Thermal Diffusion of Prototropic Ions in Water

Naokata Takeyama* and Kimie Nakashima
Department of Industrial Chemistry, Faculty of Science and Engineering, Saga University, Saga 840
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Synopsis. Regarding the Soret effect of prototropic ions of H^+ and OH^- in dilute aqueous solutions, it has been mentioned that heat-of-transport values for ions are in good agreement with those of the activation energies for ionic diffusion in the Arrhenius expression. The physicochemical significance of these facts is discussed in relation to the inclusion of thermal diffusion terms in Kramers' formula for ordinary diffusion flux.

The Soret effect regarding an aqueous ionic solution can be described with the Nernst-Hartley approximation in very dilute conditions by

$$J = - D^\circ \operatorname{grad} m - D'm \operatorname{grad} T \tag{1}$$

for ions under the Kohlrausch law which concerns the independent mobility of ions. J is the ionic diffusion flux, m the ionic molal concentration, D° the limiting ionic diffusion coefficient, D' the ionic thermal diffusion coefficient, and T the temperature which is dependent on the position coordinate.[1] At a Soret steady state of J=0, the Soret coefficient s° and the heat-of-transport Q^* are expressed[2] as

$$s^\circ = - d \ln m/dT = D'/D^\circ = Q^*/RT^2, \tag{2}$$

where R is the gas constant. The heats of transport for various ions are subject to the additivity rule for electrolytes in sufficiently dilute aqueous solutions.[2] Reversely, Q^* for ions should be derived from the observed heats of transport for various electrolytes. At present, there is no good method for dividing the heat of transport of an electrolyte into the heats of transport for constituent ions, except for a conventional method proposed by Snowdon and Turner[2] on the scale of Q^*=0 for Cl^- at 298 K and 0.01 mol kg^{-1}. It is obvious that the conventional values are not suitable for a physicochemical discussion. In this regard, the present authors have proposed a rational method for dividing the heats of transport for electrolytes into those for ions after the introduction of a reduction rule with reference to thermal diffusion coefficients of 1-1 electrolytes in aqueous solutions at 298 K and 0.01 mol kg^{-1}.[3] Although this method is quite different from the conventional method of Snowdon and Turner, the values of Q^* for H^+ and OH^- obtained from both methods are in good agreement.

On the other hand, as is well known, the Arrhenius expression for ionic diffusion coefficients shows a narrower applicability than for the reaction-rate constants.[4] An apparent activation energy E_a can still be introduced:

$$\partial \ln D^\circ/\partial T = E_a/RT^2 \tag{3}$$

for a certain temperature. However, E_a continues to be temperature dependent.[5,6]

Table 1. Ionic Quantities of Diffusion and Thermal Diffusion for H^+ and OH^- in Water at 298 K

Ion	D°	D'	Q^*	E_a
	$10^{-5}cm^2s^{-1}$	$10^{-8}cm^2s^{-1}K^{-1}$	kJ mol^{-1}	kJ mol^{-1}
H^+	9.31	161.1	12.8	12.8
OH^-	5.32	119.9	16.7	16.8

Here, we wish to discuss various relations between Q^* and E_a for H^+ and OH^- in water.

Table 1 summarizes the values of D°, D', Q^*, and E_a that were estimated for H^+ and OH^- at 298 K. The values of D° were obtained by the Nernst-Einstein relation from the limiting molar conductivities of H^+ and OH^-, of which the temperature dependences have been used to estimate the values of E_a according to Eq. 3.[6] The values of D' have been calculated from the values of Q^* using Eq. 2 with D° at 298 K.

It has been found that Q^* is equal to E_a for H^+ and OH^-, respectively. This relation is never valid for ions other than H^+ and OH^-. For example, referring to Li^+, there is a much larger difference between Q^*=−0.01 kJ mol^{-1} [3] and E_a=18.9 kJ mol^{-1}. These are obtained in a quite similar manner to the cases of H^+ and OH^-.

In order to understand this fact most simply for H^+ and OH^- in water, we use Kramers' formula for an isothermal diffusion flux[7]

$$J = - \exp(-U/RT) \operatorname{grad} D^\circ m \exp(U/RT). \tag{4}$$

The notation is the same as that mentioned above and U is an external potential which is dependent on the positions of the diffusing ions. For the present, we assume that D° is indirectly dependent on position through the position dependence of T, even in non-isothermal conditions. Thus, Eq. 4 can be expanded into

$$\begin{aligned} J = &- D^\circ \operatorname{grad} m - (\partial D^\circ/\partial T) m \operatorname{grad} T \\ &+ D^\circ m (U/RT^2) \operatorname{grad} T - (D^\circ m/RT) \operatorname{grad} U. \end{aligned} \tag{4·a}$$

The last term on the right side of Eq. 4.a is a drift term due to an external force. The second and third terms can be reduced to a thermal-diffusion term by taking the thermal-diffusion coefficient

$$D' = D^\circ(\partial \ln D^\circ/\partial T - U/RT^2). \tag{4·b}$$

In the presence of U, using Eqs. 2 and 3, the heat of transport is

$$Q^* = E_a - U. \tag{4·c}$$

In the absence of U, Eqs. 4.b and 4.c are simply

$$D' = \partial D^\circ/\partial T \tag{4·d}$$

and

$$Q^* = E_a. \qquad (4\cdot e)$$

From Eqs. 2 and 3 it is easily seen that Eq. 4.d is equivalent to Eq. 4.e, and vice versa. Equation 4.e, which is independent of U, corresponds to cases of the thermal diffusion of H^+ and OH^- in water. Moreover, it can be mentioned that Eq. 4.d agrees with an earlier proposition by Wirtz.[8]

As an important consequence of Eq. 4.e and in harmony with the empirical fact that Q^* equals E_a for H^+ and OH^-, we can consider that the values of the heat of transport of H^+ and OH^- which we used are reasonable.

In this regard, it is a well known fact that in the case of superionic solid conductors the activation energies of ionic conduction are equal to the heats of transport derived from ionic thermoelectric power.[9] These conductors are composed of mobile superions and rigid lattice ions. These are dealt with theoretically by using a lattice gas model.[10] In comparison with these superionic conductors, it can be proposed that H^+ and OH^- behave like a superion in an immobile hydrogen bonded quasi-lattice in water due to the Grotthuss' mechanism.

References

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5) In Ref. 4 the following equation is shown as the temperature dependence with rather more success:

$$D^\circ = AT^n \exp(-E/RT)$$

with constant A, n, and E within applicable temperature ranges.

For H^+, n and E are −13.7 and 46.9 kJ mol^{-1} from 273 to 329 K, and −3.31 and 18.5 kJ mol^{-1} from 329 to 373 K. For OH^- these are −27.7 and 85.4 kJ mol^{-1} from 273 to 308 K, and −5.41 and 27.5 kJ mol^{-1} from 308 to 373 K. As a reference, for Li^+ these are −17.2 and 61.6 kJ mol^{-1} from 273 to 310 K, and −8.12 and 38.1 kJ mol^{-1} from 310 to 373 K. The relationship to E_a is $E_a = E + nRT$ at a temperature T.

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