

## Molecular Origin of the Debye–Huckel–Onsager Limiting Law of Ion Conductance and Its Extension to High Concentrations: Mode Coupling Theory Approach to Electrolyte Friction

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In this paper, we present a new theoretical formulation of ion conductance in electrolyte solutions. This formulation not only offers a microscopic derivation of the well-known Debye–Huckel–Onsager (DHO) limiting law,<sup>1,2</sup> but it also allows a simple interpretation of each term of the DHO law in terms of the time correlation function of appropriate dynamical variables. It is further shown that the theory can be successfully applied to higher ion concentrations. The present theory provides a very powerful new approach to the study of conductance in electrolyte solutions.

The DHO limiting law is considered to be one of the pillars of physical chemistry, with implications in many other branches of natural science. Given the simplicity of this law, its success, without any adjustable parameter, is truly amazing. For a strong binary electrolyte, if  $\Lambda_i$  is the conductance of the  $i$ -th ionic species with concentration  $c_i$  (in moles per liter), the DHO law is given by

$$\Lambda_i(c_i) = \Lambda_i^0 - [A + B\Lambda_i^0]\sqrt{c_i} \quad (1)$$

where  $\Lambda_i^0$  is the conductance of the  $i$ -th ionic species in the limit of infinite dilution.  $A$  and  $B$  are constants which originate from electrophoretic and relaxation effects, respectively.  $B$  can be expressed as the product  $Bw$ , where  $B$  and  $A$  depend on the temperature ( $T$ ), dielectric constant ( $\epsilon$ ), and charges of the ions.<sup>1,2</sup>  $A$  also depends on the viscosity of the medium. The factor  $w$  contains the contribution from self-Brownian motion of the ion under consideration and is equal to  $2 - \sqrt{2}$  for a symmetric binary electrolyte. The initial derivation of Debye and Huckel<sup>1</sup> did not include the factor  $w$ ; this term was later introduced by Onsager.<sup>2</sup>

The original derivation of the DHO limiting law was based on macroscopic hydrodynamics and irreversible thermodynamics. Even after many years of study, precise microscopic origin of all the terms of the DHO law is not transparent. Also, the DHO law works only at very low concentrations ( $c \sim 10^{-3}$  M) and breaks down completely even at moderate concentrations.<sup>3</sup> Many attempts have been made to improve upon the DHO law,<sup>4–5</sup> the best known and the most successful being the treatment of Friedman and co-workers.<sup>5</sup> However, the theory of Friedman and co-workers treats the dynamics at a phenomenological level via the Smoluchowski equation. No microscopic generalization of the DHO law to concentrated solutions is available. Note that the latter has

remained as one of the most ill-understood problems of condensed matter chemistry. One would, therefore, like to develop a theory of ion conductance which is applicable to concentrated solutions and which is based on the time correlation function formalism of modern transport theory. Such a theory is presented in this paper.

Let us consider an ionic solution consisting of positive ions (species 1) and negative ions (species 2) and the dipolar solvent. Let us consider the diffusion of a single tagged ion of charge  $q_s$  and diffusion coefficient  $D_s$ . The diffusion of the tagged ion is in general controlled by two distinct mechanisms, the first one originates from the structural relaxation of the surrounding ions and solvent molecules; this is totally microscopic in origin. The second one is the hydrodynamic effect which arises from the coupling of the ion velocity with the natural currents of the system.<sup>6,7</sup> Thus, one can write  $D_s$  as the sum of a microscopic term and a hydrodynamic term as follows:  $D_s = D_{s,\text{mic}} + D_{s,\text{hyd}}$ . A formal derivation of the above decomposition has recently been given in ref 6 by using mode coupling theory. Use of Einstein's relation between the diffusion coefficient and the friction ( $\zeta_s$ ) provides the following decomposition of the total friction on the tagged ion:  $\zeta_s(c)^{-1} = \zeta_{s,\text{mic}}(c)^{-1} + \zeta_{s,\text{hyd}}(c)^{-1}$ . Clearly,  $\zeta_{s,\text{mic}}(c)$  includes the effects of microscopic interactions of the tagged ion with all the solvent molecules and the ions and  $\zeta_{s,\text{hyd}}(c)$  includes the effects of hydrodynamic interactions with the surrounding solvent and ion currents.

The microscopic friction  $\zeta_{s,\text{mic}}(c)$  can be calculated by using the Kirkwood equation which equates the friction to the force-force time correlation function.<sup>8</sup> This time-dependent force can be obtained by using the time-dependent density functional theory (TDDFT).<sup>9,10</sup> Since the time-dependent force on the tagged ion has contributions from surrounding solvent density and polarization fluctuations and also from ion atmosphere fluctuations, we can decompose the total microscopic friction into a solvent contribution  $\zeta_{s,\text{mic}}(c=0)$  which is assumed to be concentration independent and a concentration dependent ion contribution  $\delta\zeta_{s,\text{mic}}(c)$ . To make connection with the DHO law, we treat the solvent as a dielectric continuum and calculate the concentration dependent ion contribution to the microscopic friction. Thus, the solvent contribution is not calculated microscopically in the present work. It determines the ion diffusion at infinite dilution whose value is assumed to be known from experiments. Using TDDFT, we derive the following expression of the microscopic electrolyte friction  $\delta\zeta_{s,\text{mic}}(c)$

$$\zeta_{s,\text{mic}}(c) = \frac{k_B T}{3(2\pi)^3} \int_0^\infty dt \int_{-\infty}^\infty d\mathbf{k} k^2 [C_s][G(k,t)][C_s]^\dagger F_s(k,t) \quad (2)$$

In the above equation,  $[C_s]$  is a  $(1 \times 2)$  matrix with elements  $\sqrt{\rho_i} c_{si}(k)$ ,  $i = 1, 2$ , where  $c_{si}(k)$  is the wavevector ( $\mathbf{k}$ ) dependent direct correlation function between the tagged ion and an ion of species  $i$ , and  $\rho_i$  is the number density of the  $i$ -th species.  $[C_s(k)]^\dagger$  is the transpose of  $[C_s(k)]$ .  $F_s(k,t)$  is the self-dynamic structure factor of the tagged ion, assumed here to be equal to  $\exp(-D_s k^2 t)$ , as we are interested in the zero-frequency friction. Thus, eq 2 calls for a self-consistent solution.  $[G(k,t)]$  is the  $(2 \times 2)$  van Hove function matrix with elements  $G_{ij}(k,t)$ . The elements of the van Hove function matrix can be calculated by using an extension

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of the molecular hydrodynamic theory discussed earlier.<sup>10</sup> The time integral can be carried out analytically to derive an expression for  $\delta\zeta_{s,\text{mic}}(c)$  in terms of an integral over the wavevector  $\mathbf{k}$ .

The hydrodynamic contribution is due to the coupling of the ion velocity to the relevant current modes of the solution. Mode coupling theory directly provides an expression of the contribution of the currents or flows of the system to the diffusion coefficient, that is, inverse of the friction. Since the current modes of the solution consist of both solvent and ion currents, the hydrodynamic contribution to the diffusion ( $D_{s,\text{hyd}}$ ) can be expressed as the sum of a solvent contribution  $D_{s,\text{hyd}}(c=0)$ , which is again assumed to be concentration independent, and a concentration dependent ion contribution  $\delta D_{s,\text{hyd}}(c)$ . As before, the solvent contribution  $D_{s,\text{hyd}}(c=0)$  is not calculated in the present work. It constitutes part of the ion diffusion at infinite dilution,<sup>11</sup> which is assumed to be known from experiments. The ion contribution to the hydrodynamic term is the so-called electrophoretic effect which is calculated in the present work. By using the basic ideas of mode coupling theory and considering the coupling of the ion velocity with the charge density and current modes of ion atmosphere, a general (and somewhat complicated) expression can be derived for the hydrodynamic (or the electrophoretic) term<sup>12</sup> which in the limit of equal sized ions provides the following rather simple expression

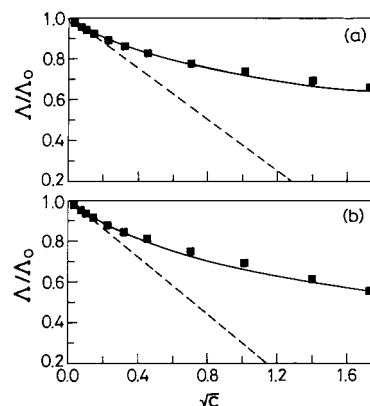
$$\delta D_{s,\text{hyd}}(c) = \frac{1}{3\pi^2 \rho N} \int_0^\infty dt \int_0^\infty d\mathbf{k} k^2 [\rho_1 G_{11}^d(k,t) - \rho_2 G_{12}^d(k,t)] C^T(k,t) \quad (3)$$

where  $\rho$  is the total ion density and  $N$  is the total number of ions present in the solution.  $G_{ij}^d(k,t)$  is the distinct van Hove function between ionic species  $i$  and  $j$ , and  $C^T(k,t)$  is the Fourier transform of the transverse current time correlation function. The above integral can be evaluated by making the so-called viscous approximation for the decay of  $C^T(k,t)$ .<sup>6</sup> Since the relaxation of the transverse current correlation function occurs much faster than the decay of distinct van Hove functions, the distinct van Hove functions in eq 3 can be replaced by the corresponding pair correlation functions and the time integral of eq 3 can then be evaluated analytically. We note that the long-range Coulombic interactions among ions and the effects of screening enter naturally in our formulation through the ion-ion correlation functions of eqs 2 and 3.

Closed-form expressions for the wavevector integrals of both eqs 2 and 3 can be obtained in the limit of very low concentration where the exact asymptotic expressions for the ionic pair correlation functions can be used. Equations 2 and 3 then lead to the following novel and essentially exact nonlinear equation for the conductance of  $i$ -th species of a strong binary electrolyte at low concentration

$$\Lambda_i(c_i) = \Lambda_i^0 - \left[ \frac{\sqrt{2\pi N_0 q_i^2 F}}{3\pi\eta(1000\epsilon k_B T)^{1/2}} + \frac{\sqrt{2\pi N_0 q_i^2 |q_i| w_i}}{3\sqrt{1000}(\epsilon k_B T)^{3/2} \Lambda_i^0} \right] \sqrt{c_i} \quad (4)$$

where  $w_i = 2[1 - \{0.5\sum_j \Lambda_j/(\Lambda_i + \Lambda_j)\}^{1/2}]$ ,  $q_i$  is the charge of an ion of species  $i$ ,  $N_0$  is the Avogadro number,  $F$  is Faraday, and  $k_B$  is the Boltzmann constant. In deriving eq 4, we have used the relation between the diffusion coefficient and the conductance and also between the concentration  $c_i$  and the number density  $\rho_i$ . The above equation is new. It is to be solved self-consistently to obtain the numerical values of the conductances of positive and



**Figure 1.** Concentration dependence of the ion conductance of aqueous (a) potassium chloride (KCl) and (b) sodium chloride (NaCl) solutions at room temperature. The ratio of the total ion conductance at finite concentration to that at infinite dilution,  $\Lambda/\Lambda_0$ , is plotted as a function of the square root of salt concentration,  $\sqrt{c}$ . The solid and the dashed curves represent respectively the predictions of the present microscopic theory and Debye-Hückel-Onsager (DHO) limiting law. The filled squares denote the experimental results (taken from refs 3 and 5). The concentration is expressed in moles/liter.

negative ions at low concentration. That  $w_i$  goes over exactly to the DHO value ( $2 - \sqrt{2}$ ) for a symmetric binary electrolyte can be seen if one assumes  $\Lambda_i = \Lambda_j$ . More importantly, in the same limit eq 4 becomes identical with the DHO limiting law.<sup>12</sup> Furthermore, the above equation reduces exactly to the expression of Friedman and co-workers<sup>5</sup> when one replaces  $\Lambda_i$  terms in the right-hand side of the above equation by  $\Lambda_i^0$ . This is exact to the order of  $\sqrt{c_i}$ . Equation 4 is valid even when the mobilities of the constituent ions of a binary electrolyte are different. This is almost always the case for real electrolytes. The original DHO limiting law does not reflect this asymmetry, which was later noticed by Onsager.<sup>13</sup>

For high ion concentrations, eqs 2 and 3 are to be solved self-consistently by evaluating the wavevector integrals numerically. We have performed these calculations by taking aqueous KCl and NaCl solutions as examples. The relevant pair correlation functions can be obtained from the recent solutions of Attard which are quite accurate even at high concentrations.<sup>14</sup> The ionic radii of  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{Cl}^-$  and their respective conductances in water at infinite dilution ( $\Lambda_i^0$ ) are readily available in the literature.<sup>15</sup> Thus, the calculations can be carried out without any major approximation and the results of the total conductance  $\Lambda$  (which is the sum of the individual conductances) are shown in figures 1a and 1b for aqueous KCl and NaCl solutions, respectively. The predictions of the DHO law and the experimental results are also included for comparison. For both solutions, the agreement between the present theory and the experimental results is quite impressive given that we have employed a theoretical approach which does not involve any adjustable parameter.

In the present theory the net mobility of an ion is determined by a subtle interplay between microscopic relaxation and hydrodynamic contributions. Nevertheless, the basic physical picture behind the DHO law remains valid. We have thus provided microscopic expressions for the constants  $A$  and  $B$  of the Debye-Hückel-Onsager theory. The theoretical formulation presented here can be extended to study several related problems, as discussed elsewhere.<sup>12</sup>

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