Paired ions: Dipolar pairs as subset of diffusion pairs

(ion pairs/association constants/electrolyte models/conductance theory)

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ABSTRACT   Previous models for which theories of electrolytic conductance have been developed are reviewed. Discrepancies between theoretically derived values of parameters and parameters characteristic of real physical systems suggested the following revised model. Ions are counted as diffusion pairs if their center-to-center distance r is in the range $a \leq r \leq R$, in which a is contact distance and R is the diameter of the Gurney cosphere. A fraction α of these pairs diffuse to contact to form nonconducting dipolar pairs; $\alpha/(1 - \alpha) = \exp(-E_s/kT)$, in which E_s is the difference in energy between a diffusion pair at $r = R$ and a contact pair, k is the Boltzmann constant, and T is the absolute temperature. This model permits separate treatment of long-range and short-range interionic effects. The former (relaxation field and electrophoresis) depend on R and the values of the dielectric constant and viscosity of the pure solvent. The latter (formation of dipolar pairs) is described by E_s, or alternatively by $K_s = \exp(-E_s/kT)$ in which K_s is the constant describing the steady state between solvent-separated diffusion pairs and dipolar (contact) pairs. For solutions of the alkali halides, a simple empirical correlation is found between R and the Pauling radii of the cations, and also between E_s and the sum of the radii of cation and anion.

The equivalent conductance Λ of symmetrical electrolytes is described by the symbolic equation

$$\Lambda(c) = p[\Lambda_0(1 + \Delta X/X) + \Delta\Lambda_e] \qquad [1]$$

in which p is the fraction of solute that contributes to transport current, Λ_0 is the limiting value $\Lambda(0)$, $\Delta X/X$ (≤ 0) is the ratio of relaxation field to external field, and $\Delta\Lambda_e$ (≤ 0) is proportional to the velocity of the electrophoretic countercurrent. The explicit formulation of Eq. 1 depends, of course, both on the model chosen to represent the system and on mathematical approximations made in the derivation of $\Delta X/X$ and $\Delta\Lambda_e$. The purpose of this communication is to present a model to replace the primitive model (rigid charged spheres of diameter a in a continuum) on which most earlier theories are based. The new model eliminates a number of artifacts that are properties of the primitive model but that cannot be correlated unambiguously with the properties of real physical systems.

The classical Debye–Hückel–Onsager (1–3) treatment of ΔX and $\Delta\Lambda_e$ begins with integration of the equation of continuity (4)

$$\text{div}_1(f_{ij} v_{ij}) + \text{div}_2(f_{ji} v_{ji}) = 0 \qquad [2]$$

in which $f_{ji} = n_j n_{ji}$ gives the probability of finding simultaneously an ion of species j in an element of volume dV_1 and an i ion in dV_2; v_{ji} is the velocity of the i ion in dV_2 (and congruently for f_{ij} and v_{ij}). Local concentrations $n_{ji} = n_i \exp(-e_i\psi_j/kT) = n_i e^\xi$, in which ψ_j is the potential at the distance r from the j ion. In the presence of an external field, the

equilibrium distribution $f^0_{ji}(r)$ and corresponding potential ψ^0_j are changed to

$$f_{ji} = f^0_{ji} + f'_{ji}, \ \psi_j = \psi^0_j + \psi'_j \qquad [3]$$

in which the primed quantities (proportional to X and to the cosine of θ, the angle between the field direction and the vector r that locates dV_2 with respect to dV_1) are the perturbations generated by the external field. The solution f'_{ji} of Eq. 2, adjusted to the boundary conditions, is then substituted in the Poisson equation

$$\Delta\psi'_j = (-4\pi/Dn_j)\sum_i e_i f'_{ji} \qquad [4]$$

which on integration gives ψ'_j. In the derivation, two approximations were made: the Boltzmann factor was set equal to the truncated series $e^\xi \approx 1 + \xi + \xi^2/2$, and terms in Eqs. 2 and 4, proportional to $e_i{}^m$ and $e_j{}^m$, $m \geq 2$, were dropped. The relaxation field and the electrophoretic term are given by

$$\Delta X = -(\partial\psi'/\partial x)_a, \ \Delta\Lambda_e = \int_a^\infty F(\kappa r)dr \qquad [5]$$

Substituting the results in Eq. 1 and setting $p = 1$ ("complete dissociation") gives the equation for the limiting tangent

$$\Lambda_{LT} = \Lambda_0(1 - \alpha_0 c^{1/2}) - \beta_0 c^{1/2} \qquad [6]$$

in which α_0 and β_0 depend only on the valence type of the ions, on the dielectric constant D and viscosity η *of the continuum*, and on absolute temperature T.

Eq. 6 assumes that all the ions participate in net transport of charge; if a fraction $(1 - \gamma)$ is assumed to form nonconducting pairs (5), Eq. 1 becomes the Fuoss–Kraus (6) conductance equation

$$\Lambda = \gamma[\Lambda_0 - Sc^{1/2}\gamma^{1/2}] \qquad [7]$$

in which $S = (\alpha_0\Lambda_0 + \beta_0)$. A mass action equilibrium between free and paired ions was postulated, with associated constant

$$K_A = (1 - \gamma)/c\gamma^2 f^2 \qquad [8]$$

where activity coefficient f was set equal to the Debye–Hückel limiting value, $-\ln f = \beta\kappa/2$, in which $\beta = e^2/DkT$ and $\kappa^2 = 8\pi n\beta$. For the primitive model (7)

$$K_A = (4\pi N/1000) \int_a^{\beta/2} r^2\exp(\beta/r)dr \qquad [9]$$

The 2-parameter equation 7, $\Lambda = \Lambda(c; \Lambda_0, K_A)$ satisfactorily reproduces observed data for systems whose conductance curves lie below the limiting tangent ($\gamma \leq 1$), but it is useless for the analysis of data for most electrolytes in solvents of high dielectric constant, for which $\Lambda(c) > \Lambda_{LT}$, because $\gamma(\Lambda_0 - Sc^{1/2}\gamma^{1/2})$ can never exceed $(\Lambda_0 - Sc^{1/2})$, because $\gamma \leq 1$.

Theoretical investigations (8–15), based on the primitive model, of the effects of the higher terms [of order $(e_{i,j})^m$], which had been neglected in the integration of the equation of con-

tinuity, subsequently led to conductance functions of the general form

$$\Lambda(c) = \Lambda_0 - Sc^{1/2} + Ec \ln c + cF_1(\varkappa a) \qquad [10]$$

which lie *above* the limiting tangent in the usual working range of concentration. Here, $E = E_1\Lambda_0 - 2E_2$, in which E_1 and E_2 (like α_0 and β_0) depend only on ionic charges, DT and η. The functional form of $F_1(\varkappa a)$ (>0, $F_1(0) = $ constant) depends on the boundary condition used in evaluating $A_0(\varkappa a)$, a coefficient that appears in the integration of the equation of continuity. The terms $(\Lambda_0 - Sc^{1/2} + Ec \ln c) = \Lambda'$ of Eq. 10 are independent of the distance parameter that defined the model, but note that $F_1(\varkappa a)$ contains a explicitly. By combining Eqs. 10, with c replaced by $c\gamma$, and 8, with $f = \exp[-\beta\varkappa/2(1 + \varkappa a)]$ (in effect, including the higher terms in the Fuoss–Kraus equation), the conductance function (15) results

$$\Lambda = \gamma[\Lambda_0 + Sc^{1/2}\gamma^{1/2} + Ec\gamma \ln c\gamma + c\gamma F_1(\gamma^{1/2}\varkappa a)] \qquad [11]$$

This equation was found to be generally useful: for small values of K_A, it gives curves that lie above the limiting tangent, and as K_A increases, the curves drop and eventually approach the sigmoid type that is characteristic of salts in solvents of lower dielectric constant, thereby providing a smooth transition from strong to weak electrolyte types. Eq. 11 involves three parameters, $\Lambda = \Lambda(c; \Lambda_0, K_A, a)$; because $K_A = K_A(a,D)$ by 9 for the primitive model, the equation can be reduced to one in two parameters, $\Lambda(c; \Lambda_0, K_A)$ or $\Lambda(c; \Lambda_0, a)$.

Two predictions based on Eq. 9 are, however, contradicted by experiment. First, because $K_A = K_A(a, D)$, a given electrolyte (a fixed) should have the *same* association constant in *different* solvents of the *same* dielectric constant. Many violations(16–18) of the isodielectric rule have been reported. Second, Eq. 9 requires that K_A decrease as D increases and that association case abruptly ($K_A = 0$) for $a = \beta/2$: for example, if a given salt is measured in a series of mixed solvents with increasing dielectric constants, then at a critical value $D = e^2/2akT$, K_A should become zero. Experimentally, K_A usually decreases as D increases, although a number of cases have been reported (19, 20) in which K_A remains constant or even *decreases* as D decreases. But K_A never decreases to zero; it may become numerically quite small but can never become less than $4\pi Na^3/3000$, the pairing constant for uncharged spheres in a continuum.

Furthermore, two physically unrealistic features of the model appear when Eq. 11 is written in the form

$$\Lambda = \gamma\{\Lambda_0 [1 + F_2(c\gamma, D, a)] + F_3(c\gamma, D, \eta, a)\} \qquad [12]$$

First, the parameter a appears in ΔX and $\Delta\Lambda_e$. But the latter are *long-range* effects, averaged over all the ions in the atmosphere of the reference ion. As such, they should depend *only* on ionic charges and on the bulk properties of the solvent, and be completely independent of any short-range parameters such as ionic diameters. Second, according to Eq. 5, Eq. 12 requires the use of continuum D and η at $r = a$. The field strength at the surface of a real ion is well over 100 MV/cm, far beyond dielectric saturation; such fields must also alter the viscosity of a hydrodynamic continuum. More significant, of course, is the fact that D and η are macroscopic properties averaged over many $[O(10^{23})]$ molecules, and for a real system, $D(r = a)$ and $\eta(r = a)$ are as meaningless as the temperature of a single ion or solvent molecule. Conclusion: although Eq. 11 fits the data in the sense that three parameters can be derived from data for a real system such that Λ calculated by Eq. 11 equals Λ (ob-

served) within experimental error, the equation describes the conductimetric behavior of a primitive model numerically equivalent to the observed system, rather than physically equivalent. The parameters refer only to the model; in particular, a is the diameter of a model ion, and not necessarily the sum of the Pauling radii of cation and anion.

In 1974, a model was proposed (21) that (*i*) permits calculation (22) of ΔX and $\Delta\Lambda_e$ in terms of solvent D and η, (*ii*) does not involve a (ionic diameter) in the formulas for ΔX and $\Delta\Lambda_e$, (*iii*) does not imply the isodielectric rule, and (*iv*) does not predict that $(\partial K_A/\partial D)$ must be negative. The model cleanly separated the problems of long-range and short-range interactions. Ions are divided into two categories, paired and unpaired. Electroneutrality requires that the volume integral of the space charge ρ around an ion of charge $\pm e$ be precisely $\mp e$. Paired cations are defined as those for which

$$4\pi \int_a^R \rho r^2 dr = -e, \ 4\pi \int_R^\infty \rho r^2 dr = 0 \qquad [13]$$

and unpaired those for which

$$4\pi \int_a^R \rho r^2 dr = 0, \ 4\pi \int_R^\infty \rho r^2 dr = -e \qquad [14]$$

in which R is the diameter of the Gurney cosphere. By definition, the properties of the solvent at distances $r \geq R/2$ are unaffected by the central ion. In calculating ΔX and $\Delta\Lambda_e$, a is replaced by R in Eq. 5; because no other ion is inside the cosphere of an unpaired ion, long-range forces acting on the sphere act on the central ion. The conductance function 12 is thereby replaced by

$$\Lambda = \gamma\{\Lambda_0[1 + F_4(c\gamma, D, R)] + F_5(c\gamma, D, \eta, R)\} \qquad [15]$$

in which ΔX and $\Delta\Lambda_e$ are calculated using $D(r \geq R)$ and $\eta(r \geq R)$ and are independent of a (as they should be). Note also that the model automatically justifies the approximation of e^ξ by $(1 + \xi + \xi^2/2)$, and because $\varkappa^2 = 8\pi n\gamma\beta$ and $\xi \leq 1$ for $r \geq R$, we may use the linearized Poisson–Boltzmann equation $\Delta\psi^0_j = \varkappa^2\psi^0_j$ in order to calculate activity coefficients. [The electrostatic energy u_k of an unpaired ion e_k is $e_k\Sigma|e_l|/Dr_{kl}$, summed over all the other ions. Consider two paired ions e_m and e_n. Their contribution $(\pm e_m/Dr_{km} \mp e_n/Dr_{kn})$ to the sum practically cancels because r_{km} and r_{kn} are nearly equal and both are much larger than $r_{mn} \leq R$. Hence unpaired ions feel paired ions as virtual dipoles, and their contribution to u_k may be neglected.] The activity coefficient (another manifestation of long-range forces) is then given by

$$-\ln f = \beta\varkappa/2(1 + \varkappa R) \qquad [16]$$

in which D ($r \geq R$) appears (implicitly in $\beta\varkappa$) and a is absent.

The conductance function 15 is a 3-parameter equation: $\Lambda = \Lambda(c; \Lambda_0, R, K_A)$. Short-range ion–ion and ion–solvent interactions are subsumed in K_A. The formulation (21) of K_A in terms of molecular parameters, however, requires too many of the latter to be practically useful [conductance data can provide three and only three parameters (21)], but at least it shows that $(\partial K_A/\partial D)$ is not necessarily negative and it does not imply the isodielectric rule. A more practical formulation of K_A will be presented below. Two other changes will also be made: (*i*) the 1975 boundary condition (equation 2.14 of ref. 22) on f'_{21} is replaced (23) by $f'_{21}(R) = 0$ in accordance with Eq. 14, whereby the 1975 approximation $A_0 \approx -1$ is replaced by an explicit function $A_0(\varkappa R)$; (*ii*) *paired* ions will be divided into two subsets, virtual dipoles and dipolar pairs. Previous conductance theories postulate that all paired ions are non-

conducting ($p = \gamma$ in Eq. 1); it will be shown that this underestimates p.

Consider first a real electrolytic solution: ions and solvent molecules are in active thermal motion within a volume V. A given particle gets from site (x,y,z) to site (x',y',z') by a series of interchanges of position with other particles; such interchanges can occur because V is greater than the close-packed volume of solute and solvent by the free volume characteristic of liquids. Examine an instantaneous configuration of the system: some of the n cations will have only solvent molecules as nearest neighbors, while others will find an anion in its first shell of neighbors. Such a grouping, adjacent cation and anion, is defined as a *contact pair*. Let n_p be the number of contact pairs found. Then consider an ensemble of such systems, and denote by $\alpha(1 - \gamma)$ the ensemble average $\langle n_p/n \rangle$. The paired configurations will be stabilized by coulomb attraction and by the caging effect of the surrounding molecules; the pair will remain in contact for a dwell time that is long compared to the time constant for thermal motion. The pair will, however, eventually dissociate by an ion–solvent interchange and the ions will then diffuse to separated sites. The mechanism for the model specified by Eqs. 13 and 14 is a steady state between unpaired anions diffusing into and out of spheres of radius R centered on the cations. Debye (24) calculated the rate constant k_1 for the diffusion of anions into a volume ΔV containing a cation and Eigen (25) calculated the rate constant k_2 for the reverse diffusion; the ratio k_1/k_2f^2 is the equilibrium constant for the "reaction"

$$A^+ + B^- \rightleftarrows (A^+ : \ldots B^-) \qquad [17]$$
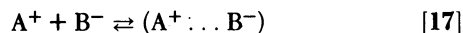
in which the symbol on the right denotes configurations in which an anion and a cation are simultaneously in ΔV, together with solvent molecules. If we set $\Delta V = 4\pi R^3/3$ and use Eigen's boundary conditions for $r = R$ (instead of for $r = a$), the result is $k_1/k_2f^2 = K_R$ in which

$$K_R = (4\pi N R^3/3000)\exp(\beta/R) \qquad [18]$$

Assume that ΔX and $\Delta\Lambda_e$ have been calculated using $c\gamma$ as the concentration of active ions, "active" in the sense that they affect the behavior of other free ions at distances $r > R$. Then we substitute the result in Eq. 1 in order to obtain an explicit $\Lambda(c)$. Former theory has set $p = \gamma$, but for the diffusion model, $p \neq \gamma$, as shown by the following. Consider an anion at a distance $r = R$ from a cation: either it will diffuse further away, or it will diffuse (interchange positions with solvent molecules inside the cosphere) towards the cation and eventually form a contact pair A^+B^-. Along its diffusion path, it is in thermal motion and subject to the force exerted by the external field. Consequently, each Brownian jump will have a component of motion in the field direction; in other words, some of the diffusion paired ions contribute to transport current and therefore $p > \gamma$. Consider next the behavior of a contact pair: when the field is applied, the pair will tend to orient in the field; if the field is turned off after a time long compared to the time characteristic of Brownian motion but short compared to the half-life of a contact pair, the pair will return to random orientation by rotational diffusion, *without changing center-to-center distance*. In other words, contact pairs behave like dipoles and contribute only to charging current but not to net transport of charge. Let α be the time average fraction of $a \leq r \leq R$ pairs that are in contact. Then by the Einstein 2-state theorem

$$\alpha/(1 - \alpha) = \exp(-E_s/kT) \qquad [19]$$

in which E_s is the difference in energy between ions in state r

$= R$ and state $r = a$. The concentration of diffusion pairs is $c(1 - \gamma)$; the concentration of dipolar pairs is $\alpha c(1 - \gamma)$; consequently $p = 1 - \alpha(1 - \gamma)$ and the final conductance equation becomes

$$\Lambda = [1 - \alpha(1 - \gamma)][\Lambda_0(1 + \Delta X/X) + \Delta\Lambda_e] \qquad [20]$$

Explicit expansion of Eq. 20 is given in the *Appendix*.

Analysis of conductance data by use of the parametric equation [20], $\Lambda = \Lambda(c; \Lambda_0, R, \alpha)$, requires relationships between α, γ and R; these are found as follows. Consider the sequence of "reactions"

$$A^+ + B^- \rightleftarrows (A^+ \ldots B^-) \rightleftarrows A^+B^- \qquad [21]$$
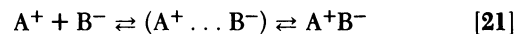
in which $(A^+ \ldots B^-)$ denotes configurations in which an anion and a cation are simultaneously in the volume $4\pi R^3/3$, separated by at least one solvent molecule ($a + s \leq r \leq R$; $s =$ diameter of solvent molecule). The first step (formation of diffusion pairs) is described by

$$K_R = (1 - \gamma)(1 - \alpha)/c\gamma^2f^2 \qquad [22]$$

and the second (formation of dipolar pairs) by

$$K_s = \alpha/(1 - \alpha) \qquad [23]$$

The pairing constant K_Λ (previous nomenclature, K_A = association constant) is then given by

$$K_\Lambda = (1 - \gamma)/c\gamma^2f^2 = K_R/(1 - \alpha) = K_R(1 + K_s) \qquad [24]$$

[The subscript Λ indicates the conductimetric origin of K_Λ, the subscript R indicates that K_R depends explicitly on the pairing distance, and the subscript s indicates that $K_s = \exp(-E_s/kT)$ describes the short-range effects.] Note that K_Λ is the product of two factors, K_R and $(1 + K_s)$. The first depends explicitly on R, the pairing distance; here we have the explanation for the previously noted close coupling between association constants and pairing distance. Note also that the complicated short-range effects of approach of anion and cation to form a dipolar pair are summarized in one parameter (given one of the three quantities K_s, E_s, or α, the other two are determined). Finally because both E_s and R must depend on molecular parameters specific to cation, anion, and solvent molecules, this model does not imply an isodielectric rule and the erratic variation of K_Λ with dielectric constant ceases to be a problem.

Determination of the parameters R and E_s from experimental data by means of Eq. 20 requires data of high precision ($\pm 0.02\%$) spanning at least a 10-to-1 range of concentration, and the highest concentration should be just under $2 \times 10^{-7} D^3$ (about 0.1 M in water at $25°$). Such data are available for 10 of the alkali halides. Analysis of these data produced R values that are nearly independent of the anion but decrease systematically with increasing atomic number of the cation. A simple empirical correlation with the Pauling radii is shown in Fig. 1 (coordinates bottom and right), where $1/R$ is plotted against a^+. The average line is given by

$$R = 11.82/(a^+ + 1.06) \qquad [25]$$

Eq. 25 was used to calculate average R values (given in Å) for the alkali halides: $R(\text{LiX}) = 7.12$, $R(\text{NaX}) = 5.88$, $R(\text{KX}) = 4.95$, $R(\text{RbX}) = 4.65$, $R(\text{CsX}) = 4.30$. Using these values, it was possible also to analyze data for the other five halides (marked with an asterisk in Table 1) which covered too low a concentration range for treatment by the 3-parameter equation $\Lambda(c; \Lambda_0, R, E_s/kT)$, which reduces to a problem in only two unknowns instead of three, if R is given. The values of K_R are as follows: $K_R(\text{LiX}) = 2.49$, $K_R(\text{NaX}) = 1.73$, $K_R(\text{KX}) = 1.30$, $K_R(\text{RbX})$

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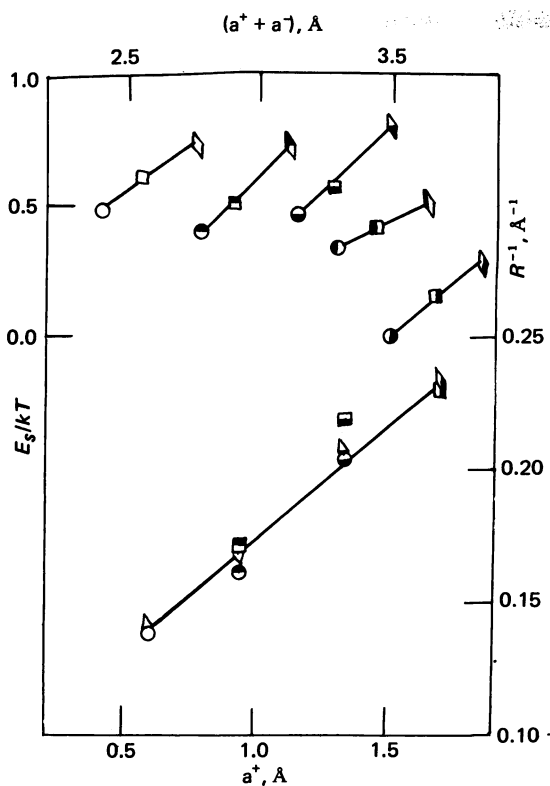Proc. Natl. Acad. Sci. USA 75 (1978)   19

FIG. 1. Dependence of conductimetric parameters on ionic radii. Code: circles, chlorides; squares, bromides; diamonds, iodides; open, Li$^+$; top black, Na$^+$; bottom black, K$^+$; left black, Rb$^+$; right black, Cs$^+$. Lowest line, coordinates bottom and right; upper lines, coordinates top and left.

$= 1.18$, $K_R(\text{CsX}) = 1.06$. Table 1 summarizes the results; σ, % represents percent deviation between observed and calculated conductances.

The correlation between R and cationic radius is consistent with the expected effects of these ions on water structure and hence on local properties. The smallest cation (Li$^+$ with $a^+ = 0.60$ Å) has the most intense surface field; the value $R(\text{LiX}) = 7.12$ Å indicates that the cosphere of Li$^+$ contains both nearest and next-nearest shells of water molecules. The average number of neighboring water molecules controlled by the central cation then decreases as the size of the cation decreases. The radii (Å)

Table 1. Parameters for the alkali halides

Salt	E_s/kT	α	K_s	K_Λ	Λ_0	σ, %	Ref.
LiCl	0.481	0.382	0.618	4.02	115.00	0.004	26
LiBr*	0.601	0.354	0.548	3.85	116.91	0.013	27
LiI	0.724	0.327	0.485	3.69	116.09	0.011	26
NaCl	0.400	0.401	0.670	2.89	126.58	0.008	28
NaBr	0.509	0.375	0.601	2.77	128.52	0.013	29
NaI	0.720	0.327	0.487	2.57	127.21	0.018	27
KCl	0.469	0.385	0.625	2.11	149.90	0.006	28
KBr	0.578	0.359	0.561	2.03	151.76	0.019	30
KI	0.794	0.311	0.452	1.89	150.64	0.013	31
RbCl*	0.341	0.416	0.711	2.02	153.64	0.009	32
RbBr*	0.420	0.397	0.657	1.96	155.44	0.004	33
RbI*	0.503	0.377	0.605	1.90	154.00	0.006	34
CsCl*	0.009	0.498	0.991	2.11	153.05	0.012	35
CsBr	0.160	0.460	0.852	1.96	155.37	0.004	36
CsI	0.284	0.430	0.753	1.86	154.18	0.003	36

* Calculated using R values from Eq. 25. See text.

of the anions $[a^-(\text{Cl}^-) = 1.81$, $a^-(\text{Br}^-) = 1.95$; $a^-(\text{I}^-) = 2.16]$ are nearly the same, hence the insensitivity of R to anionic radii. But the parameter E_s/kT, which measures the contact energy of a dipolar pair, ought to depend on the size of both anion and cation. The expected correlation is shown in Fig. 1 (coordinates left and top), where E_s/kT is plotted against $(a^+ + a^-)$; the points for the three halides of each alkali form a closed group.

APPENDIX

Using boundary conditions $f'_{21}(\infty) = 0$, $f'_{21}(R) = 0$, the equation of continuity [2] has been integrated by the 1975 method (22) of successive approximations; the result was substituted in the right side of the Poisson–Boltzmann equation [4], which was integrated subject to the boundary conditions $\nabla\psi(\infty) = 0$, $(r\ \partial\psi/\partial r - \psi)_R = 0$. The results were used to calculate the relaxation terms RX and EL in the conductance equation

$$\Lambda = [1 - \alpha(1 - \gamma)][\Lambda_0(1 + RX) + EL]$$

Expressed as functions of $t = \kappa R$, $\beta = e^2/DkT$, $q^2 = \frac{1}{2}$,

$$RX = -\beta\kappa/6\,(1 + q)\,(1 + t)\,(1 + qt) + \beta^2\kappa^2[(\ln t)/12 + FH2 + (\beta\kappa)FH3)] + DXV$$

$$EL = -\beta_0 c^{1/2}\gamma^{1/2}\,[1/(1 + t) + \beta\kappa(0.125\ln t + 0.5\,H1)]$$

$$DXV = (\beta_0 c^{1/2}\gamma^{1/2}\beta\kappa/8\Lambda_0)(0.5H2 - \ln t)$$

$H1 = 0.19295 - 0.18508\,t - 0.32106\,t^2 + 0.40243\,t^3, 0 < t \leq 0.4$

$\quad = 0.20742 - 0.31145\,t + 0.06461\,t^2, 0.4 < t < 0.8$

$H2 = -2.6851 + 18.438\,t - 35.735\,t^2 + 28.476\,t^3, 0 < t \leq 0.3$

$\quad = -2.0722 + 12.452\,t - 15.804\,t^2 + 6.0045\,t^3, 0.3 < t \leq 0.6$

$\quad = -1.0425 + 6.9012\,t - 5.8121\,t^2, 0.6 < t < 0.8$

$FH2 = 0.13842 - 0.25289\,t + 0.16281\,t^2$
$\qquad\qquad - 0.044868\,t^3, 0 < t \leq 0.4$

$\quad = 0.13558 - 0.23739\,t + 0.14034\,t^2 - 0.041583\,t^3, 0.4 < t < 0.8$

$FH3 = 0.0084869 - 0.029776\,t + 0.045001\,t^2$
$\qquad\qquad - 0.026344\,t^3, 0 < t \leq 0.4$

$\quad = 0.0067047 - 0.017767\,t + 0.018269\,t^2$
$\qquad\qquad - 0.0068686\,t^3, 0.4 < t \leq 0.8$

The nine equations above are *interpolating* polynomials, calculated to match within 0.01% (within the indicated ranges of t) the explicit terms of RX and EL, which are long and complicated functions of t and $\beta\kappa$.

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