

ASSOCIATION OF 1-1 SALTS IN WATER*

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In solvents of low dielectric constant, where the electrostatic potential energy ϵ^2/aD of an anion and a cation at contact is large compared to mean thermal energy kT , one expects and finds association of ions to nonconducting pairs. As the dielectric constant is increased the extent of association should (and does) decrease, but in principle it should never become zero, because there is always a nonzero chance that anion-cation contacts will occur, even if the ratio $b = \epsilon^2/aDkT$ becomes small. In fact, for the hypothetical extreme of infinite dielectric constant, the association constant due to encounters between ions should be given¹ by

$$K^0 = 4\pi Na^3/3000 = 0.002523\delta^3. \quad (1)$$

For $\delta = 5$, $K^0 \approx 0.3$; at 0.01 *N*, this would correspond to a decrease in conductance of about 0.3 per cent, and at 0.1 *N* to 3 per cent. Association of 1-1 salts in water has, however, been completely disregarded ever since the Debye-Hückel theory, based on the hypothesis of complete dissociation, proved to be so successful in predicting the behavior of electrolytes in the limit of extreme dilution. Experimentally, it seemed futile to look for association in aqueous solutions, for practical reasons. Application of the Fuoss-Onsager theoretical treatment^{2, 3} of conductance has been limited by their mathematical approximations to solutions no more concentrated than about 0.01 *N*. (These limitations were deliberately set; the mathematical functions to which the theory led were hopelessly intricate from the point of view of practical computation, because electronic computers were not generally available in 1955 when the theory was developed. The linearized approximation was therefore proposed; the price paid for the simplification was restriction of the range applicability of the equation. This restriction has, unfortunately, been disregarded by some authors who have applied the equation to data at higher concentrations.) The linearized conductance equation for unassociated salts is

$$\Lambda = \Lambda_0 - Sc^{1/2} + E'c \ln c + Jc, \quad (2)$$

which is modified to

$$\Lambda = \Lambda_0 - Sc^{1/2} + E'c \ln c + Jc - K_A\Lambda_0c \quad (3)$$

if slight association occurs. Clearly, since both the Jc term from long-range interaction and the $K_A\Lambda_0c$ term from pair formation are linear in concentration, empirical analysis of conductance data can only produce a net linear coefficient ($J - K_A\Lambda_0$) and there is no way to split it into components. For ordinary salts in water, the theoretical Jc term amounts to about 1.5 per cent at 0.01 *N* so a 0.3 per cent association is in any case relatively small, and difficult to find. The obvious experimental approach would be to work at higher concentrations, where the association term would not only be larger, but also would have a different functional dependence on concentration and thereby be accessible to evaluation by appropriate analysis. However, this approach has been blocked by the limitations of current theory; if

equation (2) is applied to data at concentrations above 0.01 *N*, the parameters Λ_0 and *J* begin to depend on the range of concentration over which they are determined, and deviations between calculated and observed conductances acquire a systematic plus-minus-plus pattern which becomes more pronounced, the higher the maximum concentration included in the calculation. Both of these symptoms lead to one diagnosis: the functional form of equation (2) is incorrect for concentrations much above 0.01 *N* in water.

Consideration of a large number of recent data of high precision ($\pm 0.02\%$) for several alkali halides in water^{4, 5} showed that the experimental data could be reproduced within the experimental error by a semi-empirical equation of the form

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec \log c + Ac + Bc^{3/2}, \quad (4)$$

where *S* and *E* are given by theory. A test of equation (4) is shown in Figure 1. Conductance data for potassium chloride, cesium iodide, sodium chloride, and cesium bromide were analyzed by a least-squares procedure to obtain the corresponding values of Λ_0 , *A*, and *B*. Then the quantity

$$Y = [\Lambda(\text{obs.}) - \Lambda_0 + Sc^{1/2} - Ec \log c]/c$$

was plotted against square root of concentration. The resulting plots are linear as required by equation (4). The solid circles represent Shedlovsky's earlier results^{6, 7} for potassium and sodium chlorides; perfect agreement appears. Standard deviations between calculated and observed values are 0.015, 0.018, 0.017, and 0.020 Λ -units for the four systems of Figure 1. The equation for potassium chloride is

$$\Lambda = 149.936 - 94.88c^{1/2} + 25.48c \ln c + 221.0c - 229c^{3/2}. \quad (4a)$$

It fits the Jones and Bradshaw⁸ points at 0.01 demal and 0.1 demal within 0.011 per cent and 0.010 per cent, respectively, and hence may be used for cell calibration.⁹

The coefficient *B* was found to be quite different from the J_2 of the approximate theory which included a special $c^{3/2}$ term,² the one from expansion of negative exponential integrals (all other terms of this order had been systematically dropped). Given the close fit between observed conductances and values computed by equation (4), we were encouraged to repeat the integrations which led to equation (2), this time with explicit retention of all of the terms of order $c^{3/2}$. The result (as expected) was a quite complicated expression for the conductance function, far too complicated for a desk calculator, especially when ionic association was included, but the function can be handled by an electronic computer.

The equivalent conductance Λ as a function of concentration is given by the equation

$$\Lambda = \gamma(\Lambda_0 - \Delta\Lambda)(1 + \Delta X/X)/(1 + 3\phi/2), \quad (5)$$

where γ is the ratio of free ion concentration to stoichiometric. The electrophoretic term $\Delta\Lambda$

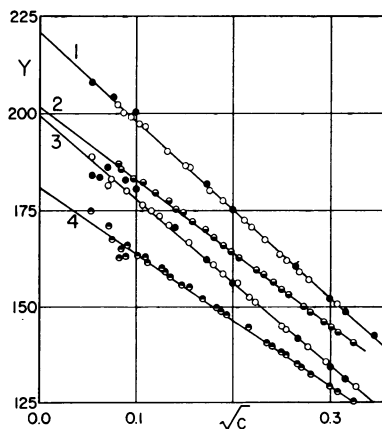


FIG. 1.—Test of empirical equation. Top to bottom: (1) $Y(\text{KCl})$, (2) $Y(\text{CsI})$, (3) $Y(\text{NaCl})$, (4) $Y(\text{CsBr}) - 10$.

and the relaxation term $\Delta X/X$ are given explicitly in the *Appendix*, equations (A39) and (A14). The fraction γ is determined by the association constant K_A

$$1 - \gamma = K_A c \gamma^2 f^2, \quad (6)$$

where the activity coefficient f is calculated by the Debye-Hückel limiting law

$$-\ln f = \beta \kappa / 2. \quad (7)$$

Both $\Delta\Lambda$ and ΔX are functions of κa , where a is the center-to-center distance at contact of the rigid charged spheres which represent the ions; ΔX also depends on a through the parameter $b = \beta/a$. The factor $(1 + 3\varphi/2)$, where φ , the volume fraction of one species of ions, is approximated by $(4\pi Nc/3000)(a/2)^3$, makes allowance for the fact that ions obstruct the motion of ions of the opposite charge.^{10, 11}

The conductance equation is a 3-constant equation:

$$\Lambda = \Lambda(c; \Lambda_0, K_A, \delta) \quad (8)$$

and is nonlinear in all three parameters. A program was designed to analyze a set of data points (c_j, Λ_j) to evaluate the parameters by the following sequence of operations: First, an arbitrary value (of the correct order of magnitude) was chosen for the association constant, and γ 's were computed from equation (6) by a convergent series of successive approximations. Then values of Λ_0 and δ were found which would minimize $\Sigma(\delta\Lambda_j)^2$, where $\delta\Lambda$ is the difference between conductance calculated by equation (5) and the observed conductances Λ_j :

$$\delta\Lambda = \Lambda(\text{calc.}) - \Lambda(\text{obs.}) \quad (9)$$

Then another value of association constant was tested and the standard deviation σ was again computed. This step was repeated until the minimizing value of association constant was bracketed. This final interval was then searched to locate K_A (min.), using appropriate subroutines to locate the corresponding values of Λ_0 and δ .

Conductance data for the following systems were analyzed by the above procedure: sodium chloride in water⁴ and in dioxane-water mixtures,¹² potassium chloride in water⁴ and in dioxane-water mixtures,¹³ and cesium iodide in water⁵ and in dioxane-water mixtures.¹⁴ An example is shown in Figure 2, where the standard deviation σ is plotted against the value of the contact distance δ ; the ordinate scales, in Λ -units, are displaced by arbitrary amounts to prevent overlap. These plots represent projections on a plane of the intersection of skew surfaces cutting the σ - (Λ_0, K_A, δ) surface at varying δ and at the Λ_0 and K_A values which minimize σ continuously for the corresponding δ -values. Curves 1-5 correspond to data for cesium iodide in dioxane-water mixtures with dielectric constants 12.81, 15.29, 18.68, 24.44, and 40.57, respectively. It will be noted that the minimum, which is very sharp at low dielectric constants, becomes progressively broader as the dielectric constant increases. These data (1961) for the dioxane-water mixtures had been designed to test the linearized² conductance equation for associated electrolytes

$$\Lambda = \Lambda_0 - Sc^{1/2}\gamma^{1/2} + Ec\gamma \log c\gamma + Jc\gamma - K_A c \gamma^2 f^2 \Lambda \quad (10)$$

and the concentration range had therefore been restricted to an upper limit such that κa did not exceed 0.1. For dielectric constants above about 40, the σ - δ

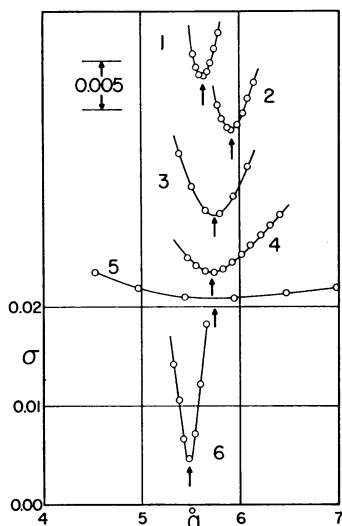


FIG. 2.—Analysis of conductance data for cesium iodide in dioxane-water mixtures; $\kappa a < 0.1$.

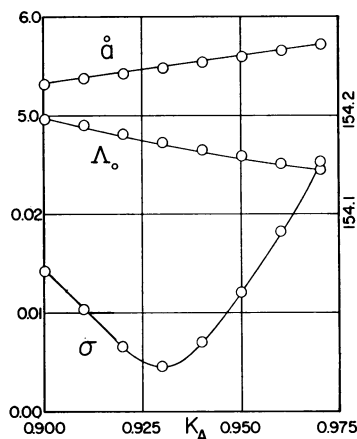


FIG. 3.—Analysis of conductance data for cesium iodide in water; $0.003 \leq c \leq 0.093$.

minima become so shallow that no unique value of a can be determined. This is to be expected, of course, because the ion pair term becomes steadily less significant as dielectric constant increases. At low concentrations in solvents of higher dielectric constant it therefore becomes impossible to conclude whether any ion pairs at all are present, because the measurements cannot distinguish between a small K_A and one equal to zero. But by going to higher concentrations, the ion pair term becomes visible again, as shown in Figure 3. The bottom curve is a plot of σ against K_A for data over the range $0.003 \leq c \leq 0.10$; the minimum at $K_A = 0.93$ is sharp. The minimizing Λ_0 and d values corresponding to the range of K_A -values are shown in the upper two plots; curve 6 of Figure 2 was constructed from the data of Figure 3. The minimizing constants $\Lambda_0 = 154.172$, $d = 5.492$, and $K_A = 0.93$ reproduce the entire set of data with $\sigma = 0.0134$, or 0.0085 per cent.

The minima of the σ - d curves of Figure 2 lie between 5.5 and 5.9. The value 5.50 from the data in water is the most precisely determined, because it is based on 70 data points covering concentrations up to about 0.1 N . In the dioxane-water runs, only five data points were available at each value of dielectric constant. Inspection of Figure 2 suggests that the *same* value of contact distance should describe cesium iodide in *all* mixtures. Accordingly, the inverse calculation was made; d was fixed at the water value of 5.50, and the corresponding values of Λ_0 and K_A which would minimize σ were determined. Data for sodium chloride (water value of $d = 6.10$) and potassium chloride (water value of $d = 5.65$) were treated in the same fashion. The results of these calculations are summarized in Table 1. In every case, a single contact distance serves to predict the conductance of the salt over the entire range of dielectric constant from that of water down to about 12. This result, that d is a parameter independent of solvent composition, shows that the previously observed variation¹³ of d was an arithmetical artifact produced by the neglect of ion association at the higher dielectric constants. The association con-

TABLE 1
CALCULATION OF CONDUCTANCE USING WATER VALUE OF \bar{d} FOR MIXTURES

D	Λ_0	K_A	ϵ
Cesium Iodide, $\bar{d} = 5.50$			
60.18	99.42	1.0	0.013
40.57	66.89	3.0	0.005
29.79	56.52	11.4	0.006
24.44	52.28	30	0.006
18.68	48.27	109	0.010
15.29	45.44	336	0.021
12.81	41.95	865	0.012
Potassium Chloride, $\bar{d} = 5.65$			
60.16	100.73	1.6	0.010
41.46	69.16	5.9	0.009
30.26	56.48	24	0.004
25.84	52.40	46	0.006
19.32	46.39	184	0.005
15.37	42.73	575	0.005
12.74	39.46	1720	0.016
Sodium Chloride, $\bar{d} = 6.10$			
49.54	71.21	3.0	0.009
32.77	53.31	16	0.009
26.85	48.78	34	0.010
18.74	42.75	177	0.021
16.67	41.11	330	0.003
13.51	38.60	1035	0.022
12.12	37.52	2050	0.010

stants in water are 0.93 for cesium iodide, 0.80 for potassium chloride, and 0.92 for sodium chloride.

The dependence of association constant on dielectric constant is shown in Figure 4, where logarithm of association constant is plotted against reciprocal dielectric constant. Theory¹ predicts linearity, from

$$K_A = (4\pi N a^3 / 3000) \exp(\epsilon^2 / a D k T). \quad (11)$$

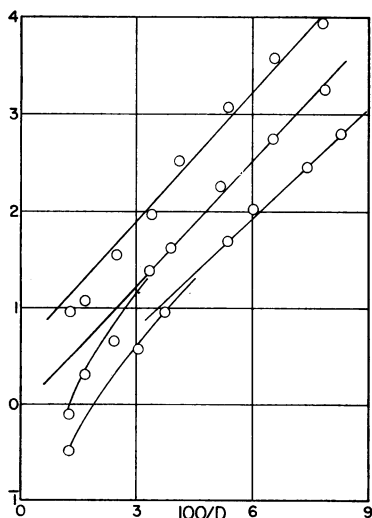


FIG. 4.—Dependence of association constant on dielectric constant. *Top to bottom:* cesium iodide ($1.0 + \log K_A$); potassium chloride ($\log K_A$); and sodium chloride ($-0.5 + \log K_A$).

The linear segments in the figure are drawn with slopes calculated from the water values of the parameter \bar{d} which minimized the difference between observed conductances and values calculated by equation (5). Reasonably good agreement is found for cesium iodide over the whole range of dielectric constants. For potassium and sodium chlorides the fit is good at the lower dielectric constants, but the values curve down from the straight line for water-rich mixtures, and earlier for sodium than for potassium. The agreement between slopes calculated from a single value of \bar{d} , at least for a large part of the dielectric range, is most gratifying, because it is convincing evidence that the association constants reported here have real physical meaning and are not merely the results of curve-fitting.

The curvature for sodium and potassium chlorides at higher dielectric constant suggests the

obvious *ad hoc* hypothesis that K_A should contain an entropy factor¹⁷ to allow for the differences in water structure around free ions and around ion pairs as the cation varies through the series of the alkali metals. In the dioxane-rich systems, where the $\log K_A - D^{-1}$ slope has the predicted value, the water structure is presumably destroyed by the dioxane; hence the agreement there. The values of a are all considerably larger than the sum of the lattice radii of the ions and clearly must include the diameters of several water molecules. This observation suggests that conductance measures the association constant for solvent-separated ion pairs.

Appendix.—The relaxation field is given by

$$\Delta X/X = -\alpha c^{1/2} \gamma^{1/2} (1 - \Delta_1) + \Delta X_B/X + \Delta X_{2,3}/X + \Delta X_a/X + \Delta X_P/X + \Delta X_v/X, \quad (A1)$$

where the symbols are those defined in reference 2. The following terms remain unchanged

$$\alpha c^{1/2} \Delta_1 = (\beta^2 \kappa^2 / 12 p_3 b^2) (1 + b) \quad (A2)$$

$$\Delta X_B/X = [\beta^2 \kappa^2 / 3 p_2 (1 + \kappa a)^2] [1/8 - (1 + \kappa a)/4b + T_2/4] \quad (A3)$$

$$\begin{aligned} \Delta X_a/X &= -\{\beta^2 \kappa^2 / 3 p_2 p_3 (1 + \kappa a)^2\} [0.5 - 2q/3] \\ &= -0.0286 \{ \dots \}. \end{aligned} \quad (A4)$$

The cross-gradient term becomes

$$\Delta X_{2,3}/X = -(\beta^2 \kappa^2 / 3) [F_{23}(\kappa a) - (\kappa a/b) F_b(\kappa a) + (3T_2 + p_1 T_1 - 4p_1 p_2 T_0) / 16 p_2 (1 + \kappa a)^2] \quad (A5)$$

with
$$F_{23}(\kappa a) = N_{23}(\kappa a) / 4 p_2 p_3 (1 + \kappa a)^2 \quad (A6)$$

$$N_{23}(\kappa a) = -9/4 + 9q/2 + (7q/3 - 7/12)\kappa a + (7q/12 + 1/24)\kappa^2 a^2 \quad (A7)$$

and
$$F_b(\kappa a) = N_b(\kappa a) / 8 p_2 p_3 (1 + \kappa a) \quad (A8)$$

$$N_b(\kappa a) = q/2 + (2q - 2/3)\kappa a + (5/12 - q/3)\kappa^2 a^2. \quad (A9)$$

The function $F_b(\kappa a)$ and the κa and $\kappa^2 a^2$ terms in N_{23} are new. The kinetic term to next approximation is now

$$\Delta X_P/X = (\beta^2 \kappa^2 / 12 b^2) [(1 + \kappa a/2) / (1 + \kappa a)(1 + q\kappa a) - 1/b], \quad (A10)$$

where the bracketed quantity replaces the former $[1 - 1/b]$. The velocity term¹⁵ is replaced by

$$\Delta X_v/X = [\beta \kappa^2 / 6 \pi \eta (\omega_1 + \omega_2)] [F_v(\kappa a) + F(\kappa a) / 2(1 + \kappa a)^2 - 1/6b p_3 (1 + \kappa a)], \quad (A11)$$

where
$$F_v(\kappa a) = N_v(\kappa a) / 48 p_2 (1 + \kappa a)^2$$

$$N_v(\kappa a) = 16 + 6q + (7 + 10q)\kappa a + (3 + 4q)\kappa^2 a^2 \quad (A12)$$

and
$$F(\kappa a) = (7T_2 + p_3 T_1 - p_2 p_3 T_0) / 8 p_2. \quad (A13)$$

Here the κa and $\kappa^2 a^2$ terms in $N_v(\kappa a)$ are new. Also, the constant $(16 + 6q)$ replaces the former¹⁵ $(13 + 6q)$; the 13 was either a misprint or a mistake.

The integrations actually gave higher polynomials in the numerators $N(\kappa a)$. By numerical test, we found that terms of order $\kappa^3 a^3$ in the polynomials could be neglected without significantly changing the values obtained for the conductance parameters, provided κa did not exceed 0.4. (Terms of order $\kappa^2 a^2$ in the polynomials are equivalent to terms of order c^2 in the Λ - c equations.) Therefore, these equations should not be used in a range of variables beyond $\kappa a \approx 0.3$ on account of this algebraic approximation. Also, of course, for such values of κa , the distance κ^{-1} is only three times the mean ionic diameter, and the average implied in using an ionic atmosphere as a model is certainly no longer valid.

The above relaxation field terms are combined by substituting in (A1). The result, in which electrostatic and hydrodynamic terms (coefficients E_1' and E_2' , respectively) are separated, is

$$(1 + \Delta X/X) = 1 - \alpha c^{1/2} \gamma^{1/2} + E_1' c \gamma F_1(\kappa a, b) - (E_2' c \gamma / \Lambda_0) F_2(\kappa a, b), \quad (A14)$$

where

$$F_1 = -4F_{11} - F_{12} + F_{13}/b + F_{14}/b^2 - 2/b^3 \quad (A15)$$

$$F_2 = -8F_{21} - 4F_{11} + 4/3bp_2(1 + \kappa a) \quad (A16)$$

with

$$F_{11} = (7T_2 + p_1T_1 - 4p_1p_2T_0)/8p_2(1 + \kappa a)^2 \quad (A17)$$

$$F_{12} = 2N_{12}(\kappa a)/p_2p_3(1 + \kappa a)^2 + 1/p_2(1 + \kappa a)^2 + 0.4576/2p_2p_3(1 + \kappa a)^2 \quad (A18)$$

$$N_{12} = -9/4 + 9q/2 + (-7/12 + 7q/3)\kappa a + (1/24 + 7q/12)\kappa^2 a^2 \quad (A19)$$

$$F_{13} = 4N_{13}/p_2p_3(1 + \kappa a) \quad (A20)$$

$$N_{13} = 1 + (9q/8 + 1/2)\kappa a + (q + 1/24)\kappa^2 a^2 \quad (A21)$$

$$F_{14} = 4(1 + 3\kappa a/4)/p_3(1 + \kappa a) \quad (A22)$$

$$F_{21} = N_{21}/48p_2(1 + \kappa a)^2 \quad (A23)$$

$$N_{21} = 16 + 6q + (7 + 10q)\kappa a + (3 + 4q)\kappa^2 a^2. \quad (A24)$$

The polynomials p_j have the following values

$$p_1 = 1 + \kappa a + \kappa^2 a^2/2 \quad (A25)$$

$$p_2 = 1 + q\kappa a + \kappa^2 a^2/4, \quad q^2 = 1/2 \quad (A26)$$

$$p_3 = 1 + q\kappa a + \kappa^2 a^2/6 \quad (A27)$$

and the transcendental functions $T_j(\kappa a)$ are defined by the expressions

$$T_j(\kappa a) = \exp[(j + q)\kappa a] E_n[(j + q)\kappa a], \quad j = 0, 1, 2 \quad (A28)$$

$$E_n(x) = \int_x^\infty e^{-u} du/u. \quad (A29)$$

The following relationships among various constants¹⁸ are used in converting the coefficients to practical units:

$$\beta = \epsilon^2/DkT = ab \quad (A30)$$

$$\beta^2 \kappa^2/3 = 8E_1' c \quad (A31)$$

$$\alpha c^{1/2} = \beta \kappa/6(1 + q) \quad (A32)$$

$$\beta_0 = 8E_2'/(6E_1')^{1/2} \quad (A33)$$

$$\tau^2 = 6E_1' c = \beta^2 \kappa^2/4 \quad (A34)$$

$$\kappa/3\pi\eta(\omega_1 + \omega_2) = \beta_0 c^{1/2}/\Lambda_0 \quad (A35)$$

$$\kappa^2 = \pi\beta N c \gamma/125. \quad (A36)$$

(Note that the definition of κ^2 includes a factor γ , where $\gamma = [A^+]/c = [B^-]/c$.)

$$\lambda^{\circ j} = |\epsilon_j| \mathcal{F} \sigma \omega_j \quad (A37)$$

$$\beta_0 = \mathcal{F} \epsilon \kappa \sigma/3\pi\eta c^{1/2} \quad (A38)$$

The electrophoretic term $\Delta\Lambda$, to a very close approximation, is given by

$$\Delta\Lambda = \beta_0 c^{1/2} \gamma^{1/2}/(1 + \kappa a). \quad (A39)$$

Retaining higher terms in the hydrodynamic equation¹⁶ gives

$$\Delta\Lambda = \beta_0 c^{1/2} \gamma^{1/2} EL(\kappa a, b), \quad (A40)$$

where $EL(\kappa a, b)$ is a very complicated function of κa and b . It is, however, numerically almost

exactly equal to $1/(1 + \kappa a)$, as shown by the typical example (calculated for potassium chloride in water) in Table 2.

Conductance data have also been analyzed¹⁹ by the Pitts equation,²⁰ which is based on an expansion in powers of $\beta\kappa$. Two of the boundary conditions, however, seem physically unrealistic. One requires that the velocity vector "vanishes on the surface of the ion." For rigid spheres in a continuum, only the radial component must vanish; the tangential component, which corresponds to one sphere rolling or slipping around another,¹⁵ need not vanish. Our treatment therefore requires only that $\mathbf{v} \cdot \mathbf{r}$ vanish at contact. Also, Pitts specifies that the perturbation potential must vanish at $r = a$ (i.e., precisely where the relaxation force is to be computed). Our electrostatic boundary conditions are the classical continuity of potential and field at the boundary $r = a$.

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TABLE 2

c	ELECTROPHORESIS TERM	
	$\Delta\Delta(39)/\Delta_0$	$\Delta\Delta(40)/\Delta_0$
0.0797	0.0867	0.0855
0.0725	0.0837	0.0828
0.0597	0.0776	0.0774
0.0485	0.0715	0.0716
0.0388	0.0652	0.0656
0.0246	0.0539	0.0545
0.0109	0.0378	0.0383
0.0050	0.0265	0.0268