Recalling (B.5) we find

$$\prod_{l=1}^{N} \exp\{if_l\mathbf{w}\cdot[\mathbf{b}_l + \mathbf{b}_l^+(1 + G_l)^{-1}]\} =$$

$$\exp\left[-\frac{1}{2}\sum_{l=1}^{N} f_l^2(1 + G_l)^{-1}w^2\right]\theta \exp[i\mathbf{w}\cdot\mathbf{r}_{ij}^{M_0}] \tag{B.9}$$

where θ designates an ordering operator whose action is to place, in the boson expansion of $\mathbf{r}_{ij}^{M_0}$, every $\mathbf{b}_l$ on the right of every $\mathbf{b}_l^+$. The average is then

$$\prod_{l=1}^{N} \langle 0|\exp\{if_l\mathbf{w}\cdot[\mathbf{b}_l + \mathbf{b}_l^+(1 + G_l)^{-1}]\}0|\rangle =$$

$$\exp\left[-\frac{1}{2}\sum_{l=1}^{N} f_l^2(1 + G_l)^{-1}w^2\right] \tag{B.10}$$

and

$$\langle 0|\delta(\mathbf{r} - \mathbf{r}_{ij})|\rho\rangle_{\mathrm{eq}} = (2\pi)^{-3}\int \mathrm{d}\mathbf{w} \times$$

$$\exp\left[-i\mathbf{w}\cdot\mathbf{r} - \frac{w^2}{2}\sum_{l=1}^{N} f_l^2(1 + G_l)^{-1}\right] \tag{B.11}$$

Integration over $\mathbf{w}$ gives

$$\langle 0|\delta(\mathbf{r} - \mathbf{r}_{ji})|\rho\rangle_{\mathrm{eq}} = \left[2\pi\sum_{l=1}^{N} f_l^2(1 + G_l)^{-1}\right]^{-3/2} \times$$

$$\exp\left[-\frac{r^2}{2\sum_{l=1}^{N} f_l^2(1 + G_l)^{-1}}\right] \tag{B.12}$$

Appendix C

The average $\langle \nabla_j U\rangle$ translates into boson language as

$$\langle \nabla_j U\rangle = \sum_{l=1}^{N} Q_{jl}\left\langle\frac{\partial U}{\partial \mathbf{q}_l}\right\rangle = \sqrt{2}\sum_{l=1}^{N} Q_{jl}\alpha_l\langle 0|[(\mathbf{b}_l, U]|\rho\rangle \tag{C.1}$$

where the commutator is

$$[\mathbf{b}_l, U] = kT(1 + G_l)(\mathbf{b}_l^+ + \mathbf{b}_l) \tag{C.2}$$

Then

$$\langle 0|(\mathbf{b}_l^+ + \mathbf{b}_l)|\rho\rangle = -\frac{1}{2}(1 + G_l)^{-1}\langle 0|(\mathbf{b}_l^+ + \mathbf{b}_l)\mathbf{b}_l^+\cdot$$

$$\left[G_l\mathbf{b}_l^+ - \frac{(2N)^{1/2}f}{kT\alpha_l}\frac{\langle F_{0l}\rangle_{\mathrm{eq}}}{\langle F_{ll}\rangle_{\mathrm{eq}}}\mathbf{e}_x\right]|0\rangle =$$

$$\left(\frac{N}{2}\right)^{1/2}(1 + G_l)^{-1}\frac{f}{kT\alpha_l}\frac{\langle F_{0l}\rangle_{\mathrm{eq}}}{\langle F_{ll}\rangle_{\mathrm{eq}}}\mathbf{e}_x \tag{C.3}$$

since $[\mathbf{b}_l, \mathbf{b}_l^+\cdot\mathbf{e}_x] = \mathbf{e}_x$. Combining (C.2) and (C.3) we get

$$\langle \nabla_j U\rangle = N^{1/2}f\mathbf{e}_x\sum_{l=1}^{N} Q_{jl}\frac{\langle F_{0l}\rangle_{\mathrm{eq}}}{\langle F_{ll}\rangle_{\mathrm{eq}}} \tag{C.4}$$

Conductance of the Alkali Halides. XI. Cesium Bromide and Iodide in Water at 25°[1]

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Contribution from the Sterling Chemistry Laboratory of Yale University, New Haven, Connecticut 06520. *Received November 22, 1967*

Abstract: The conductances at 25° in water of cesium bromide and cesium iodide have been determined over the range $0.003 \leqslant c \leqslant 0.10\,N$. About 65 sets of data are given for each salt, sufficient to permit a statistical analysis of the differences $\delta\Lambda$ between calculated and observed values of the conductance. The semiempirical screening equation $\Lambda = \Lambda_0 - Sc^{1/2} + E'c \ln c + Ac + Bc^{3/2}$ accurately reproduces the data within about 0.01%, with a random pattern of $\delta\Lambda$'s, and the constants are independent of the concentration range, provided c_{min} does not exceed 0.01. The explicit equation $\Lambda = \gamma(\Lambda_0 - \Delta\Lambda)(1 + \Delta X/X)/(1 + 3\varphi/2)$ reproduces the data over the same range, and with the same precision. The distribution of $\delta\Lambda$'s is likewise random, independent of concentration. The values of the parameters Λ_0 = limiting conductance, K_{A} = association constant, and $\mathring{a}$ = contact distance are independent of the upper limit of the concentration range, provided c_{max} does not exceed 0.10 N. Deviations between Λ_{calcd} and Λ_{obsd} are very nearly proportional to c^2 in the range $0.10 \leq c \leq 1.0$. The following values summarize the results: for cesium iodide, $\Lambda_0 = 154.17$, $K_{\mathrm{A}} = 0.93$, $\mathring{a} = 5.49$; for cesium bromide, $\Lambda_0 = 155.37$, $K_{\mathrm{A}} = 1.07$, $\mathring{a} = 5.55$.

Association of 1:1 electrolytes in water has not been seriously considered since the advent of the Debye–Hückel theory of electrolytes in 1923. This theory was so successful in accounting for the limiting behavior of dilute solutions of strong electrolytes in water that the Arrhenius hypothesis was completely rejected for such systems. In 1926, Bjerrum revived the idea that less than the stoichiometric concentration of electrolyte functioned as free ions, by proposing ion pairs to account for the activity coefficients of 2:2 electrolytes in water. In 1933, Fuoss and Kraus combined the Debye and the Bjerrum theories to obtain a conductance equation which accurately reproduced observations in solvents of dielectric constant of about 25 or less, where the conductance curve lies well below

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[1] Grateful appreciation is expressed to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Table I. Conductance of Cesium Iodide in Water at 25°[a]

10^4c	Λ	$10^3\delta$	10^4c	Λ	$10^3\delta$	10^4c	Λ	$10^3\delta$
1052.97	131.626	10^n	428.740	137.758	1^l	188.691	142.354	14^b
952.43	132.347	20^m	393.822	138.270	14^n	188.362	142.369	7^c
931.95	132.520	4^q	385.218	138.405	13^j	179.786	142.615	-9^m
910.36	132.675	18^o	370.717	138.624	27^f	173.326	142.795	-10^i
865.82	133.057	-5^p	367.915	138.679	17^h	166.834	142.984	-16^e
786.71	133.723	7^q	364.316	138.750	5^m	159.534	143.164	17^c
754.96	134.014	4^o	331.961	139.297	9^i	157.536	143.254	-14^h
746.62	134.086	10^p	329.390	139.354	-2^k	144.694	143.635	-2^g
698.73	134.560	-6^l	304.513	139.830	-24^h	141.269	143.752	-10^d
670.52	134.841	-4^m	296.498	139.972	-14^l	134.616	143.970	-11^f
664.85	134.911	-16^q	293.013	140.029	-4^f	117.281	144.571	-14^k
640.98	135.140	3^o	283.925	140.174	29^e	116.205	144.595	1^a
630.55	135.267	-13^p	283.863	140.200	4^j	113.113	144.731	-22^c
593.97	135.643	12^n	261.858	140.649	3^g	98.349	145.299	-19^d
585.60	137.766	-16^q	253.147	140.833	4^i	96.246	145.388	-23^j
572.85	135.899	-3^l	240.931	141.086	18^d	95.123	145.407	4^a
554.81	136.091	15^k	232.714	141.292	-2^h	72.156	146.444	-4^a
536.12	136.350	-19^p	227.748	141.398	6^e	70.817	146.525	-19^g
530.20	136.403	1^m	222.923	141.530	-14^k	66.430	146.745	-18^f
508.49	136.693	-17^o	210.088	141.811	13^g	54.840	147.334	23^b
502.68	136.733	17^n	201.741	142.031	0^n	51.298	147.573	-8^a
478.13	137.049	22^j	196.070	142.175	1^d	36.689	148.519	6^c
444.45	137.531	3^k	190.570	142.320	-2^j	27.768	149.218	7^b

[a] Superscripts in the δ columns designate runs.

the limiting tangent. In 1955, Fuoss and Onsager derived a theoretical conductance equation which accounted for the approach from above to the limiting tangent for aqueous solutions of 1:1 electrolytes. The transition region from high to lower dielectric constant, where the conductance curve swings from above to below the tangent, was tacitly assumed to be the transition from negligible to appreciable ionic association, but quantitative support for the hypothesis was completely lacking, on account of a practical dilemma. The available theory[2] was limited to concentrations less than about 0.01 *N*; at this concentration in water, ion pairs are not detectable. There was no point in making measurements at higher concentrations because the magnitude of the electrophoresis and relaxation terms in the conductance at concentrations beyond $c = 0.01$ was theoretically unknown, and these obviously would have to be subtracted from the observed total conductance before one could look for the effects of ion pairs. Recently[3] the Fuoss–Onsager equation was extended to include explicitly terms of order $c^{3/2}$, which had previously been neglected; it is precisely those terms which are needed to extend the range amenable to theoretical treatment by one order of magnitude. The purpose of this paper is to present conductance data for cesium bromide and iodide in water in the concentration range $0.003 \leq c \leq 0.10$ and to show that these salts have association constants of 1.06 and 0.93, respectively. At 0.1 *N*, about 4% of the ions are present as nonconducting pairs. The conductance equation[3] used to analyze the data is

$$\Lambda = \gamma(\Lambda_0 - \Delta\Lambda)(1 + \Delta X/X)/(1 + 3\varphi/2) \qquad (1)$$

where Δ is equivalent conductance at concentration c, Λ_0 is limiting conductance, γ is the ratio of free ion concentration to stoichiometric concentration, $\Delta\Lambda$ is the electrophoretic correction, $\Delta X/X$ represents the effect of the relaxation field, and $3\varphi/2$ allows for the effect of finite ion size on path length.

Experimental Section

The cesium bromide and iodide were obtained from the Harshaw Chemical Co., as "random cuttings" from crystals grown from melts of purified salt. The salts were used as received; samples were weighed in platinum boats or glass weighing bottles, after drying overnight at 80°. Weighings were made on a Mettler-type M microbalance. In order to allow for the slow drift of the zero point of the balance, alternate readings were made for unloaded and loaded balance; by interpolation to the same time, weights were determined to ± 2 μg. All solutions were made up by weight and corrected to vacuum (density of salt, 4.51 g/cc). The density ρ of the solutions in the range up to 0.1 *N* is given by $\rho = \rho_0(1 + \gamma w)$, where w is weight concentration (equiv/kg of solution). The constant γ equals 0.169 for cesium bromide; it averages the following data: $w = 0.102549$ equiv/kg, $\rho = 1.01436$ g/ml at 25°; $w = 0.076147$, $\rho = 1.00987$; $w = 0.052280$, $\rho = 1.00583$. For cesium iodide, $\gamma = 0.198$ from the following: $w = 0.097604$, $\rho = 1.01731$; $w = 0.059484$, $\rho = 1.01026$; $w = 0.038621$, $\rho = 1.00571$. The water conductance of $1\text{–}2 \times 10^{-6}$ was subtracted from solution conductance; the correction was less than 0.5% at the most dilute points (about 0.003 *N*). It was determined by measuring the resistance of the cell with the water for the first point in it, parallel to a calibrated 100,000-ohm resistor. Concentrations were changed by adding water to the cell, mixing thoroughly, and reweighing.

The cell constant was 9.4904 ± 0.0020, determined by measuring the resistance of solutions of potassium chloride[4] in the range $0.0025 \leq c \leq 0.012$ (resistances, 5400–27,000 ohms). All resistances were determined at 1, 2, and 5 kHz, and extrapolated to infinite frequency linearly on a $1/f$ scale. The bridge has already been described.[5]

The experimental results are summarized in Tables I and II, where c is volume concentration, equiv/l. at 25°, and Λ is equivalent conductance. Also included in the tables are the values of $\delta\Lambda = \Lambda_{\text{calcd}} - \Lambda_{\text{obsd}}$; the calculated conductances will be discussed in the next section. The data are arranged in sequence of decreasing concentrations; runs are identified by the superscripts in the δ columns. Several runs were also made at higher concentrations for cesium iodide, using a cell with constant 33.962 ± 0.001; the results are given in Table III.

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(2) R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 668 (1957).

(3) R. M. Fuoss and K.-L. Hsia, *Proc. Natl. Acad. Sci., U. S.*, **57**, 1550, 1818 (1967). Equation A28 is correct only for $j = 1$ and 2. $T_0(\kappa a) = \exp(\kappa a)E_n(\kappa a)$.

(4) J. E. Lind, Jr., J. J. Zwolenik, and R. M. Fuoss, *J. Am. Chem. Soc.*, **81**, 1557 (1959).

(5) J. E. Lind, Jr., and R. M. Fuoss, *J. Phys. Chem.*, **65**, 999 (1961).

Table II. Conductance of Cesium Bromide in Water 25°[a]

10^4c	Λ	$10^3\delta$	10^4c	Λ	$10^3\delta$	10^4c	Λ	$10^3\delta$
1036.24	132.174	10^{l}	375.483	139.369	-5^{i}	149.573	144.467	4^{e}
1027.38	132.256	-6^{m}	352.063	139.781	-13^{k}	141.481	144.706	28^{d}
948.01	132.860	10^{n}	338.885	140.020	-16^{j}	125.422	145.282	3^{f}
900.95	133.251	7^{o}	334.700	140.073	7^{g}	124.715	145.303	8^{c}
839.48	133.772	19^{k}	325.870	140.262	-19^{h}	120.574	145.473	-12^{b}
838.13	133.786	17^{m}	298.205	140.749	28^{f}	109.755	145.843	26^{a}
789.24	134.243	8^{l}	285.851	141.029	-3^{i}	105.869	146.015	6^{d}
782.49	134.288	26^{n}	276.436	141.238	-16^{g}	103.893	146.099	2^{e}
731.54	134.807	3^{o}	251.075	141.766	7^{e}	97.433	146.387	-22^{i}
706.16	135.059	8^{k}	242.526	141.966	2^{f}	86.890	146.800	22^{b}
655.39	135.641	-36^{l}	239.408	142.054	-14^{j}	84.744	146.933	-14^{c}
566.94	136.636	-7^{n}	236.508	142.119	-11^{h}	82.930	147.027	-25^{h}
561.83	136.680	12^{j}	216.287	142.594	3^{g}	80.862	147.304	21^{a}
554.80	136.801	-22^{m}	207.084	142.800	30^{o}	71.646	147.536	10^{d}
551.97	136.836	-22^{l}	201.572	142.975	-2^{e}	68.629	147.721	-20^{g}
549.91	136.846	-6^{o}	193.599	143.193	-9^{i}	64.729	147.931	-25^{f}
477.44	137.798	4^{i}	183.964	143.451	-3^{o}	59.546	148.160	30^{b}
457.68	138.084	-2^{j}	180.443	143.534	12^{f}	57.432	148.304	6^{a}
410.35	138.801	-4^{h}	169.167	143.881	-10^{k}	52.022	148.640	-10^{e}
376.53	139.360	-13^{o}	169.150	143.865	6^{c}	29.380	150.245	-12^{a}
375.74	139.372	-12^{n}	161.548	144.114	-16^{h}	29.351	150.246	-11^{b}

[a] Superscripts in the δ columns designate runs.

Table III. Conductance of Cesium Iodide in Water at 25°

c	Λ	c	Λ
0.44585	121.682	0.29337	124.348
0.38398	122.543	0.18712	127.478
0.32146	123.740	0.14957	129.125
0.22301	126.242	1.02476	118.450
0.64620	119.801	0.78534	119.207
0.42873	122.033	0.61094	120.143

Table IV. Constants of Eq 2 for Cesium Iodide

$c_{\max}$	Λ_0	A	$-B$	σ
0.012	154.139 ± 0.043	219.3 ± 18.8	318.1 ± 147.0	0.0171
0.021	154.140 ± 0.022	216.8 ± 7.1	282.2 ± 44.1	0.0154
0.033	154.173 ± 0.015	205.9 ± 2.8	206.6 ± 14.1	0.0127
0.043	154.166 ± 0.010	205.7 ± 1.8	204.5 ± 8.1	0.0105
0.051	154.170 ± 0.010	205.0 ± 1.4	200.7 ± 5.7	0.0112
0.063	154.175 ± 0.008	203.1 ± 0.9	193.3 ± 3.6	0.0096
0.070	154.172 ± 0.008	204.0 ± 0.9	195.8 ± 3.1	0.0099
0.079	154.173 ± 0.005	203.7 ± 0.6	195.0 ± 1.9	0.0072
0.091	154.173 ± 0.006	203.3 ± 0.5	193.2 ± 1.5	0.0080
0.105	154.179 ± 0.006	202.9 ± 0.5	191.9 ± 1.5	0.0086

Discussion

The explicit conductance equation can be solved for the parameters Λ_0, $\mathring{a}$, and K_A only by successive approximations, a procedure which obviously requires considerably more machine time than is needed to solve a three-parameter equation which is linear in its constants. For preliminary screening of the data, the following equations were therefore used

$$\Lambda = \Lambda_0(1 - \alpha c^{1/2} + E_1'c \ln c) - \beta_0 c^{1/2} - E_2 c \ln c + Ac + Bc^{3/2} \quad (2)$$

$$= \Lambda_0 - Sc^{1/2} + E'c \ln c + Ac + Bc^{3/2} \quad (3)$$

in which the theoretically known leading terms in $c^{1/2}$ and $c \ln c$ are included explicitly and all other concentration dependence of conductance is thrown into empirical c and $c^{3/2}$ terms. It has been shown[3] that (3) will reproduce conductance data for 1:1 salts in water up to about 0.1 N; a third empirical term in c^2 will extend the fit to about 1.0 N. About half a dozen points showed differences between calculated and observed conductances equal to or greater than 2σ (σ = standard deviation = $[\Sigma\delta\Lambda^2/(n-3)]^{1/2}$) and were discarded. The remaining data were reanalyzed, giving the values $\Lambda_0 = 154.185 \pm 0.005$, $A = 202.7 \pm 0.4$, $B = -191.5 \pm 1.2$, $\sigma = 0.013$ for cesium iodide.

That the equation really is a function which closely matches the much more complicated explicit equation is shown by the results summarized in Table IV. Blocks of 12–15 data points were analyzed separately; each block started at $c = 0.0028$ and ended at a higher concentration given as $c_{\max}$, in the first column of Table IV. For small values of $c_{\max}$, the uncertainty in A and B is of course large because most of the difference between the limiting conductance and the observed value is already accounted for by the theoretical terms $Sc^{1/2}$ and $E'c \ln c$; at $c = 0.01$, $Ac \approx 2.0$ and $Bc^{3/2} \approx -0.6$; the net sum of 1.4 of the empirical terms is a little less than 1% of the total value of Λ. Considering this fact, we may conclude that the values of Λ_0, A, and B are *independent of the concentrating range over which they are determined*, provided $c_{\max}$ does not exceed 0.1 N.

One interesting variation of eq 3 was considered: the equation obtained by inserting the theoretically significant factor $(1 + \kappa a)$ as denominator in the theore-

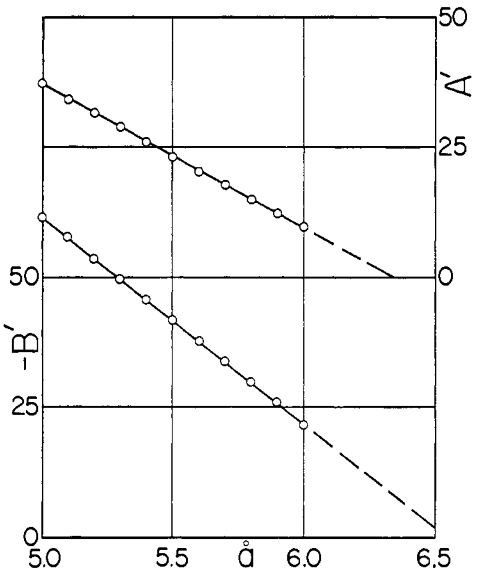

Figure 1. Variation of A and B of eq 2 with preset $\mathring{a}$ values.

tical terms. The four-parameter equation

$$\Lambda = \Lambda_0 - (Sc^{1/2} - E'c \ln c)/(1 + \varkappa a) + A'c + B'c^{3/2} \qquad (4)$$

could not be solved for Λ_0, a, A', and B'; the discriminant vanished, showing that the variation equations were homogeneous. In other words, no unique solution could be found: within reasonable limits, values of A' and B' which would minimize σ to values well within the experimental error could be found for any value of the a parameter. This result is shown in Figure 1 where values of A' and B' corresponding to preset values of a are plotted against a. We note that for $\mathring{a} = 6.45$, a very close fit to the data could be obtained by the simple two-parameter equation

$$\Lambda = \Lambda_0 - (Sc^{1/2} - E'c \ln c)/(1 + \varkappa a) \qquad (5)$$

As will be shown later, the explicit equation gives $\mathring{a} = 5.5$ for cesium iodide in water. If one wanted only an extrapolation to Λ_0 and an interpolation formula for conductance, eq 5 would suffice, but the $\mathring{a}$ parameter would not correlate with a physical model; in (5), it is merely a catch-all for the neglected terms of higher order.

Having screened the data to eliminate erratic points, the explicit conductance equation (1) was used for a final analysis by electronic computer. The program calls for the following sequence of operations. For a selected value of association constant, γ_j is calculated at each concentration c_j by the mass action equation

$$1 - \gamma_j = K_A c_j \gamma_j^2 f_j^2 \qquad (6)$$

where the limiting law

$$-\ln f = \beta\varkappa \qquad (7)$$

is used to calculate activity coefficients. Estimated initial values of Λ_0 and $\mathring{a}$ are used to start the cycle of approximations; for Λ_0, we used the value from the $c^{1/2}$ extrapolation and, for $\mathring{a}$, 5.0 Å was usually the first trial value. Then variations $\Delta\Lambda_0$ and $\Delta\mathring{a}$ from the preliminary estimates of Λ_0 and $\mathring{a}$ are computed which minimize the quantity

$$(n - 3)\sigma^2 = \Sigma[\Lambda_{\text{calcd}} - \Lambda_{\text{obsd}}]^2$$

where Λ_{calcd} is the value of conductance calculated by (1), using iterated values of $(\Lambda_0 + \Delta\Lambda_0)$ and $(\mathring{a} + \Delta\mathring{a})$; iteration is considered converged when $\Delta\mathring{a}/\mathring{a} \leq 0.001$. Then K_A is incremented and the calculation is repeated. After computing for a sequence of K_A values, σ and the converged values of Λ_0 and $\mathring{a}$ are plotted against K_A, and final values of the parameters are interpolated to the value of K_A which minimizes the σ's. For the first scan, a rather wide range of K_A values is chosen; then in one or two successive scans, narrower ranges are used. For the first scan, the K_A range usually was chosen to bracket the theoretical $(4\pi Na^3/3000) \exp(\epsilon^2/aDkT)$, using $a = 5 \times 10^{-8}$ cm. (It is possible, of course, to program a search for all three parameters. We prefer the above approach for two reasons. First, one has a better feeling for the uncertainty in K_A when the σ–K_A plots are used, as will be shown later. Second, several spurious higher minima exist and the computer can trap itself in a pointless search to deliver absurd $\mathring{a}$ values.)

For cesium iodide, the following values of the parameters are found: $\Lambda_0 = 154.172$, $K_A = 0.93$, $\mathring{a} = 5.492$, $\sigma = 0.013$. The limiting conductance agrees exactly with the value found by Lind,[6] whose data covered the range $0.002 \leq c \leq 0.01$; this value is given as 154.16 ± 0.02. The differences between calculated and observed values are given as $\delta\Lambda$ in Table I. It will be noted that these are completely random; a plot of $\delta\Lambda$ against concentration shows no systematic trend.

The dependence of the parameters on concentration range was next tested. The results are summarized in Table V. For maximum concentrations less than 0.03 N, the calculation would not converge; association was so slight that K_A became indeterminate. But for larger values of c_{max}, the parameters are independent of the concentration range over which they are determined. For the above calculations, the set of points for each value of c_{max} was started at 0.003 N. We also determined the parameters, keeping c_{max} fixed at 0.105 N and varying the initial concentration. For the range $0.019 \leq c \leq 0.105$, we found $\Lambda_0 = 154.177$, $K_A = 0.935$, $\mathring{a} = 5.499$, $\sigma = 0.005$. For higher values of initial concentration, Λ_0 and K_A began to decrease and $\mathring{a}$ to increase in a systematic way; clearly, the range was then too narrow (*i.e.*, the extrapolation to Λ_0 was too long) to give reliable values. But the significant result is simply this: in order to evaluate Λ_0, K_A; and $\mathring{a}$ for 1:1 salts in water, it suffices to work in the range 0.01–

Table V. Constants of Eq 1 for Cesium Iodide

c_{max}	Λ_0	K_A	$\mathring{a}$	σ
0.03	154.167 ± 0.022	0.95	5.624 ± 0.041	0.011
0.04	154.168 ± 0.021	0.96	5.586 ± 0.037	0.010
0.05	154.172 ± 0.024	0.94	5.508 ± 0.040	0.011
0.06	154.182 ± 0.021	0.92	5.436 ± 0.031	0.008
0.07	154.173 ± 0.022	0.93	5.467 ± 0.033	0.010
0.08	154.174 ± 0.015	0.93	5.481 ± 0.023	0.007
0.09	154.173 ± 0.025	0.93	5.485 ± 0.034	0.009
0.10	154.173 ± 0.015	0.94	5.504 ± 0.020	0.006

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(6) J. E. Lind, Jr., and R. M. Fuoss, *J. Phys. Chem.*, **65**, 1414 (1961).

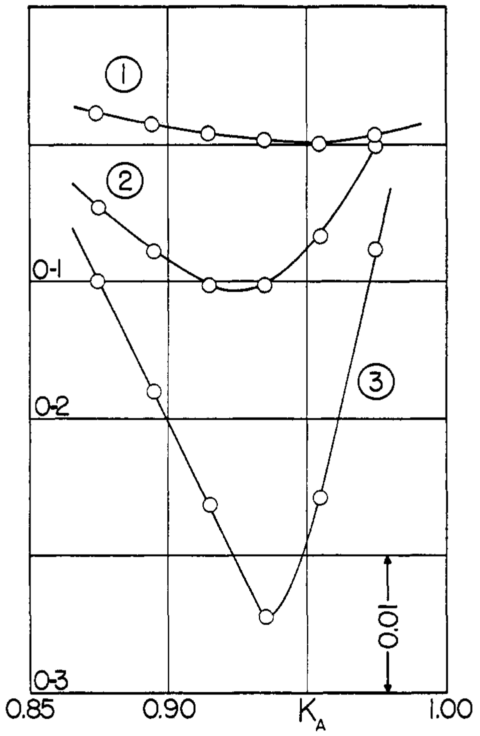

Figure 2. Sensitivity of minimum in σ–K_A curves to concentration range: curve 1, $c_{max} = 0.04$; curve 2, $c_{max} = 0.07$; curve 3, $c_{max} = 0.105$.

0.10 N, thereby avoiding the technical difficulties involved in handling more dilute solutions.

The precision in determination of the association constant is quite sensitive to the concentration range of the data from which it is evaluated. This point becomes obvious from an examination of the leading terms of the conductance equation which can be put in the form

$$\Lambda = \Lambda_0 - Sc^{1/2} + E'c \ln c + Jc - K_A\Lambda_0 c f^2 + O(c^{3/2}) \quad (8)$$

The only detail which distinguishes the leading ion-pair term from the linear terms is the factor f^2; if the concentration range is too low, f^2 does not differ much from unity and does not change enough for the computer to separate the K_A and J terms, and therefore it delivers a broad band of association constants paired off with a wide band of contact distances. This effect is illustrated in Figure 2 for cesium iodide. (The ordinate scale is 0.01 Λ unit. The zero for σ for each curve is indicated at the left.) Curve 1 is for the data up to $c_{max} = 0.04$. A minimum in σ appears at K_A around 0.94, but it is very shallow; K_A could easily be chosen much larger or smaller and still give a σ smaller than 0.02 Λ unit. For $c_{max} = 0.07$, curve 2, the situation is improved; to keep σ less than 0.02, K_A must lie in the range 0.85–0.98. With $c_{max} = 0.105$, curve 3, the minimum at $\sigma = 0.006$ at $K_A = 0.935$ pins the association constant within a per cent.

The rule, "the higher c_{max}, the sharper the precision in K_A," has its limit, of course. When higher terms than $c^{3/2}$ start to be significant, the three-parameter equation obviously must break down. The diagnostic symptoms are clear: the values of the parameters begin to depend on c_{max} when the latter is too large, a systematic pattern in the dependence of $\delta\Lambda$ on concentration appears, and the minimum value of σ exceeds the estimated experimental error. For the four salts so far examined by this method (CsI, CsBr, NaCl, KCl in water), the upper limit for application of eq 1 is about 0.10 N. This is illustrated in Figure 3 for the data of Table III. Using the constants obtained from the range $0.003 \leq c \leq 0.105$, the inverse program (no. 93) was used to compute conductances for the range $0.15 \leq c \leq 1.02$. The difference $\delta\Lambda$ between calculated and observed values is plotted against the square of the concentration in Figure 3. The curve is nearly linear with slope 11.6 between $c = 0.1$ and $c \approx 0.8$, and then goes concave-down. Below 0.1 N, the deviations are, as already mentioned, completely random. The figure clearly shows that eq 1 will fail very soon after 0.1 N is passed.

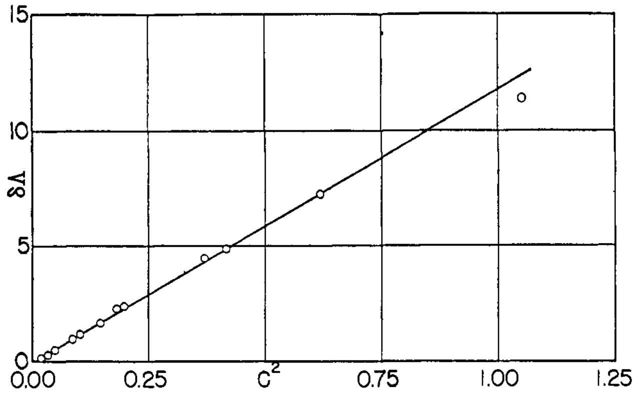

Figure 3. Difference between calculated and observed conductance for cesium iodide at higher concentrations.

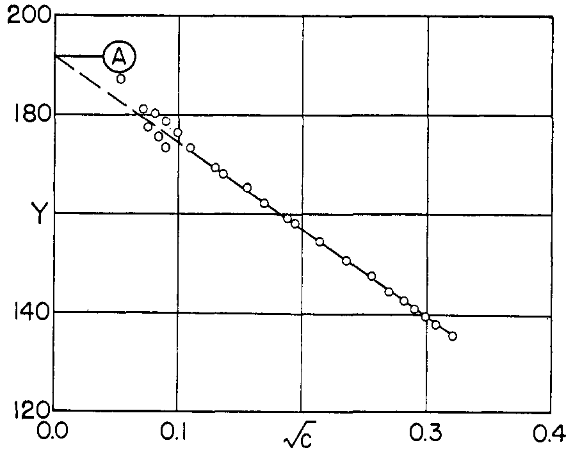

Figure 4. Test of $c^{3/2}$ equation for cesium bromide in water.

Cesium bromide is, as expected, quite similar to cesium iodide. Empirically, the data of Table II can be reproduced by the semiempirical eq 2, as shown in Figure 4, where

$$Y = [\Lambda_{obsd} + Sc^{1/2} - E'c \ln c - \Lambda_0]/c \quad (9)$$

is plotted against the square root of concentration. A least-squares analysis of the data gives $\Lambda_0 = 155.361 \pm 0.006$, $A = 191.7 \pm 0.5$, $B = -174.9 \pm 1.5$, $\sigma = 0.016$, averaged over 64 data points in the range 0.003–0.10 N. The value of A from the least-squares calculation is shown by the horizontal line at the left. Using the above value of Λ_0, values of Y for Figure 4 were calculated. The quantity Y obviously is an extremely sensitive function of concentration, especially at low concentrations. Above 0.01 N, the points are quite precisely on a straight line; below this concentration they start to scatter. Two points should be mentioned: first, at $c = 0.01$, the numerator in (9) is 1.37, a little less than 1% of the total conductance; and, second, an error in Λ_0 would make Y diverge to $\pm\infty$ as the concentration decreased to zero.

The data were then analyzed for the constants of the explicit conductance function (1); the results (for all the points of Table II) are shown in the first line of Table VI. The value of Λ_0 agrees within better than 0.01% with the value obtained by the $c^{3/2}$ extrapolation. The parameters Λ_0, K_A, and $å$ showed little sensitivity to the range (lines 1, 2, 5, 6, 7) over which they were determined, provided the lowest concentration was not higher than 0.01 N. If this value is exceeded, then Λ_0 and $å$ begin to vary in a systematic way with concentration, as they did for cesium iodide. Based on results for cesium bromide and iodide, and also on those for sodium[7] and potassium[7] chloride and for sodium bromide[8] over the concentration range $0.003 \leq c \leq 1.0$ N, we conclude that the $c^{3/2}$ equation may be used for extrapolation for Λ_0 for conductance data for 1:1 salts in water over the range up to 0.10 N, and the eq 1 may be used to determine the three parameters Λ_0, K_A, and $å$ over the same range. In both cases, the range should start at concentrations not greater than 0.01 N; data at lower concentrations, down to perhaps 0.005 N, are desirable but not necessary.

Table VI. Constants of Eq 1 for Cesium Bromide

c (range)	Λ_0	K_A	$å$	σ
0.003–0.10	155.374	1.065	5.548	0.016
0.01 –0.10	155.366	1.07	5.607	0.012
0.02 –0.10	155.516	1.05	5.345	0.011
0.03 –0.10	155.539	1.05	5.323	0.011
0.003–0.04	155.372	1.03	5.443	0.011
0.003–0.06	155.360	1.06	5.570	0.014
0.003–0.08	155.349	1.07	5.627	0.010
0.003–0.01[a]	155.432	0.00	2.602	0.019

[a] Calculated by 1965 program for eq (2.2): R. M. Fuoss, L. Onsager, and J. F. Skinner, *J. Phys. Chem.*, **69**, 2581 (1965).

The linearized form of (1)

$$\Lambda = \Lambda_0 - Sc^{1/2}\gamma^{1/2} + E'c\gamma \ln c\gamma + Jc\gamma - K_A c\gamma f^2 \Lambda \qquad (10)$$

which we have previously used to analyze conductance data at low concentrations,[9] always gave unsatisfactory results for aqueous solutions; the association constants were completely uncertain (*i.e.*, the "±" on the calculated K_A was often as large as K_A itself) because the last term of (10) was so small that the computer could not distinguish between slight association and no association. If K_A were set equal to zero, reducing (10) to a two-parameter equation, the values of the contact distance obtained always seemed rather small. As an example, the data for cesium bromide for which $c \leq 0.01$ were analyzed by the 1965 program (last line of Table VI); assuming $K_A = 0$, which reduces (10) to

$$\Lambda = \Lambda_0 - Sc^{1/2} + E'c \ln c + Jc \qquad (11)$$

leads to the unreasonably small value $å_J = 2.602$. It is now clear that this and similar small $å$ values for other alkali halides in water are merely the consequence of absorbing the association term into a net linear term. Equation 10 should only be used for systems in which the association constant is at least 10, and for concentrations such that κa does not exceed 0.1. Equation 11 probably should be restricted to the very dilute range, with $c_{\max} < 0.005$. For systems with small association constants, the complete eq 1 should be used, and the data should extend to concentrations high enough to make γ at least 3–4% less than unity. The concentration range should, of course, not run too high, because then terms of order higher than $c^{3/2}$ will perturb the calculation (*cf.* Figure 3). An empirical rule based on experience is to work below the concentration at which the calculated activity coefficient is 0.7 which corresponds to $c_{\max} < 2 \times 10^{-7}D^3$. This limit is a little lower than $3.2 \times 10^{-7}D^3$, the critical concentration above which it is statistically impossible to assign unique partners to ions to form pairs.[10]

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(7) Unpublished work by Ying-Chech Chiu at this laboratory.

(8) A. F. Reynolds, Thesis, Yale University, 1966.

(9) R. M. Fuoss, L. Onsager, and J. F. Skinner, *J. Phys. Chem.*, **69**, 2581 (1965); see eq (2.2) and (2.3). Corrections to ref 9: $b^{-1/2}$ in (1.42); $b^n/n \cdot n!$ in (1.46); $\Sigma_{n=0} b^n$ in (1.50).

(10) R. M. Fuoss, *J. Am. Chem. Soc.*, **57**, 2604 (1935).