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Nonequilibrium Thermodynamics of Ionic Diffusion Coefficients in Binary Electrolyte Solutions

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Synopsis. Ionic diffusion coefficients were treated on the basis of nonequilibrium thermodynamics. They were calculated for alkali metal chloride solutions and compared with the experimental data of self-diffusion coefficients.

Miller,[1)] and Paterson *et al.*[2)] treated transport phenomena in terms of nonequilibrium thermodynamics and calculated the phenomenological coefficients $l_{\alpha\beta}$ from the conductance λ, salt diffusion coefficient D_s, and transference number t_α in solutions of alkali and alkaline earth chlorides. However, no mention was given of the ionic diffusion coefficient which is an important transport coefficient describing the motion of an ion in an electrolyte solution.

In this paper, the ionic diffusion coefficient has been expressed as a function of $l_{\alpha\beta}$ and related to the other transport coefficients. The ionic diffusion coefficient D_α calculated from the $l_{\alpha\beta}$ coefficients has been compared with the self-diffusion coefficient D_α^* as well as $(D_\alpha)_{\text{N.E.}}$ calculated from the ion conductance by means of the Nernst-Einstein equation. The diffusion coefficient of a salt D_s calculated from the ionic self-diffusion coefficients by means of the Nernst equation was compared with the observed one.

Results and Discussion

The independent flow J_α for the binary electrolyte system is given by

$$J_\alpha = -l_{\alpha\alpha}\nabla\bar{\mu}_\alpha - l_{\alpha\beta}\nabla\bar{\mu}_\beta, \tag{1}$$

where the subscripts α and β refer to either cation or anion, and $\nabla\bar{\mu}_\alpha$ denotes the electrochemical potential gradient for ion α. In the absence of the electric current, we find by eliminating $\nabla\bar{\mu}_\beta$

$$-J_\alpha/\nabla\bar{\mu}_\alpha = z_\beta(l_{\alpha\alpha}l_{\beta\beta} - l_{\alpha\beta}^2)/(z_\alpha l_{\alpha\beta} + z_\beta l_{\beta\beta}), \tag{2}$$

where z is the charge number of ion. The $l_{\alpha\beta}$ is related to the element of mobility matrix $u_{\alpha\beta}$ as follows[3)]

$$l_{\alpha\beta} = u_{\alpha\beta}|z_\beta/z_\alpha z_\beta|c_\beta/F, \tag{3}$$

where c_β and F are the concentration of ion β and Faraday constant, respectively. Substituting Eq. 3 into the right hand side of Eq. 2, we have

$$-J_\alpha/\nabla\bar{\mu}_\alpha = c_\alpha/f_\alpha, \tag{4}$$

where f_α denotes the friction coefficient of ion α:

$$f_\alpha = F(z_\alpha|z_\beta|u_{\alpha\beta} + z_\beta|z_\alpha|u_{\beta\beta})/z_\beta(u_{\alpha\alpha}u_{\beta\beta} - u_{\alpha\beta}^2). \tag{5}$$

Defining an ionic diffusion coefficient D_α by the Einstein equation

$$D_\alpha = \frac{RT}{f_\alpha} = RT\frac{z_\beta(l_{\alpha\alpha}l_{\beta\beta} - l_{\alpha\beta}^2)}{c_\alpha(z_\alpha l_{\alpha\beta} + z_\beta l_{\beta\beta})}, \tag{6}$$

and substituting Eq. 6 into Eq. 2, we obtain the Nernst-Planck equation

$$J_\alpha = -\frac{D_\alpha c_\alpha}{RT}\nabla\bar{\mu}_\alpha. \tag{7}$$

Thus we see that the Nernst-Planck equation holds only in the limited case of no electric current in the binary electrolyte system, and that the ionic diffusion coefficient is given by Eq. 6 as a function of $l_{\alpha\beta}$. Since the equivalent conductance λ_α is given by[3)]

$$\lambda_\alpha = |z_\alpha|F^2(z_\alpha l_{\alpha\alpha} + z_\beta l_{\beta\alpha})/z_\alpha c_\alpha, \tag{8}$$

we obtain by dividing Eq. 6 by Eq. 8

$$\frac{|z_\alpha|F^2D_\alpha}{RT\lambda_\alpha} = 1 - \lambda_{\alpha\beta}\left(\frac{1}{\lambda_\alpha} + \frac{1}{\lambda_\beta}\right) \equiv F(\lambda_{\alpha\beta}), \tag{9}$$

where

$$\lambda_{\alpha\beta} = z_\alpha z_\beta F^2 l_{\alpha\beta}/|z_\beta|c_\beta. \tag{10}$$

On the other hand, the diffusion coefficient of the salt D_s is expressed in terms of $l_{\alpha\beta}$ as

$$D_s^0 \equiv \frac{D_s}{1 + \dfrac{\mathrm{d}\ln\gamma_s}{\mathrm{d}\ln m_s}} = -\frac{z_\alpha z_\beta(\nu_\alpha + \nu_\beta)(l_{\alpha\alpha}l_{\beta\beta} - l_{\alpha\beta}^2)\nu_\alpha RT}{\nu_\alpha\nu_\beta(z_\alpha^2 l_{\alpha\alpha} + 2z_\alpha z_\beta l_{\alpha\beta} + z_\beta^2 l_{\beta\beta})c_\alpha}, \tag{11}$$

where γ_s and m_s are the activity coefficient and molality of the salt, respectively.[1)] Comparing Eq. 11 with Eqs. 8 and 9 and rearranging, we get

$$\nu_\alpha|z_\alpha|F^2D_s^0/(\nu_\alpha + \nu_\beta)RT\lambda t_\alpha t_\beta = F(\lambda_{\alpha\beta}), \tag{12}$$

where λ is the equivalent conductance of the salt. Equations 9 and 12 are reduced to the Nernst-Einstein equation

$$(D_\alpha)_{\text{N.E.}} = RT\lambda_\alpha/|z_\alpha|F^2, \tag{13}$$

and the Nernst-Hartley equation

$$(D_s)_{\text{N.H.}} = \frac{(\nu_\alpha + \nu_\beta)RT\lambda t_\alpha t_\beta}{\nu_\alpha|z_\alpha|F^2}\left(1 + \frac{\mathrm{d}\ln\gamma_s}{\mathrm{d}\ln m_s}\right), \tag{14}$$

respectively, provided $l_{\alpha\beta}=0$. Substituting Eq. 13 into Eq. 9, we get

$$D_\alpha/(D_\alpha)_{\text{N.E.}} = 1 - \lambda_{\alpha\beta}/\lambda t_\alpha t_\beta = F(\lambda_{\alpha\beta}), \tag{15}$$

which relates D_α to $(D_\alpha)_{\text{N.E.}}$. Eliminating $F(\lambda_{\alpha\beta})$ from Eqs. 9 and 12, we have

$$D_s^0/(\nu_\alpha + \nu_\beta)t_\beta = D_\alpha/\nu_\alpha, \tag{16}$$

which serves to estimate D_α from D_s^0 and t_β. Since $F(\lambda_{\alpha\beta})$ is a characteristic parameter for a given system, we have from Eq. 9

$$|z_\alpha|D_\alpha/|z_\beta|D_\beta = \lambda_\alpha/\lambda_\beta = t_\alpha/t_\beta. \tag{17}$$

Further, Eq. 16 leads to the Nernst equation

$$(\nu_\alpha + \nu_\beta)/D_s^0 = \nu_\alpha/D_\alpha + \nu_\beta/D_\beta. \tag{18}$$

It should be noted that Eqs. 16—18 also hold on the basis of nonequilibrium thermodynamics, although these equations can also be derived from the Nernst-Planck equation.

In Tables 1 and 2 are listed the ionic diffusion coefficients calculated by means of Eq. 6 from $l_{\alpha\beta}$ evaluated by Miller,[1] and Paterson *et al.*,[2] the results being compared with $(D_\alpha)_{\mathrm{N.E.}}$ and D_α^* compiled by Anderson and Paterson.[4] D_α is closer to D_α^* than $(D_\alpha)_{\mathrm{N.E.}}$, indicating that the isotope-isotope interaction is much smaller than the cation-anion interaction. It should be also noted that D_α is greater than $(D_\alpha)_{\mathrm{N.E.}}$. According to Eq. 15, this can be accounted for by negative $\lambda_{\alpha\beta}$ or positive $l_{\alpha\beta}$. The positive values of the interionic interaction, $l_{\alpha\beta}$, have been verified with many electrolytes.[1,2] The increase in the values of $D_\alpha/(D_\alpha)_{\mathrm{N.E.}}$ with increase in concentration (Tables 1 and 2) indicates the increase in the cation-anion interaction. This is also reflected in the decrease in λ with increasing concentration. The difference between D_α and D_α^* shows no conspicuous concentration dependence except for Li^+ and Na^+. The D_α values are larger than the D_α^* values for these ions, the order of magnitude being reversed for the other ions. The magnitudes of cationic and anionic diffusion coefficients are in the order $D_{\mathrm{Li}}<D_{\mathrm{Na}}<D_{\mathrm{K}}<D_{\mathrm{Cs}}$ and $D_{\mathrm{Cl}}(\mathrm{LiCl})<D_{\mathrm{Cl}}(\mathrm{NaCl})<D_{\mathrm{Cl}}(\mathrm{KCl})<D_{\mathrm{Cl}}(\mathrm{CsCl})>D_{\mathrm{Cl}}(\mathrm{RbCl})$, respectively, the same as those in the case of the self-diffusion coefficients.

TABLE 1. CATIONIC DIFFUSION COEFFICIENTS

Salt	Concn / mol dm^{-3}	$D_\alpha\times10^5$ / cm^2 s^{-1}				
		D_α^*	D_α	$(D_\alpha)_{\mathrm{N.E.}}$	$\frac{D_\alpha}{D_\alpha^*}$	$\frac{(D_\alpha)_{\mathrm{N.E.}}}{D_\alpha^*}$
LiCl	0.2	0.962	0.967	0.746	1.01	0.78
	0.5	0.946	0.896	0.648	0.95	0.68
	1.0	0.919	0.799	0.556	0,87	0.61
	2.0	0.868	0.653	0.442	0.75	0.51
	3.0	0.821	0.527	0.360	0.64	0.44
NaCl	0.2	1.295	1.307	1.033	1.01	0.80
	0.5	1.279	1.269	0.9350	0.99	0.73
	1.0	1.234	1.200	0.8424	0.97	0.68
	2.0	1.133	1.073	0.7187	0.95	0.63
	3.0	1.033	0.9521	0.6214	0.92	0.60
KCl	0.2	1.92	2.01	1.62	1.05	0.84
	0.5	1.87	2.03	1.53	1.09	0.82
	1.0	1.85	2.04	1.45	1.10	0.78
	2.0	1.84	2.02	1.36	1.10	0.74
	3.0	1.84	1.98	1.29	1.08	0.70
CsCl	0.5	1.947	2.197	1.565	1.13	0.80
	1.0	1.935	2.207	1.483	1.14	0.77
	1.5	1.921	2.199	1.430	1.14	0.74
	2.0	1.906	2.191	1.387	1.15	0.73
	2.5	1.888	2.185	1.345	1.16	0.71
	3.0	1.868	2.175	1.301	1.16	0.70

TABLE 2. ANIONIC DIFFUSION COEFFICIENTS

Salt	Concn / mol dm^{-3}	$D_\beta\times10^5$ / cm^2 s^{-1}				
		D_β^*	D_β	$(D_\beta)_{\mathrm{N.E.}}$	$\frac{D_\beta}{D_\beta^*}$	$\frac{(D_\beta)_{\mathrm{N.E.}}}{D_\beta^*}$
LiCl	0.2	1.907	2.145	1.654	1.12	0.87
	0.5	1.817	2.099	1.518	1.16	0.84
	1.0	1.683	1.990	1.384	1.18	0.82
	2.0	1.494	1.777	1.203	1.19	0.81
	3.0	1.296	1.529	1.045	1.18	0.81
NaCl	0.2	1.925	2.117	1.673	1.10	0.87
	0.5	1.854	2.112	1.556	1.14	0.84
	1.0	1.772	2.068	1.440	1.17	0.81
	2.0	1.614	1.895	1.269	1.17	0.79
	3.0	1.449	1.722	1.124	1.19	0.78
KCl	0.2	1.966	2.097	1.686	1.07	0.86
	0.5	1.963	2.123	1.596	1.08	0.81
	1.0	1.955	2.142	1.524	1.10	0.78
	2.0	1.907	2.131	1.437	1.12	0.75
	3.0	1.835	2.095	1.360	1.14	0.74
RbCl	0.5	1.961	2.133	1.601	1.09	0.82
	1.0	1.971	2.198	1.540	1.12	0.78
	1.5	1.997	2.241	1.503	1.12	0.75
	2.0	2.042	2.264	1.471	1.11	0.72
	2.5	*2.105*	*2.272*	*1.439*	*1.08*	*0.68*
	3.0	2.180	2.271	1.406	1.04	0.64
CsCl	0.5	1.952	2.221	1.583	1.14	0.81
	1.0	1.963	2.274	1.527	1.16	0.78
	1.5	2.000	2.297	1.494	1.15	0.75
	2.0	2.076	2.316	1.466	1.12	0.71
	2.5	2.123	2.333	1.436	1.10	0.68
	3.0	2.189	2.345	1.403	1.07	0.64

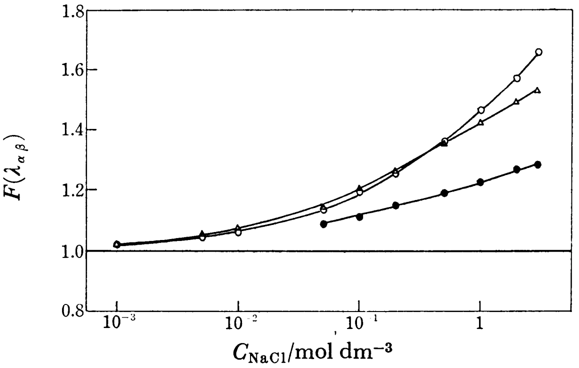

Fig. 1. $F(\lambda_{\alpha\beta})$ calculated from various origins. ○: From D_{Na}^*, ●: from D_{Cl}^*, △: from D_α. $F(\lambda_{\alpha\beta})=1$ corresponds to the calculated value from $(D_\alpha)_{\mathrm{N.E.}}$. D_{Na}^* or D_{Cl}^* in the range 10^{-3}—10^{-1} mol/dm^3 were obtained from Mills' review.[5]

$F(\lambda_{\alpha\beta})$ in Eqs. 9 and 12 is a characteristic parameter for a given system and can be evaluated from $l_{\alpha\beta}$. Equation 9 also indicates that the values of the left hand side evaluated for both cation and anion should be the same. Since the ionic diffusion coefficient can not be measured directly, the self-diffusion coefficients were used for approximate evaluation of the value of the left hand side and the results compared with $F(\lambda_{\alpha\beta})$. An example is shown for aqueous sodium chloride solution in Fig. 1. $F(\lambda_{\alpha\beta})$ is closer to the values estimated from the self-diffusion coefficient than those predicted from the Nernst-Einstein equation or the Nernst-Hartley equation, $F(\lambda_{\alpha\beta})=1$.

Since the values of D_α are closer to those of D_α^* than $(D_\alpha)_{\mathrm{N.E.}}$, the calculation of D_{s} from D_α^* by using Eq. 18 was also carried out. The difference between $(D_{\mathrm{s}})_{\mathrm{calcd}}$ and $(D_{\mathrm{s}})_{\mathrm{obsd}}$ is almost independent of concentration, the deviation being less than 15% for NaCl, KCl, and CsCl except for LiCl. $(D_{\mathrm{s}})_{\mathrm{calcd}}$ is much closer to $(D_{\mathrm{s}})_{\mathrm{obsd}}$ than $(D_{\mathrm{s}})_{\mathrm{N.H.}}$.[6]

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