[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WESTERN AUSTRALIA]

The Electrophoretic Corrections to the Diffusion Coefficient of an Electrolyte Solution

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The number of terms which should be included for the computation of the electrophoretic effect in the diffusion of a single electrolyte is discussed in the light of the principle of linear superposition of ionic fields. It is shown that both first- and second-order terms in the potential are mathematically justified for symmetrical valence-types, but that only the first-order term is admissible for unsymmetrical types. This point is emphasized by developing an expression for the n'th-order term in the potential arising from a Boltzmann distribution law: computation of terms up to the fifth order then shows that for 1:1 electrolytes the electrophoretic terms converge sharply after the second-order term, while for unsymmetrical electrolytes the series converge slowly or diverge. A "self-consistent" equation for the diffusion coefficient is obtained by taking two electrophoretic terms for 1:1 electrolytes, but only one for other types. It accounts satisfactorily for the observed diffusion coefficients of dilute calcium chloride solutions, which deviate markedly from the Onsager–Fuoss theory. The cases of aqueous lithium, calcium and lanthanum chlorides at 25° are considered in detail.

The theory developed by Onsager and Fuoss[1] results in an expression for the diffusion coefficient D of a dilute electrolyte solution, which may conveniently be written as

$$D = (1 + c\,\mathrm{d}\ln y_{\pm}/\mathrm{d}c)(D^0 + \Delta_1 + \Delta_2) \qquad (1)$$

Here Δ_1 and Δ_2 are small concentration-dependent corrections to the Nernst limiting value D^0, and originate in the electrophoretic effect, *i.e.*, the transfer of velocity from one ion to another *via* the solvent. On working through the theory as presented in references (1), one finds that Δ_1 and Δ_2 arise, respectively, from the first and second terms of the expansion of an exponential function

$$n_i' - n_i = n_i[-z_ie\psi/kT + (1/2!)(z_ie\psi/kT)^2 - (1/3!)(z_ie\psi/kT)^3 +] \qquad (2)$$

A closely related expansion occurs in the derivation of the Debye–Hückel equation 3 for the potential ψ at a distance r from a chosen central ion of valency z_j

$$\psi = \frac{z_je}{\epsilon}\,\frac{e^{\kappa a}}{1 + \kappa a}\,\frac{e^{-\kappa r}}{r} \qquad (3)$$

The expansion involved in the derivation of equation 3 is that for the time-averaged charge density ρ at the point where the potential is ψ, *viz.*

$$\rho = \sum_i n_iz_iee^{-z_ie\psi/kT} \qquad (4)$$

Equation 4 is combined with the Poisson equation to obtain the differential equation for the potential. In order that this differential equation should be *linear* in ψ, (a condition required by the principle of linear superposition of ionic fields, which demands that ρ be proportional to ψ), the exponentials in equation 4 are expanded and terms in higher powers of ψ than the first are rejected, giving after introducing the condition of electrical neutrality the result

$$\rho = -\sum_i n_iz_i^2e^2\psi/kT \qquad (5)$$

This means in effect that the Boltzmann distribution has to be abandoned in favor of a linear distribution law

$$n_i' = n_i(1 - z_ie\psi/kT) \qquad (6)$$

since the Boltzmann distribution and the Poisson equation are fundamentally incompatible.[2]

List of Symbols and Definitions

D	= differential diffusion coefficient at concn. c, in cm.^{2} sec.$^{-1}$
D^0	= Nernst limiting value of D at infinite dilution $= \dfrac{\nu_1 + \nu_2}{\nu_1\lvert z_1\rvert}\dfrac{RT}{\mathbf{F}^2}\Lambda^0t_1^0t_2^0$
Δ_n,	nth order electrophoretic correction to D (eqn. 1 and 8)
ν_1, ν_2,	numbers of cations and anions, respectively, formed by 1 "molecule" of electrolyte
z_1, z_2,	*algebraic* valencies of cation and anion, respectively
t_1^0, t_2^0,	transference numbers of cation and anion, respectively, at infinite dilution
Λ^0,	limiting equivalent conductance of electrolyte
R,	molar gas constant = 8.314 joule mole^{-1} deg.$^{-1}$
T,	absolute temperature
c,	concentration of electrolyte in moles/liter
$y_{\pm}$,	mean molar activity coefficient
n_i,	number of ions of species i in gross unit volume
n_i',	number of ions of species i in microscopic unit volume at distance r from a particular "central" ion
e,	charge of proton = 4.803 × 10^{-10} e.s. units
ψ,	potential at distance r from central ion
k,	Boltzmann's constant = 1.380 × 10^{-16} erg deg.$^{-1}$ molecule^{-1}
η,	viscosity of solvent = 0.008937 poise for water at 25°
$\mathbf{F}$,	Faraday = 96493 coulombs/g. equiv.
ϵ,	dielectric constant of solvent = 78.54 for water at 25°
κ,	quantity in Debye–Hückel theory, given by $\kappa^2 = [4\pi Ne^2/(1000\epsilon kT)]c(\nu_1z_1^2 + \nu_2z_2^2)$
N,	Avogadro number = 6.024 × 10^{23}
a,	mean distance of closest approach of ions, in cm.
$å$,	mean distance of closest approach, in Å.
$E_i(x)$,	exponential integral function, here defined as $\int_x^{\infty} e^{-y}y^{-1}dy$ (This integral is called $-E_i(-x)$ in Jahnke and Emde's Tables, reference 4.)
$S_n(\kappa a)$,	nth order functions of (κa) given by equation 10
$\phi_n(\kappa a)$,	nth order functions of (κa) given by equation 11
$F_n(\kappa a)$,	abbreviation for quantity in square bracket of eq. 12

There is however an important special case where the Boltzmann distribution is more nearly applicable: For a single symmetrical electrolyte where $z_1 = -z_2$ and $n_1 = n_2$, the expansion of (4) becomes

$$\rho = 0 - 2n_1z_1^2e^2\psi/kT + 0 - n_1z_1e(z_1e\psi/kT)^3/_3 + 0 + \cdots \qquad (7)$$

in which all terms in even powers of ψ vanish. In this case therefore the Boltzmann distribution is represented by equation 5 without errors of order ψ^2, the approximation being in terms of order ψ^3 only. One would therefore expect the expression (3) for the potential to be most satisfactory for

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[1] L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932). See also H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943 and 1950.

[2] See R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge University Press, 1952, Ch. IX.

symmetrical electrolytes; and especially for 1:1 electrolytes, since 2:2 electrolytes and higher types are affected by ion-pair formation. Furthermore, there is no inconsistency involved in taking the series (2) as far as the second term when calculating the electrophoretic effect for 1:1 electrolytes. For unsymmetrical electrolytes however there is a definite mathematical inconsistency in accepting the square term in series (2), and then using for ψ the expression (3) obtained by neglecting square terms. This was recognized by Onsager and Fuoss,[1] who commented that their expressions for Δ_1 and Δ_2 were scarcely changed by using the expressions for the potential obtained by La Mer[3] and co-workers, in which higher powers were considered. This is however not entirely relevant, since the La Mer formulas have been criticized[2] as inconsistent with the superposition principle. The point is rather that in the general case only the first-order electrophoretic term Δ_1 is mathematically consistent with the formula adopted for the charge density and with expression (3) for the potential. In the case of single 1:1 electrolytes however there is logical justification for including the second-order electrophoretic correction Δ_2 in the diffusion problem, since formulas 1, 3 and 5 are then all self-consistent as far as square terms in the potential. It will now be shown, by evaluating higher electrophoretic contributions from the higher terms in series (2), that for 1:1 electrolytes the series $\Delta_1 + \Delta_2 + \cdots$ converges sharply after Δ_2, the higher terms being negligible, but that for unsymmetrical electrolytes such convergence does not occur. It follows that there is no justification, either logical or numerical, for accepting the second-order electrophoretic term for unsymmetrical electrolytes, though for 1:1 electrolytes its acceptance is not only logically justifiable and experimentally necessary, but is also sufficient to ensure convergence. For unsymmetrical electrolytes the first-order term, which alone is justifiable, also gives results corresponding better to the experimental observations than are obtained by including Δ_2 and higher terms.

Evaluation of the Higher Order Electrophoretic Corrections.—This task turns out to be less difficult than might be imagined from an examination of the usual expressions for Δ_1 and Δ_2. One finds, by a straightforward generalization of the procedure by which Δ_1 and Δ_2 were obtained,[1] that the nth electrophoretic correction, Δ_n, arising from the nth term of the series in equation (2), is given by

$$\Delta_n = \frac{1.546 \times 10^{-7} RT}{6\pi\eta \mathbf{F}^2} \cdot \frac{(-1)^n}{n!} \left(\frac{e^2}{\epsilon k T}\right)^{n-1} 10^{8n} \times$$
$$(\kappa a)^2 \left(\frac{e^{\kappa a}}{1 + \kappa a}\right)^n a^{n-2} \int_a^\infty \frac{e^{-n\kappa r}}{r^{n-1}}\, \mathrm{d}r \times$$
$$\frac{1}{|z_1 z_2|} \frac{(z_1{}^n t_2^0 + z_2{}^n t_1^0)^2}{\mathring{a}^n} \qquad (8)$$

The factors in equation 8 have been arranged in three groups, each given on a separate line. The first group contains only physical constants and properties of the solvent; the second group is a function only of the dimensionless concentration-dependent quantity (κa); and the third group contains only specific characteristics of the ions, *viz.*, their valences and transference numbers, and the "distance of closest approach" $\mathring{a}$. It should be noted that $\mathring{a}$ in the third line is to be expressed in ångström units; the compensating factor 10^{8n} has been introduced into the first line. The second line appears to contain a^{n-2} in addition to functions of (κa) only, but this factor actually cancels with a similar one which appears upon evaluating the integral. The integral in the second line of (8) can be expressed in terms of the exponential integral function $E_i(x) = \int_x^\infty e^{-y}y^{-1}\mathrm{d}y$, which is available in tables,[4] and simple exponential functions. Successive values of the integral are given by

$$a^{n-2} \int_a^\infty \frac{e^{-n\kappa r}}{r^{n-1}}\, \mathrm{d}r = S_n(\kappa a) \qquad (9)$$

where

$$S_1(\kappa a) = \frac{e^{-\kappa a}}{\kappa a}; \qquad S_2(\kappa a) = E_i(2\kappa a);$$
$$S_3(\kappa a) = e^{-3\kappa a} - 3\kappa a E_i(3\kappa a);$$
$$S_4(\kappa a) = e^{-4\kappa a}\left(\frac{1}{2} - 2\kappa a\right) + 8(\kappa a)^2 E_i(4\kappa a);$$

etc.

The S_n for $n > 2$ are obtained by repeated integration by parts; the general expression is

$$S_n(\kappa a) = e^{-n\kappa a}\left[\frac{1}{n-2} + \frac{(-n\kappa a)}{(n-2)(n-3)} + \frac{(-n\kappa a)^2}{(n-2)(n-3)(n-4)} + \cdots + \frac{(-n\kappa a)^{n-3}}{(n-2)!}\right] + \frac{(-n\kappa a)^{n-2}}{(n-2)!} E_i(n\kappa a) \qquad (10)$$

there being $(n - 2)$ terms in the series enclosed in square brackets in (10). The concentration-dependent factors in the second line of equation (8) may therefore be written

$$\phi_n(\kappa a) = (\kappa a)^2 \left(\frac{e^{\kappa a}}{1 + \kappa a}\right)^n S_n(\kappa a) \qquad (11)$$

Values of $\phi_n(\kappa a)$ at round values of (κa) for n up to 5 are given in Table I.

TABLE I

VALUES OF THE FUNCTION $\phi_n(\kappa a)$ AT ROUND VALUES OF (κa)

κa	$100\phi_1(\kappa a)$	$100\phi_2(\kappa a)$	$100\phi_3(\kappa a)$	$100\phi_4(\kappa a)$	$100\phi_5(\kappa a)$
0	0.000	0.0000	0.0000	0.0000	0.0000
0.05	4.762	0.4566	0.1609	.0884	.0584
.1	9.091	1.235	0.4761	.2624	.1693
.2	16.67	2.911	1.166	.6192	.3764
.3	23.08	4.405	1.734	.876	.499
.5	33.33	6.628	2.425	1.100	.552
.7	41.18	7.987	2.686	1.096	.491
1.0	50.00	9.032	2.678	0.938	.37

For the case of water as solvent at 25°, one finds on substituting the values of η, ϵ, k, e and $\mathbf{F}$ (given in the list of symbols) that equation (8) reduces to

$$\Delta_n = (-1)^n\left[3.425 \times 10^{-6} \frac{(7.134)^n}{n!} \phi_n(\kappa a)\right] \frac{1}{|z_1 z_2|} \frac{(z_1^n t_2^0 + z_2^n t_1^0)^2}{\mathring{a}^n} \qquad (12)$$

The quantity in the square bracket of (12) may be

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(3) T. H. Gronwall, V. K. La Mer and K. Sandved, *Physik. Z.*, **29**, 358 (1928).

(4) E. Jahnke and F. Emde, "Tables of Functions," Dover Publications, N. Y., 1945.

abbreviated to $F_n(\kappa a)$; values of this quantity at round (κa) are given in Table II, and are valid only for aqueous solutions at 25°.

TABLE II

VALUES OF THE QUANTITY $F_n(\kappa a)$ FOR AQUEOUS SOLUTIONS AT 25°

κa	$F_1(\kappa a) \times 10^6$	$F_2(\kappa a) \times 10^6$	$F_3(\kappa a) \times 10^6$	$F_4(\kappa a) \times 10^6$	$F_5(\kappa a) \times 10^6$
0	0	0	0	0	0
0.05	1.163	0.398	0.334	0.327	0.308
.1	2.221	1.076	0.987	0.970	0.893
.2	4.072	2.537	2.417	2.289	1.985
.3	5.64	3.839	3.595	3.238	2.63
.5	8.14	5.78	5.03	4.07	2.91
.7	10.06	6.96	5.57	4.05	2.59
1.0	12.22	7.87	5.55	3.47	1.95

Thus the diffusion coefficient is now given by

$$D = (1 + c\ \mathrm{d} \ln y_{\pm}/\mathrm{d}c) \times (D^0 + \Delta_1 + \Delta_2 + \cdots + \Delta_n +) \cdots \quad (13)$$

where

$$\Delta_n = (-1)n \frac{F_n(\kappa a)}{|z_1 z_2|} (z_1^n t_2^0 + z_2^n t_1^0)^2/\mathring{a}^n \quad (14)$$

A glance across the rows of Table II shows that for a given (κa) value, the quantity $F_n(\kappa a)$ decreases only slowly with increasing n: it remains of the same order of magnitude for n up to 5. This means that responsibility for the early convergence of the series $\Sigma\Delta_n$ is thrown upon the factor $(z_1^n t_2^0 + z_2^n t_1^0)^2/\mathring{a}^n$ in equation 14; if this decreases rapidly with increasing n, convergence is assured. For 1:1 electrolytes, the factor takes alternately the values $(t_2^0 - t_1^0)^2/\mathring{a}^n$ (odd n) and $1/\mathring{a}^n$ (even n); and since $\mathring{a}$ for most 1:1 electrolytes lies in the range 3 to 5, it follows that the factor $\mathring{a}^n$ in the denominator will mean that Δ_3 and Δ_4 are at least an order of magnitude smaller than Δ_1 and Δ_2, respectively. The original Onsager–Fuoss expression 1 is therefore adequate for 1:1 electrolytes.

For higher valence type electrolytes however the position is quite different; it is easily seen that if the higher-valence ion present has valence z, the factor $(z_1^n t_2^0 + z_2^n t_1^0)^2$ will be approximately proportional to z^{2n}, the approximation improving as n increases. Hence if z^2 is greater than $\mathring{a}$ (or not much smaller), the series $\Sigma\Delta_n$ will converge only slowly, if at all, for small n values. Since for electrolytes of the 2:1 and 3:1 categories the $\mathring{a}$ values usually lie in the range 4–7, it follows that early convergence will not occur in these cases, and the Onsager–Fuoss expression 1 will therefore fail. It is hardly justifiable to consider 2:2, 3:2 or 3:3 electrolytes, since these always show marked ion-pair formation effects which make the theory in its usual form inapplicable; but the same convergence troubles would clearly arise in these cases. It is thus clear that there are sound theoretical reasons for the observations that the Onsager–Fuoss expression 1 is satisfactory for potassium chloride,[5] lithium chloride,[6] and other 1:1 electrolytes in water at 25°, but that it fails for calcium chloride[7] and lanthanum chloride.[8]

These two last-named salts are the only polyvalent ones for which both accurate diffusion coefficients and accurate values of the activity factor $(1 + c\ \mathrm{d} \ln y^{+}/\mathrm{d}c)$ are available in dilute solutions. Some other cases where there is apparently a reasonable degree of conformity with equation 1, *e.g.*, sodium sulfate, do not in fact provide convincing evidence since the activity factor has to be obtained by a long extrapolation from the region where reliable activity coefficients are available.

Some numerical examples will now be discussed.

(a) **Lithium Chloride:**

$z_1 = -z_2 = 1, t_1^0 = 1 - t_2^0 = 0.3364;\ \mathring{a} = 4.32;\ \Lambda^0 = 115.03$
$D^0 = 1.3683 \times 10^{-5}$
$\Delta_1 = -(0.3272^2/4.32)F_1(\kappa a) = -0.0248F_1(\kappa a)$
$\Delta_2 = +(1/4.32^2)F_2(\kappa a) = +0.0536F_2(\kappa a)$
$\Delta_3 = -(0.3272^2/4.32^3)F_3(\kappa a) = -0.00133F_3(\kappa a)$
$\Delta_4 = +(1/4.32^4)F_4(\kappa a) = +0.00287F_4(\kappa a)$

The values of c corresponding to the round (κa) values are now calculated from the relation $0.3286\ \mathring{a}c^{1/2} = \kappa a$, which in this case gives $c = 0.4963\ (\kappa a)^2$. We now obtain the Δ_n with the help of Table II, as shown in Table III.

TABLE III

ELECTROPHORETIC TERMS FOR LITHIUM CHLORIDE SOLUTIONS AT 25°

κa	c	$\Delta_1 \times 10^5$	$\Delta_2 \times 10^5$	$\Delta_3 \times 10^5$	$\Delta_4 \times 10^5$
0.05	0.00124	−0.0029	+0.0021	...	+0.0001
.1	.00496	− .0055	+ .0058	−0.0001	+ .0003
.3	.0447	− .0140	+ .0260	− .0005	+ .0009
1.0	.4963	− .0303	+ .0422	− .0007	+ .0010

This tabulation merely confirms the conclusion reached above, that the error involved in stopping at Δ_2 is negligible, so that equation 1 is applicable.

(b) **Calcium Chloride:**

$z_1 = 2,\ z_2 = -1,\ t_1^0 = 1 - t_2^0 = 0.4380,\ \Lambda^0 = 135.85,\ \mathring{a} = 4.73$
$D^0 = 1.3364 \times 10^{-5},\ c = 0.1380(\kappa a)^2$

κa	c	$\Delta_1 \times 10^5$	$\Delta_2 \times 10^5$	$\Delta_3 \times 10^5$	$\Delta_4 \times 10^5$	$\Delta_5 \times 10^5$
0.05	0.00035	−0.0058	+0.0064	−0.0026	+0.0029	−0.0020
.1	.00138	− .0110	+ .0173	− .0077	+ .0086	− .0058
.2	.00552	− .0203	+ .0409	− .0188	+ .0203	− .0129
.3	.0124	− .0281	+ .0619	− .0280	+ .0288	− .0171
.5	.0345	− .0405	+ .0932	− .0391	+ .0362	− .0189
.7	.0676	− .0500	+ .1122	− .0433	+ .0360	− .0168
1.0	.1380	− .0608	+ .1269	− .0432	+ .0308	− .0127

We see that the series $\Sigma\Delta_n$ is converging very slowly, if at all. It is therefore not surprising that the Onsager–Fuoss equation 1, which includes Δ_1 and Δ_2 only, fails to give agreement with experiment. However, we have remarked earlier that on grounds of self-consistency only the first-order term Δ_1 is acceptable for unsymmetrical electrolytes; we shall therefore make a comparison between theory and experiment using this term only, *i.e.*, using the formula

$$D = (1 + c\ \mathrm{d} \ln y_{\pm}/\mathrm{d}c)(D_0 + \Delta_1) \quad (15)$$

The factor $(1 + c\ \mathrm{d} \ln y_{\pm}/\mathrm{d}c)$ can be computed from the activity coefficient data of McLeod and Gordon,[9] and takes the values 0.949, 0.935, 0.922, 0.911, 0.901 and 0.892 at $\sqrt{c}$ = 0.03, 0.04, 0.05, 0.06, 0.07, and 0.08, respectively. Using these values

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(5) H. S. Harned and R. L. Nuttall, THIS JOURNAL, **69**, 736 (1947).

(6) H. S. Harned and C. L. Hildreth, *ibid.*, **73**, 650 (1951).

(7) H. S. Harned and A. L. Levy, *ibid.*, **71**, 2781 (1949).

(8) H. S. Harned and C. A. Blake, *ibid.*, **73**, 4255 (1951).

(9) H. G. McLeod and A. R. Gordon, THIS JOURNAL, **68**, 58 (1946).

in equation (15) we obtain the calculated D values shown by the continuous curve in Fig. 1; the measured values[7] are plotted as circles. The superiority of the "self-consistent" equation 15 over equation 1, shown as a broken line, is evident.

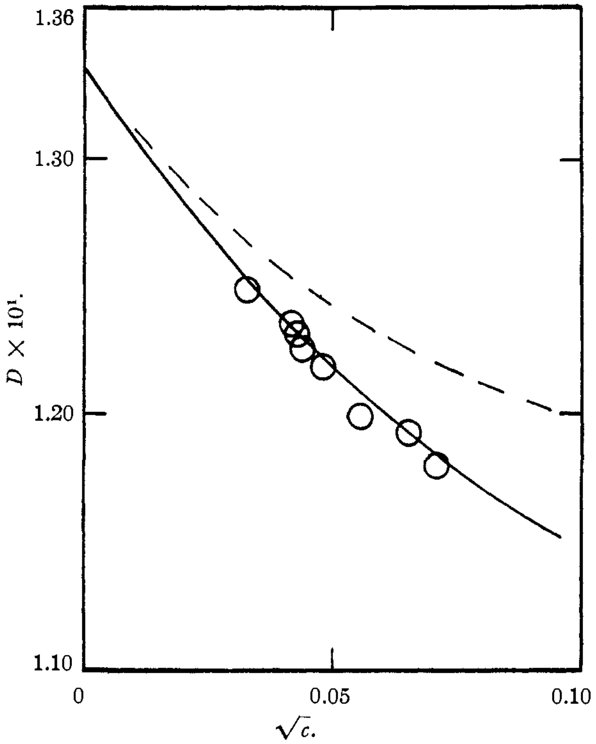

Fig. 1.—Diffusion coefficient of aqueous calcium chloride solutions at 25°: ⊙, experimental values (Harned and Levy)[1]; —, "self-consistent" equation 15; — — —, Onsager–Fuoss equation 1.

(c) Lanthanum Chloride:

$z_1 = 3$, $z_2 = -1$, $t_1^0 = 1 - t_2^0 = 0.477$, $\Lambda^0 = 145.9$, $\mathring{a} = 6.8$
$D^0 = 1.294 \times 10^{-5}$, $c = 0.0334(\kappa a)^2$

These values lead to the Δ_n values below

κa	c	$\Delta_1 \times 10^5$	$\Delta_2 \times 10^5$	$\Delta_3 \times 10^5$	$\Delta_4 \times 10^5$	$\Delta_5 \times 10^5$
0.2	0.00134	−0.024	+0.049	−0.048	+0.065	−0.073
.3	.00301	− .033	+ .074	− .071	+ .093	− .097
.5	.00835	− .048	+ .112	− .099	+ .116	− .107
.7	.01637	− .059	+ .135	− .110	+ .116	− .095
1.0	.0334	− .071	+ .153	− .110	+ .099	− .072

Here the non-convergence of the series $\Sigma\Delta_n$ is, as expected, even more marked. The "self-consistent" equation 15 is here less satisfactory, giving a curve lying well below the experimental results, while the Onsager–Fuoss equation 1 gives a curve lying above them. This is a different order-relation to that shown by calcium chloride (Fig. 1), and may perhaps indicate that some ion-pair formation is occurring; this would have the effect of increasing the diffusion coefficient. Electrolytes of 3:1 valency type are in any case difficult to deal with theoretically, but it is noteworthy that the activity coefficient curve of lanthanum chloride[10] at the concentrations considered here falls *below* that given by the Debye–Hückel expression $\log y_{\pm} = -\frac{3.74\sqrt{c}}{1 + 5.5\sqrt{c}}$ in which the factor 5.5 corresponds to an ionic diameter of 6.8 Å.; this also suggests that some ion-pair formation is occurring.

There are of course many other assumptions and approximations inherent in the computation of the electrophoretic terms, whatever choice be made in terminating the expansion of the series in equation 2: (a) Stokes' law is used in treating the motion of a series of shells proceeding outwards from the central ion to infinity. These exist only as a time-average, and are a convenient mathematical fiction rather than a physical reality; furthermore when a different central ion is chosen it becomes impossible for any normal imagination to picture the resulting interpenetrating system of shells at all. In these circumstances it is difficult to make any analysis of the justification of using Stokes' law, and one must merely note that the resulting formulas do work, for 1:1 electrolytes at least. (b) Other approximations made involve binomial expansions of the form $1/(1 + x) \approx (1 - x)$; the quantities involved as x in these expansions are of the order of magnitude of Δ_n/D_0, which the examples quoted show to be small enough to permit the neglect of their squares at the concentrations considered. The same applies to an approximation in which the "forces" acting on the diffusing ions are evaluated in terms of the velocities they have before the electrophoretic corrections are applied: since this assumption is made only for the purpose of calculating the electrophoretic corrections themselves, it follows that the error it introduces will be of the second order.

Conclusion.—Thus the present investigation has succeeded to the extent of: (a) demonstrating the *theoretical* adequacy and self-consistency of the Onsager–Fuoss equation 1 for 1:1 electrolytes; (b) showing that the same equation applied to unsymmetrical electrolytes is neither self-consistent nor convergent; and (c) showing that the "self-consistent" equation 15, in which only the first-order electrophoretic term is accepted, is satisfactory in the case of calcium chloride. (Its failure for lanthanum chloride must however be attributed to ion-pair formation, for which there is other evidence.)

I am indebted to Dr. J. N. Agar of the University of Cambridge for valuable discussions on the problem of self-consistency.

Nedlands, Western Australia

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[10] T. Shedlovsky, This Journal, **72**, 3680 (1950).