, in particular, alkali ions in methanol at ambient conditions. Takahata et. al measured [24] molar conductivities of alkali halides at high temperatures in alcohols along the liquid-vapor coexistence curve and found that the friction coefficients of ions obtained by the molar conductivities are reasonably explained by the HO theory. Thus, if we were able to investigate linear correlations between $\ln(\lambda_\infty)$ and $\ln(D_s/T)$ for alkali and halogen ions in methanol at high temperatures, a relationship between $\ln(\lambda_\infty)$ and $\ln(D_s/T)$ that does not depend on the type of ions may be obtained because ion-solvent interaction near the ion is considered to become weak at high temperatures from the results in Ref. [24].

5. Conclusion

In this work, we studied the linear correlation between $\ln(\lambda_\infty)$ and $\ln(D_s/T)$ for alkali cations (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+), tetra-alkyl ammonium cations (R_4N^+ , where $\text{R} = \text{Me}$, Et , or Pr), and halogen

anions (Cl^- , Br^- , I^-) in ordinary water and for these ions except for Rb^+ and Cs^+ in methanol, together with those for Na^+ and K^+ in D_2O . From the results shown in Figure 1, Figure 2, Table 1, and Table 2, we consider that the linear correlation between $\ln(\lambda_\infty)$ and $\ln(D_s/T)$ for any electrolyte solution would be generally strong. This indicates that the λ_∞ of an ion is strongly dominated by D_s of the pure solvent. Since linear correlations between $\ln(\lambda_\infty)$ and $\ln(D_s/T)$ depend on both the ion and solvent, further study on the linearity between $\ln(\lambda_\infty)$ and $\ln(D_s/T)$ is necessary. In future, we will investigate the empirical linear relationships between λ_∞ and D_s in aprotic solvents such as *N,N*-dimethylformamide and acetonitrile.

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Figure captions

Figure 1. Linear correlations between $\ln(\lambda_\infty)$ and $\ln(D_s/T)$ in ordinary water for Cl^- (circles), Me_4N^+ (triangles), and Li^+ (squares).

Figure 2. Linear correlations between $\ln(\lambda_\infty)$ and $\ln(D_s/T)$ in methanol for Cl^- (circles), Me_4N^+ (triangles), and Li^+ (squares).

Table 1

Fitting parameters $\ln(q)$ and t of Eq. (4b) for ordinary water and D₂O. CC and AAD are the correlation coefficient and the average absolute deviation (%), respectively. NDP is the number of data points.

The figures in parentheses for $\ln(q)$ and t are standard deviations.

Ion	NDP	CC	AAD	$\ln(q)$	t
Li ⁺	7	1.00	0.34	20.9(0.5)	1.04(0.02)
Na ⁺	7	1.00	0.22	20.2(0.3)	1.00(0.01)
Na ⁺ a)	6	1.00	0.31	20.7(0.7)	1.02(0.03)
K ⁺	7	1.00	0.08	18.3(0.1)	0.91(0.00)
K ⁺ a)	6	1.00	0.30	18.0(0.7)	0.89(0.03)
Rb ⁺	6	1.00	0.04	17.9(0.1)	0.89(0.00)
Cs ⁺	6	1.00	0.04	17.7(0.1)	0.88(0.00)
Me ₄ N ⁺	5	0.98	0.44	15(3)	0.8(0.1)
Et ₄ N ⁺	5	0.95	0.64	16(4)	0.9(0.2)
Pr ₄ N ⁺	5	0.96	0.62	17(4)	0.9(0.2)
Cl ⁻	7	1.00	0.07	19.4(0.1)	0.95(0.00)
Br ⁻	6	1.00	0.04	19.0(0.1)	0.93(0.00)
I ⁻	6	1.00	0.03	18.8(0.1)	0.93(0.00)

a) The values of λ_{∞} were measured in D₂O.

Table 2

Fitting parameters $\ln(q)$ and t of Eq. (4b) for methanol. CC and AAD are the correlation coefficient and the average absolute deviation (%), respectively. NDP is the number of data points. The figures in parentheses for $\ln(q)$ and t are standard deviations.

Ion	NDP	CC	AAD	$\ln(q)$	t
Li^+	5	1.00	0.22	26.7(0.8)	1.26(0.03)
Na^+	5	1.00	0.19	24(1)	1.13(0.04)
K^+	5	1.00	0.20	23(1)	1.11(0.04)
Me_4N^+	5	1.00	0.19	20.4(0.9)	0.99(0.04)
Et_4N^+	5	1.00	0.07	19.7(0.3)	0.97(0.01)
Pr_4N^+	5	1.00	0.19	22(1)	1.05(0.04)
Cl^-	5	1.00	0.18	22(1)	1.06(0.04)
Br^-	5	1.00	0.18	21.4(0.9)	1.04(0.04)
I^-	5	1.00	0.19	21.1(0.9)	1.02(0.04)

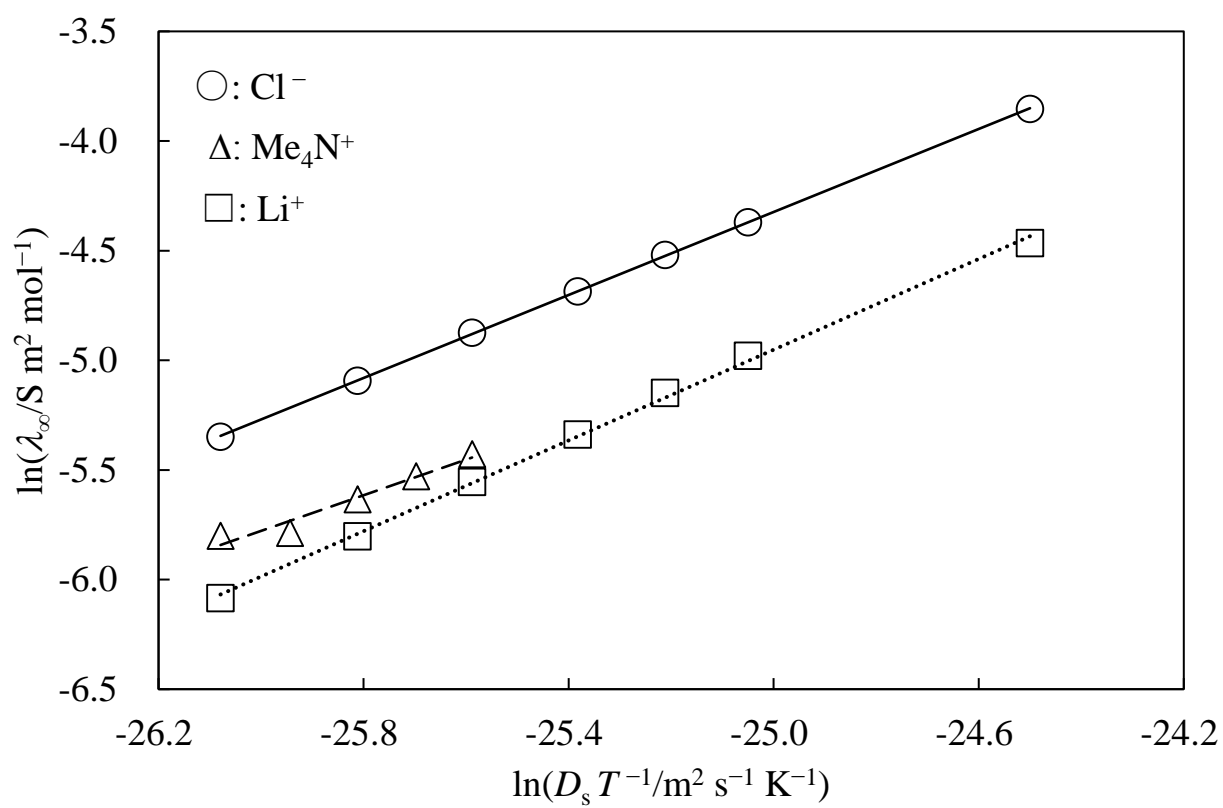


Figure 1

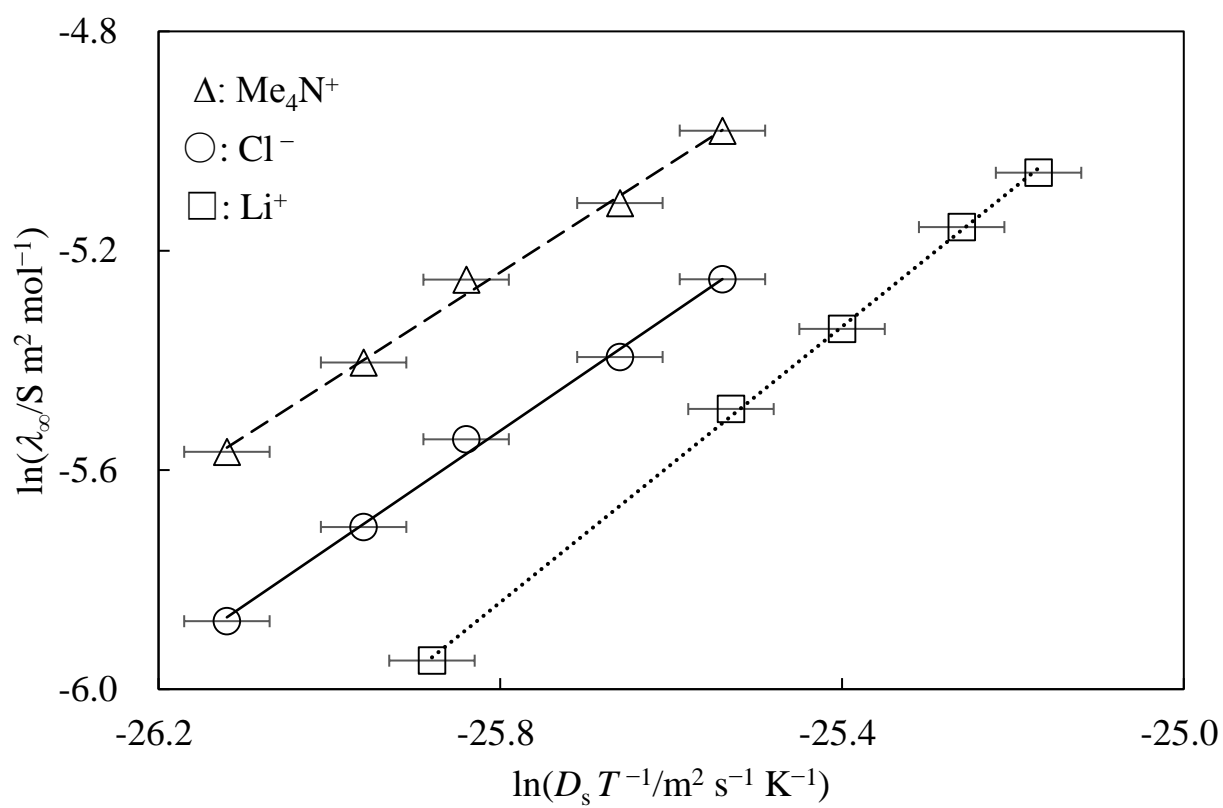


Figure 2