Wien Effect on Ionic Conductance of Binary Strong Electrolyte Solutions in a High External Electric Field

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(Date text: May 2, 2014)

Abstract

In the preceding paper, the exact solution of Stokes equation was obtained for a binary strong electrolyte solution in an external electric field. In the present paper, the solution is applied to calculate the Wien effect on deviation from the Coulombic law of conduction in high fields. One of the important aims of the present line of work was in removing or avoiding the divergence difficulty in calculating the electrophoretic and relaxation time coefficients. The present work achieves that aim by calculating on the basis of computing the axial velocity profiles the position of the center of the ion atmosphere as a function of the reduced field strength and therewith computing the electrophoretic and relaxation time coefficients for the migrating spherical ion atmosphere at each value of the reduced field strength. With the electrophoretic and relaxation time coefficients thus calculated along the trajectory of the center of the ion atmosphere with regard to the reduced field strength, the equivalent ionic conductance of a magnesium sulfate solution is calculated and compared with experimental data in very good accuracy. It is also compared with the prediction by Wilson’s theory and is found very much improved over the latter. Moreover, the present method is divergence-free unlike Wilson’s theory. It therefore not only sheds a new light on the nonequilibrium liquid structure of ionic solutions and the motion of ion atmosphere in an electric field, but also shows how the Onsager–Wilson theory of conductance in electrolyte solutions should be applied to account for the Wien effect on ionic conductance.
I. INTRODUCTION

In the preceding companion paper [1], henceforth referred to as paper I or simply I, we have obtained the exact solutions for the governing equations for nonequilibrium pair distribution functions and potentials in a Brownian motion model, and also the solutions for the Stokes equation [2–4], which yield the velocity of the countercurrent induced by the motion of ions in a binary strong electrolyte solutions under the influence of an external electric field. Therewith we obtained the general formulas for the electrophoretic and relaxation time factors that can be made use of to define the divergence-free electrophoretic and relaxation time coefficients with which we may calculate ionic conductance of binary electrolyte solutions. Since the electrophoretic and relaxation time factors, \( f(x, r; \xi) \) and \( g(x, r; \xi) \), obtained are for all allowable values of position \( (x \text{ and } r) \), it is necessary to select an appropriate position or a set of positions that must yield divergence-free electrophoretic and relaxation time coefficients. Since \( x \) and \( r \) represent the position of the center ion of the ion atmosphere at the given value of external field strength \( \xi \) we have first determined the shape of ion atmosphere from the projection \( C_P \) of the axial velocity profile and obtained the coordinates of its center position. Then therewith we can calculate the electrophoretic and relaxation time coefficients as functions of external field strength \( \xi \). The salient point of the procedure put forward here is that since the center position \((x_c, 0)\) of the ion atmosphere moves along the \( x \) axis from the origin as \( \xi \) increases, the electrophoretic coefficient for the center ion must be calculated for the moving spherical ion atmosphere at each value of \( \xi \), which follows the trajectory described in Fig. 7 of paper I, and therewith the ionic conductance. In this connection, it should be recalled that Wilson [5] evaluated the electrophoretic coefficient for the center ion located at the coordinate origin \( x = r = 0 \) for all values of \( \xi \), which consequently gives rise to a divergent term that must be discarded to obtain a finite electrophoretic coefficient. Such a divergent integral arises mainly because \( x = r = 0 \) is taken for the center ion position for the ion atmosphere even if \( \xi > 0 \). Moreover, his procedure ignores the fact that the ion atmosphere not only is distorted, but also migrates in the field direction under the influence of an external field. Therefore the coordinate position in the electrophoretic and relaxation time factors must be other than \( x = r = 0 \) and also a function of \( \xi \).

In the present paper, we would like to apply this important point of observation to calculate the electrophoretic coefficient and the corresponding relaxation time coefficient, and therewith the equivalent ionic conductance in the nonlinear regime of the field strength as a function of \( \xi \); in particular, the Wien effect [6] on equivalent conductance. Thus we would like to show that the Onsager–Wilson theory [5, 7, 8] is basically capable of predicting in an excellent accuracy
a marked deviation from Coulomb’s law of conduction if we avoid Wilson’s procedure of taking $x = r = 0$ in the electrophoretic and relaxation time coefficient formulas. When they are calculated according to our procedure, the equivalent ionic conductance compares well with experimental data on magnesium sulfate solution available in the literature\[9\]. As a matter of fact, when the electrophoretic coefficient $f(x)$ and the relaxation time coefficient $g(x)$ thus calculated according to our procedure, the present method becomes not only divergence-free, but also improves the accuracy of the Onsager–Wilson theory qualitatively and quantitatively over Wilson’s original theoretical prediction made with $x = r = 0$ used for the center position for all values of $\xi$.

The present paper is organized as follows: In Sec. II, the electrophoretic and the relaxation time factors are briefly reviewed and the corresponding coefficients are defined. In Sec. III, the constitutive equations for velocities in terms of diffusion coefficients and mean external forces are discussed within the framework of thermodynamics of linear irreversible processes. In Sec. IV, the theory of ionic conductance is presented and, upon use of the electrophoretic and relaxation time coefficients defined according to the procedure mentioned, the relative ionic conductance is calculated as a function of reduced external field strength $\xi$ for magnesium sulfate solution in excellent agreement with experimental data. Sec. V is for discussion and conclusion.

II. ELECTROPHORETIC AND RELAXATION TIME FACTORS

A. Electrophoretic Coefficient

From the axial velocity $v_x (x, r; \xi)$ completely calculated from the formal Fourier transform solutions we have shown the electrophoretic factor $f(x, r; \xi)$ may be identified:

$$v_x (x, r; \xi) = \frac{k_B T \kappa^2}{8 \pi \eta_0} \frac{x}{(x^2 + r^2)^{3/2}} - \frac{ze X \kappa}{6 \sqrt{2 \pi} \eta_0} f(x, r; \xi),$$

where $f(x, r; \xi)$ is given by

$$f(x, r; \xi) = \frac{3}{2 (x^2 + r^2)^{1/2}} - \frac{3r^2}{4 (r^2 + x^2)^{3/2}} - \frac{3 (2x^2 - r^2)}{2 (r^2 + x^2)^{5/2}} + \frac{3}{2} [\psi_1 (x, r, \xi) + 2 \psi_2 (x, r, \xi) - \psi_1 (x, r, \xi) - 2 \psi_2 (x, r, \xi)],$$

where

$$\psi_1 (x, r, \xi) = \frac{1}{x^2 + r^2} \int_0^\infty (x^2 + r^2)^{1/2} e^{-\frac{(x^2 + r^2) s}{(x^2 + r^2) + x^2 + r^2}} ds$$

and

$$\psi_2 (x, r, \xi) = \frac{1}{x^2 + r^2} \int_0^\infty (x^2 + r^2)^{1/2} e^{-\frac{(x^2 + r^2) s}{(x^2 + r^2) + x^2 + r^2}} ds.$$
with \( C_1(x, r, \xi) \), \( C_2(x, r, \xi) \), \( S_1(x, r, \xi) \), and \( S_2(x, r, \xi) \) defined by the integrals

\[
C_1(x, r; \xi) = \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{(1-y^2 + \sqrt{1+2\xi^2y^2})}{1+2\xi^2y^2} e^{-xy} I_0(\overline{\omega}_1 r),
\]

\[
C_2(x, r; \xi) = \int_0^1 dy \frac{2\xi^2y^2 (1-y^2)}{1+2\xi^2y^2} e^{-xy} I_0(\overline{\omega}_3 r),
\]

\[
S_1(x, r; \xi) = \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{2\xi y \left(1-y^2 + \sqrt{1+2\xi^2y^2}\right)}{(1+2\xi^2y^2) \left(1+\sqrt{1+2\xi^2y^2}\right)} e^{-xy} I_0(\overline{\omega}_1 r),
\]

\[
S_2(x, r; \xi) = \int_0^1 dy \frac{\sqrt{2}\xi y (1-y^2)}{1+2\xi^2y^2} e^{-xy} I_0(\overline{\omega}_3 r).
\]

It is useful to remind the reader that the second term on the right of Eq. (1) is in the same form as the electrophoretic effect term—i.e., the last term in Eq. (3) of paper I—in the velocity formula obtained on the basis of a heuristic argument. Here the notation is the same as in Paper I, but we reiterate that \( \xi = zeX/\kappa k_B T \) is the reduced external field strength and

\[
\overline{\omega}_1 = \sqrt{1-y^2 + \sqrt{1+2\xi^2y^2}}, \quad \overline{\omega}_2 = \sqrt{1-y^2 - \sqrt{1+2\xi^2y^2}}, \quad \overline{\omega}_3 = \sqrt{1-y^2}, \quad \overline{\omega} = \frac{\sqrt{1+2\xi^2}}{\sqrt{2\xi}}.
\]

Therefore, we see that \( f(x, r; \xi) \) is a measure of variation in the external body-force on the nonequilibrium ion atmosphere that has resulted from the originally spherical ion atmosphere of radius \( (1/\sqrt{2}) \kappa^{-1} \) (in reduced units).

In Fig. 1, an example of a three-dimensional surface of \( f(x, r; \xi) \) in the case of \( \xi = 3 \) is plotted and the projections of the level curves on the surface are plotted in Fig. 2. The level curves appear as quasi-ellipses in the \((x, r)\) plane. In particular, the outermost curve \( C_P \) denotes the locus of zero of the surface as the intersection with the \((x, r)\) plane. The appearance of two quasi-ellipses making up the locus \( C_P \) implies that there are two velocity components, axial and transversal, developing as the external field is increased from zero. It also means that the spherical ion atmosphere formed in the electrolyte solution at equilibrium when the external field is absent deforms into two quasi-ellipses, one along the \( x \) axis and the other along the \( r \) axis transversal to the \( x \) axis. (This phenomenon in fact gives rise to a Hall effect. It is interesting, but will not be a subject of investigation in this paper. We hope to return to this aspect in a future work. Our main interest has been and is the quasi-ellipsoid along the axial field direction and its associated ion atmosphere in the present series of work.) As is evident from Fig. 1 and Fig. 2, the spherical ion atmosphere is now distorted into a quasi-ellipse (a quasi-ellipsoid if rotated about the \( x \) axis which is the symmetry axis) described by the level curve \( C_p \) with its center displaced to \((x_c, 0)\) and tracing the trajectory in the \((x_c, \xi)\) plane shown in Fig. 7 of paper I and also in Table 1, as
ξ increases. Since it would be useful to discuss the feature of \( f(x, r; \xi) \) in a little more detail, we would like to elaborate on it below:

Since the exact velocity profile consists of a purely mechanical part \((\bar{v}_x)_{me}\) and the Brownian motion (i.e., stochastic) part \((\bar{v}_x)_{Brown}\), which are opposite in their numerical effects in some region of space, the electrophoretic factor \( f(x, r; \xi) \), which is a surface in the plane of coordinates \( x \) and \( r \), has a locus of zero defined by \( f(x, r; \xi) = 0 \); see curve \( C_P \) in Fig. 2 of this paper and also Fig. 6 of paper I. The center of the region bounded by this locus \( C_P \) not only migrates along the \( x \) axis (the field direction) as the field strength increases, but also \( C_P \) changes its shape as \( \xi \) varies. When graphically examined, the coordinate \( x_c \) of the center of \( C_P \) traces a certain trajectory as \( \xi \) increases from \( \xi = 0 \), as shown in Fig. 7 of paper I. Furthermore, \( f(x, r; \xi) < 0 \) if \((x, r)\) is within the domain defined by \( C_P \) whereas \( f(x, r; \xi) > 0 \) if \((x, r)\) is exterior to \( C_P \). This feature implies that the spherically symmetric ion atmosphere at \( \xi = 0 \) (i.e., equilibrium) with the center at the coordinate origin polarizes to a negative velocity domain within \( C_P \) and a positive velocity domain exterior to \( C_P \) in the velocity space while the center of the quasi-elliptic domain of \( C_P \) at \((x_c, 0)\), where \( x_c > 0 \), is displaced from the coordinate origin where the center of equilibrium ion atmosphere was located. Therefore, the spherical ion atmosphere displays two regions of opposite signs and the conductance of ions is contributed by ions in the exterior shell, and the electrophoretic coefficient should be calculated with the force by the flowing medium acting on the sphere (i.e., ion atmosphere) of radius \( x_c \), part of which is exterior to \( C_P \), but centered at \((x_c, 0)\). This means the transversal distance to the \( x \) axis (i.e., the radial distance) on the spherical ion atmosphere of radius \( x_c \) (in reduced units used here) in question is \( r = x_c \) from the coordinate origin (the original center). Therefore, the electrophoretic coefficient at \( \xi > 0 \) for the spherical ion atmosphere at \((x_c, 0)\) is given by \( f(\xi) \equiv f(x_c, r_c; \xi) = f(x_c, x_c; \xi) \), if the Stokes law is applied to this spherical

\[
\begin{array}{|c|c|c|c|}
\hline
x_c & \xi & x_c & \xi \\
\hline
0.2 & 0.5670 & 2.4 & 0.5960 \\
0.4 & 0.5795 & 2.6 & 0.5930 \\
0.6 & 0.5900 & 2.8 & 0.5910 \\
0.8 & 0.5975 & 3.0 & 0.5895 \\
1.0 & 0.6050 & 3.2 & 0.5890 \\
1.2 & 0.6070 & 3.4 & 0.5885 \\
1.4 & 0.6080 & 3.6 & 0.5880 \\
1.6 & 0.6075 & 3.8 & 0.5880 \\
1.8 & 0.6065 & 4.0 & 0.5875 \\
2.0 & 0.6030 & 4.2 & 0.5875 \\
2.2 & 0.5995 & 4.4 & 0.5870 \\
\hline
\end{array}
\]
ion atmosphere. This, in essence, is the content of the aforementioned procedure for selecting $x$ and $r$ in the electrophoretic factor $f(x, r; \xi)$. This procedure makes the selected values for $x = x_c$ and $r = x_c$ unique because there is only one center and one spherical ion atmosphere of radius $(1/\sqrt{2})\kappa^{-1}$ for each value of $\xi$. Note, of course, the set $(x_c, r_c)$ is axially symmetric, because the system is axially symmetric around the $x$ axis, which is parallel to the field direction.

Therefore, the Stokes law should be applied to the spherical ion atmosphere of radius $x_c$ in reduced units, whose center is located at $(x_c, 0)$. Thus, the electrophoretic coefficient at $\xi$ is defined by
\[
f(\xi) \equiv f(x_c, r_c; \xi) = f(x_c, x_c; \xi).
\] (8)

It should be noted that $f(x, r; \xi)$ now is everywhere finite for $x > 0$ and $r > 0$ for all $\xi > 0$. We have calculated $f(\xi)$ defined in Eq. (8) according to the procedure formulated in paper I and mentioned earlier. In Table 1, the dependence on $\xi$ of $x_c$ in the reduced units employed in this work is tabulated for the purpose of future use in computing the $f(\xi)$ and $g(\xi)$ for binary electrolytes. It is interesting to note that this trajectory has a maximum and thereafter diminishes to an asymptote as the field strength increases.

B. Relaxation Time Coefficient

In paper I, it is shown that the local ionic field $e_j\Delta X$ can be obtained from the solutions of the governing equations in the form
\[
e_j\Delta X(x) = -\frac{e_j^2\kappa^2}{2D} g_s(x, r; 0) - \frac{e_j\xi\kappa^2}{2D} g(x, r; \xi),
\] (9)

where the relaxation time factor $g(x, r; \xi)$ is given by the formula
\[
g(x, r; \xi) = g_c(x, r; \xi) + \Delta g_s(x, r; \xi)
\] (10)

with $g_s(x, r; 0)$, $g_c(x, r; \xi)$ and $\Delta g_s(x, r; \xi)$, respectively, defined by the integrals
\[
\begin{align*}
g_s(x, r; 0) &= \int_0^{\sqrt{2}} dy e^{-xy} y I_0 \left( r \sqrt{2 - y^2} \right), \\
g_c(x, r; \xi) &= \frac{1}{\sqrt{2}} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{e^{-xy} y I_0 (\overline{w}_1 r)}{1 + 2\xi^2 y^2} - \sqrt{2} \int_0^1 dy \frac{e^{-xy} y I_0 (\overline{w}_1 r)}{1 + 2\xi^2 y^2}, \\
\Delta g_s(x, r; \xi) &= \frac{1}{\xi} \left[ \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{e^{-xy} y \left( 1 + \sqrt{1 + 2\xi^2 y^2} \right) I_0 (\overline{w}_1 r)}{1 + 2\xi^2 y^2} ight. \\
&\left. - \int_0^{\sqrt{2}} dy e^{-xy} y I_0 \left( r \sqrt{2 - y^2} \right) \right] + 2\xi \int_0^1 dy \frac{y^3 e^{-xy} I_0 (\overline{w}_3 r)}{1 + 2\xi^2 y^2}.
\end{align*}
\]
It should be noted that $\Delta g_s(x, r; \xi)$ tends to a constant as $\xi \to 0$. The integrals in Eqs. (12) and (13) are also subject to Ineq. (90) or (A20) of paper I. Using this form of relaxation time factor $g(x, r; \xi)$, we have shown in Paper I that Wilson’s formula\(^5, 10\) $g(\xi)$ for the relaxation time coefficient can be recovered as an approximation if both $x$ and $r$ are taken equal to zero. It is an approximation since the contribution from $\Delta g_s(x, r; \xi)$ must be discarded although its magnitude is not negligible when the results of the integrals are evaluated at $x = r = 0$.

To be consistent with the electrophoretic coefficient defined earlier, we define the relaxation time coefficient $g(\xi)$ with the relation

$$g(\xi) = g_c(x_c, r_c; \xi) + \Delta g_s(x_c, r_c; \xi) = g_c(x_c, x_c; \xi) + \Delta g_s(x_c, x_c; \xi). \quad (14)$$

This relaxation time coefficient $g(\xi)$ will be used in the calculation of ionic conductance as a function of the external field strength and, in particular, the Wien effect on the ionic conductance\(^9, 10\) of magnesium sulfate solution. In Fig. 3 and Fig. 4, $f(\xi)$ and $g(\xi)$ defined in Eqs. (8) and (14) are, respectively, calculated and compared with the Wilson’s results. Compare these results for $f(\xi)$ and $g(\xi)$ with the examples for $f(x, r; \xi)$ and $g(x, r; \xi)$ for $x = r = 0.5$ shown in Figs. 8 and 10, respectively, of Paper I. The values of $x$ and $r$ chosen are arbitrary.

III. CONSTITUTIVE EQUATION FOR DIFFUSION AND CONDUCTANCE

Macroscopic description of ionic motions in solution in an external electric field must be subjected to the laws of irreversible thermodynamics. Since the macroscopic process of interest here is steady, we first assume that it obeys steady-state linear irreversible thermodynamic constitutive equations—namely, linear thermodynamic force–flux relations. On close examination of the OW theory\(^5\) it is evident that the linear irreversible thermodynamic constitutive equations for diffusion underlie it. If they are found inadequate for constitutive equations in the linear regime then we will have to seek a way to extend them to the nonlinear regime. For this, see, for example, Refs. 14 and 15.

Here the ionic diffusion flux $J_k$ of ion $k$ is assumed to follow a linear constitutive relation according to the linear irreversible thermodynamics\(^11, 13\). According to the kinetic theory of fluids\(^14–16\), for binary mixtures at steady state the thermodynamic force $d_k$ for diffusion is given by the linear thermodynamic force

$$d_k = x_k \nabla p_k - \frac{p_k}{p} F_k, \quad (15)$$

where $x_k = n_k/n$ is the mole fraction, $p_k$ is the partial pressure, $p$ is the pressure, $p_k$ is the mass density of species $k$, and $F_k$ is the external force on the species per mass. In the conductance
experiment considered in this work, the partial pressure is uniform in space, so that the pressure
gradient is equal to zero in first order. In the case of a binary electrolyte solution in which the
continuum solvent is assumed spatially uniform, there is only one independent diffusion coefficient,
and the linear thermodynamic force–flux relation or the constitutive equation for diffusion may be
written as

$$J_k = -\omega_k p d_k,$$

(16)

where $\omega_k$ is the diffusion coefficient of species $k$. Since the diffusion flux is defined relative to a
reference velocity by the formula

$$J_k = v_k - u,$$

(17)

where $u$ is the reference velocity suitably chosen, such as the barycentric velocity, which obeys
the hydrodynamic equations of the solution. There are other possibilities chosen for the reference
velocity in the literature. However, in the theory of conductance in electrolyte solutions the
barycentric velocity is generally used, and if the kinetic theory of diffusion is developed, $u$
is exactly what appears in the equation for the diffusion flux. Since we are generally interested in
mobilities in the conductance experiments, it is required to calculate $v_k$ itself of species $k$ instead
of the diffusion flux $J_k$. Thus we have

$$v_k = -\omega_k p d_k + v(r) = \omega_k \rho_k F_k + v(r),$$

(18)
in which we have taken $u \equiv v(r)$, the hydrodynamic velocity calculated previously and presented
in the previous section. It should be noted that there is no arbitrariness about the identification of
$u$ with $v(r)$, because generally $u$ in Eq. (17) is certainly the barycentric velocity obeying the
momentum balance equation—the Navier–Stokes equation or the Stokes equation at the level
of linear irreversible thermodynamics. By this consideration, we now see that the electrophoretic
coefficient considered in the theory of conductance is intimately associated with the hydrodynamic
flow velocity $v(r)$, which is the solution of the Stokes equation for flow of the medium in the binary
electrolyte solution in the present theory. However, this hydrodynamic velocity to be used is that
evaluated at $(x_c, r_c)$ at which the electrophoretic coefficient $f(x_c, r_c; \xi)$ is computed.

IV. CONDUCTANCE

The velocity $v_k$ of ion $k$ at $(x_c, r_c)$ is computed relative to a suitable reference velocity—for
example, the solution of the Stokes equation. Identifying $\rho_k F_k$ with $e_k X_t = e_k X + e_k \Delta X$ and taking
the reference velocity \( u(x_c, r_c) \) with the axial velocity \( v_x \) at \((x_c, r_c)\), we find

\[
v_k(\xi) = \omega_k e_k X - \frac{\omega_k e_k \mu' \kappa}{2D} g(\xi) - \frac{|z_k| e X \kappa}{6\sqrt{2\pi}\eta_0} f(\xi) \quad (k = i, j).
\] (19)

Here we have taken the ionic field \( \Delta X \) as for the relaxation time effect in Eq. (9)

\[
e_j \Delta X = -e_j \xi \kappa^2 \frac{2D}{2D} g(x_c, r_c; \xi) = -e_j \xi \kappa^2 \frac{g(\xi)}{2D} \]

(20)

without the field-independent term which has nothing to do with the relaxation of distorted ion atmosphere, because the relaxation time coefficient is representative of the relaxation of asymmetry of the ionic atmosphere. Similarly, the electrophoretic effect is represented by

\[
v_x(\xi) = -\frac{ze X \kappa}{6\sqrt{2\pi}\eta_0} f(x_c, r_c; \xi) = -\frac{ze X \kappa}{6\sqrt{2\pi}\eta_0} f(\xi)
\]

(21)

without the field-independent term.

The mobility in electrostatic units is then given by

\[
u_k = \frac{v_k(\xi)}{X},
\]

(22)

and it may be written in practical units as

\[
u_k = \frac{1}{300} \left( |e_k| \omega_k - \frac{\omega_k e_k \mu' \kappa}{2D} g(\xi) - \frac{|e_k| \kappa}{6\sqrt{2\pi}\eta_0} f(\xi) \right).
\]

(23)

At infinite dilution, \( \kappa \to 0 \) and the limiting mobility is given by

\[
u_k^0 = \frac{|e_k| \omega_k}{300}
\]

(24)

Since the limiting equivalent conductance is

\[
\Lambda_k^0 = F \nu_k^0,
\]

(25)

where \( F \) is the Faraday constant \( (F = 96493.1) \), we have the equivalent conductance of ion \( k \) in practical units given in the form

\[
\Lambda_k = \Lambda_k^0 - \frac{(ze)^2 \kappa \Lambda_k^0}{2D k_B T} g(\xi) - \frac{F |e_k| \kappa}{6 \times 300 \sqrt{2\pi} \eta_0} f(\xi).
\]

(26)

Define the equivalent conductance of the binary electrolyte

\[
\Lambda = \Lambda_+ + \Lambda_- \equiv \Lambda_1 + \Lambda_2.
\]

(27)

Then the equivalent conductance for a binary electrolyte is given by

\[
\Lambda(\xi) = \Lambda^0 - \frac{(ze)^2 \kappa \Lambda^0}{2D k_B T} g(\xi) - \frac{F (|e_1| + |e_2|) \kappa}{6 \times 300 \sqrt{2\pi} \eta_0} f(\xi)
\]

(28)
with $\Lambda^0 = \Lambda_1^0 + \Lambda_2^0$.

In experiment, the relative equivalent conductance

$$\Delta \Lambda (\xi) = \Lambda (\xi) - \Lambda (0)$$

(29)

is reported as a function of the field strength $\xi$. Since in the limit of $\xi = 0$

$$\Lambda (0) = \Lambda^0 - \frac{(ze)^2 \kappa \Lambda^0}{2DK_B T} g(0) - \frac{F (|e_1| + |e_2|) \kappa}{6 \times 300 \sqrt{2} \pi \eta_0} f(0),$$

(30)

we obtain the relative equivalent conductance

$$\Delta \Lambda (\xi) = \frac{(ze)^2 \kappa \Lambda^0}{2DK_B T} \left[ g(0) - g(\xi) \right] + \frac{F (|e_1| + |e_2|) \kappa}{6 \times 300 \sqrt{2} \pi \eta_0} \left[ f(0) - f(\xi) \right].$$

(31)

This formula is computed for various values of reduced field strength $\xi$, and $\Delta \Lambda (\xi) / \Lambda (0)$ calculated is plotted against $\xi$ and compared with experimental data [9, 10] on a MgSO$_4$ solution in Fig. 5. It is the only data of this kind available in the literature for strong binary electrolytes which we can use for comparison on the Wien effect. We have taken $d = 2R_{MgSO_4} = 2 \times 3.12 = 6.24$ for the diameter of MgSO$_4$, $T = 291$ K, $D = 81$, $c = 1.22 \times 10^{-3}$ mole/liter, $\eta_0 = 0.0105$ poise, the limiting conductance values [10] $\lambda_0^+ = 53.06$ for Mg$^{2+}$ and $\lambda_0^- = 80.0$ for SO$_4^{2-}$, respectively, and 120.36 g/mole for the molecular weight for MgSO$_4$. In Fig. 5, the solid curve is the prediction by the present theory, the solid squares are experimental data, and the broken curve is the prediction by Wilson’s method, that is, the prediction with the electrophoretic coefficient $f(\xi)$ and the relaxation time coefficient $g(\xi)$ calculated by Wilson in his dissertation [5, 10]. Note that they are tabulated in the monograph of Harned and Owen [10]. The OW theory prediction is much smaller than the experimental conductance. Furthermore, the low field ($\xi < 1$) behavior predicted by the Wilson’s result appears to be markedly different from the experimental data and the present theoretical prediction, the latter being almost linear with respect to $\xi$, while Wilson’s prediction appears to be nonlinear, i.e., $\xi^\alpha$ with $\alpha > 1$. We believe that the procedure used for selecting the $x$ and $r$ used for calculation of the electrophoretic and relaxation time coefficients and thus the ionic conductance appears to be well supported by the comparison made.

V. DISCUSSION AND CONCLUDING REMARKS

Ionic liquids are ubiquitous and it is important to understand their physical behaviors in physical, chemical, and biological systems under the influence of external electromagnetic fields. Onsager’s theory [7] of conductance is an important benchmark in the development of the theory of transport processes in ionic solutions, although his theory appears to have been almost forgotten.
about and paid little attention these days except one recent work[17]. We believe it is unwarranted to ignore his basic ideas on the subject matter because the theory seems to provide much valuable insight for further development of theories of transport processes in ionic solutions and plasmas. 

In the present series of papers, we have revisited and examined the details of his theories and have been able to obtain full evaluations of the formal results of the OW theory. The preceding[1] and present papers describe our understanding of the inner workings of his theories and their application to an experimental system. We have found that the solutions of the OF equations[18], the Poisson equations[19], and Stokes equation[3] for the velocity of the medium would require a more mathematically complete treatment than originally implemented in Wilson’s dissertation[5], especially, to avoid divergence difficulty that was unfortunately not dealt with squarely. In paper I[1] we have exactly evaluated the formulas for the axial and transversal velocities in a binary electrolyte solution, which may be deemed one of the goals of the theory of ionic conductance. In the present paper, we have applied the axial velocity formula to calculate the equivalent conductance of a binary strong electrolyte, having elucidated the appropriate set of \( (x, r) \) to use by a computation-based procedure to select a unique set of \( (x, r) \) as a function of \( \xi \). Although this procedure lacks a precise theoretical foundation based on irreversible thermodynamics or hydrodynamics, it does provide us with an unambiguous procedure to obtain correct estimates of conductance over the entire range of \( \xi \) experimentally studied. In this sense, we may conclude that it is a practical and useful procedure for understanding the experimental data. In any case, the procedure is founded on the observation of how the ion atmosphere behaves in the applied external field. The study of its behavior with respect to the field not only provides much insight into the interplay between the long-range Coulombic interactions between charged particles and the interaction of the ion atmosphere with the external field producing a rather intricate ionic liquid structure, but also shows how charged species diffuse in such a liquid under the influence of the applied electric field. This picture of the ionic liquid behavior that we have gained in the present paper owes to the fact that the Brownian movement model, namely, the solutions of the governing equations, provides us with exact nonequilibrium distribution functions, ionic potentials, and velocity profiles that can be evaluated rigorously either numerically or analytically. This latter feature is an indispensable aspect of the OW theory of ionic solutions we have shown possible in this work. We emphasize that the present work disposes of the divergence difficulty inherent to Wilson’s procedure[3], which arose from an inadequate treatment of the Fourier transform integrals for the solutions, and the theory of Wien effect is thereby made practically amenable to theoretical investigation and satisfactorily accountable theoretically.
The theoretical significance of the Onsager theory of electrolytic conductance\cite{7} lies in its ability to take into account the non-linear field dependence in the form of local body-force that is obtained through the Onsager–Fuoss equations\cite{18} for the pair distribution functions and the Poisson equations\cite{19} which are coupled together. The local body-force thus obtained is then made use of in the Stokes equation for the velocity of the medium subjected to the external electric field. The present paper enables us to conclude that the Onsager theory is now made capable of treating conduction phenomena of dilute electrolyte solutions irrespective of the applied field strength and predicts a correct behavior qualitatively and quantitatively in contrast to the conclusion drawn in the literature in the past that it predicts too small values for equivalent conductance\cite{10}. Thus it, in fact, appears to provide a great deal of insights into diverse electrical conduction phenomena in subjects other than traditional electrolyte solutions studied in physical chemistry, which are lately studied under different guises and subject names, such as semiconductors\cite{20,21}, ionic liquids\cite{22,23}, ion channels\cite{24}, plasmas\cite{25}, etc., but still involve charged species subjected to an external electric field gradient, often rather strong because of small system sizes commonly studied in recent years. Therefore the basic physics underlying the phenomena in the aforementioned subject fields is unchanged other than sizes of the systems and conditions, and in this respect Onsager’s theory can give us a valuable lesson on how to treat ionic solutions and ionized gases in external electromagnetic fields.

In this work and also in the OW theory\cite{5}, the treatment of the thermodynamic force–flux relation is still that of linear irreversible processes, that is, the constitutive relations for ionic motion and flow of the medium are those of the theory of linear irreversible processes\cite{11}. In addition to this restriction, it is a theory limited to sufficiently dilute electrolyte solutions. Therefore these two important restrictions must be removed for a more comprehensive theory of electric conductivity in experimental systems of current interest. We leave these aspects to future studies, but just refer to reader to Refs. 14 and 15 for nonlinear constitutive equations.

Acknowledgement

This work was supported in part by the Discovery grants from the Natural Sciences and Engineering Research Council of Canada.

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Figure Captions

Fig. 1 The electrophoretic factor \( f(x,r,\xi) \) is plotted in the \((x,r)\) plane in 3D in the case of \( \xi = 3 \).

Fig. 2 The level curves of the surface \( f(x,r,\xi) \) in Fig. 1 is projected onto the \((x,r)\) plane. The level curves form two sets of quasi-ellipses with the major axes on the \( x \) and \( r \) axes, respectively. The outermost level curve \( C_P \) represents the zero of \( f(x,r,\xi) \), namely, \( f(x,r,\xi) = 0 \). This outermost level curve \( C_P \) indicates how the spherical ion atmosphere assumed by the equilibrium ion atmosphere when \( \xi = 0 \) migrates from \((x,r) = (0,0)\) to a point on the positive \( x \) axis and also is distorted to a quasi-ellipse with the major axis lying on the \( x \) axis by the action of the external electric field as \( \xi \) increases, and similarly to the quasi-ellipse with the major axis lying on the \( r \) axis perpendicular to the \( x \) axis. The center of the curve \( C_P \) follows a trajectory described by the curve shown in Fig. 7 in paper I. The trajectory grows from zero at \( \xi = 0 \) to a maximum and then decreases to a plateau value as \( \xi \) increases. See also Table 1 of the present paper.

Fig. 3 Comparison of the electrophoretic coefficients of the present and Wilson’s theories. The solid line: the present theory; the dotted line: Wilson’s result.

Fig. 4 Comparison of the relaxation time coefficients of the present and Wilson’s theory. The solid line: the present theory; the dotted line: Wilson’s result.

Fig. 5 Relative equivalent conductance compared with experiment and the prediction by the Onsager–Wilson formula. The solid symbols are the experimental data on MgSO\(_4\) solution, the solid curve the present theory, and the broken curve the prediction by the Onsager–Wilson formula. It should be noted that the behaviors of the relative conductance of the present and Wilson’s theories are qualitatively and also quantitatively different.
FIG. 3:
FIG. 4:
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