



Research paper

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

Hisashi Matsuyama*, Kota Motoyoshi

Applied Chemistry Research Unit, Graduate School of Engineering, Muroran Institute of Technology, Muroran, Hokkaido 050-8585, Japan

ARTICLE INFO

Article history:

Received 9 February 2018

In final form 27 March 2018

Available online 28 March 2018

Keywords:

Limiting molar conductivity

Self-diffusion coefficient

Water

Methanol

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 to 1.26. This is the first report showing an affirmative linear correlation between λ_{∞} and D_s .

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

The limiting molar conductivity λ_{∞} ($S\ m^2\ mol^{-1}$) 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:

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

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 $R = Me, Et, \text{ or } Pr$), and halogen anions (Cl^- , Br^- , I^-) in ordinary water and for these ions except for Rb^+ and

* Corresponding author.

E-mail address: hisashi@mmm.muroran-it.ac.jp (H. Matsuyama).

Cs⁺ in methanol, together with the experimental values of λ_∞ for Na⁺ and K⁺ in heavy water, D₂O, 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:

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

The symbols a (S m² 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

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

where c (m² s⁻¹ 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 :

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

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

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 (Me₄N⁺, Et₄N⁺, Pr₄N⁺), 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 D₂O.

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 R₄N⁺ 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 R₄N⁺ 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 $f_1 = 3.484 \times 10^{-13}$ m² s⁻¹, $f_2 = -1.512 \times 10^{-10}$ m² s⁻¹, and $f_3 = 1.641 \times 10^{-8}$ m² 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 1.530×10^{-9} m² s⁻¹ at 10 °C and 2.026×10^{-9} m² 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, D₂O, 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⁺, Me₄N⁺, Pr₄N⁺) 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 I⁻, $\lambda_\infty(\text{I}^-)$, 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 $\lambda_\infty(\text{I}^-)$ at the five temperatures from 0 °C to 56.9 °C [16] with the five experimental values of $\lambda_\infty(\text{I}^-)$ 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 $\lambda_\infty(\text{I}^-)$ from -15 °C to 25 °C [15] into the function, yielding $h_1 = -1162$ K and $h_2 = -1.175$. The largest and smallest deviations of the experimental $\lambda_\infty(\text{I}^-)$ 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 $\lambda_\infty(\text{I}^-)$ well, we used this function to calculate the five $\lambda_\infty(\text{I}^-)$ values from 0 °C to 56.9 °C. The values of $\lambda_\infty(\text{I}^-)/10^{-4}$ S m² mol⁻¹ obtained using the function were: 43.92 (0 °C), 62.74 (25 °C), 71.19 (35 °C), 82.37 (47.4 °C),

Download English Version:

<https://daneshyari.com/en/article/7837836>

Download Persian Version:

<https://daneshyari.com/article/7837836>

[Daneshyari.com](https://daneshyari.com)