

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORIES OF BROWN UNIVERSITY]

An Application of the Fuoss-Onsager Conductance Theory to the Alkali Halides in Several Solvents¹

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A method of solving the Fuoss-Onsager conductance equation with the aid of a high speed digital computer is outlined for both associated and unassociated electrolytes. The results of an analysis of conductance data for the alkali halides in water, 50 mole % methanol-water, methanol, ethanol, 1-propanol and liquid ammonia at various temperatures, as well as for other alkali metal salts in aqueous solution, are presented. The ion size parameter, a , shows a consistent decrease from lithium to cesium in all salts studied and the values are lower than would be expected from the crystallographic radii. This is explained in terms of ion association as confirmed by the association pattern obtained in ethanol, propanol-1 and liquid ammonia solutions where the degree of association is appreciable, and the association constants increase $\text{Li} < \text{Na} < \text{K}$. The order of magnitude of the association constants, which must be postulated to account for the low a values in aqueous solutions, have been calculated using Latimer's ionic "cavity" values as a measure of the solvated radii. The a values are shown to be independent of temperature from 5 to 55°.

In a number of publications Fuoss and Onsager^{2,3} have outlined a theory of electrolytic conductance based on the Debye interionic attraction theory. Their main contribution has been the solution of the equation of continuity for spherical ions with the inclusion of higher order terms. They applied the resulting conductance equation to some of the available data for the potassium halide salts in aqueous solution at several temperatures² and obtained ion size parameters which were reasonable, showed a consistent increase from chloride to iodide and appeared to be independent of temperature.

Since the publication of these results, Fuoss⁴ has revised the equation making it more consistent in the retention of higher order terms. At present the only extensive results that have been published using this revised equation involve large ions, such as those obtained from the quaternary ammonium salts,⁵ in associating solvents. It was felt that, before the new equation could be used with much confidence for the determination of association constants, its ability to reproduce the concentration dependence of the equivalent conductance of unassociated electrolytes should be demonstrated thoroughly and the magnitude of the parameters used, particularly the ion size parameter, should be shown to be reasonable. The alkali halides were most suitable for this purpose since a large number of data with the required precision were available. They are generally considered to be relatively unassociated in aqueous solution and they involve relatively small ions. This latter fact was most important since Fuoss has shown⁶ that a viscosity correction must be made if large ions are involved. At this stage of the theory, such a correction must be avoided if an unambiguous analysis is to be made.

It is the purpose of this paper to present a thorough investigation of the alkali halides in

several solvents and at various temperatures. For comparison, several alkali metal salts other than the halides have been included. All data were obtained from the literature. An exhaustive search of the literature was not undertaken but rather a representative group of data was used to show what can be obtained from the new theory.

Due to the large number of data that had to be processed (over 100 separate systems) and since the calculations involved were quite extensive, a high speed digital computer, the I.B.M. 650, was used to carry out all calculations. Programs, involving a least squares treatment, have been written for both associated and unassociated electrolytes.

Method of Calculation

The revised Fuoss-Onsager equation for an associated electrolyte, involving only relatively small ions, is

$$\Lambda = \Lambda_0 - S c^{1/2} \gamma^{1/2} + E c \gamma \log c \gamma + J c \gamma - K_{AA} f^2 c \gamma \quad (1)$$

where S , the Onsager limiting slope, and E are both known functions of Λ_0 and the solvent properties. These functions are given elsewhere.⁷ The coefficient J is a function of the solvent properties, Λ_0 , and the ion size a . It can be expressed⁴ as a cubic and logarithmic function of a .

The method of calculation was designed primarily for ease of computation on the I.B.M. 650 computer. The graphical methods developed by Fuoss⁶ were discarded in favor of a least squares treatment which was more compatible with computer programming and from which the standard deviations in each unknown could be obtained with very little extra calculation. This latter point was particularly important in the handling of data for the same systems but which had been obtained in different laboratories.

Equation 1 is essentially a linear equation in the three unknowns Λ_0 , J and K_A , the ion pair association constant. Since a , the ion size parameter, and not J was the quantity whose evaluation was required, the expression for J in terms of a was substituted in equation 1.⁸ Although this produced an equation non-linear in a , it was linearized⁹ quite easily by taking the total differential of Λ which is linear in the new unknowns $\Delta\Lambda_0$, Δa and ΔK_A .

$$\Delta\Lambda = \frac{\partial\Lambda}{\partial\Lambda_0} \Delta\Lambda_0 + \frac{\partial\Lambda}{\partial a} \Delta a + \frac{\partial\Lambda}{\partial K_A} \Delta K_A \quad (2)$$

The calculation was started by selecting initial values for Λ_0 , a and K_A . The literature values for Λ_0 and K_A , ob-

(7) J. E. Lind, J. J. Zwolenik and R. M. Fuoss, *ibid.*, **81**, 1557 (1959). Two misprints in the expressions for b and T in this paper should be noted: $b = e^2/aDkT$ and $T = 273.160 + t^\circ\text{C}$.

(8) It would appear that equation 1 could be solved more rapidly in its linear form to obtain J followed by an iteration procedure to obtain a . However, when programmed in this manner, the calculations involved were almost as long as those required in the above procedure and the solution of the equation converged no more rapidly.

(9) E. T. Whittaker and G. Robinson, "The Calculus of Observations," 3rd Ed., Blackie and Son Limited, London, 1940, p. 214.

(1) Presented at the International Symposium on Electrolytes, Congresso della Società Italiana per il Progresso delle Scienze, Trieste, 4-9 June, 1959, and, in part, at the American Chemical Society Meeting in Boston, April, 1959.

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

(3) R. M. Fuoss and L. Onsager, *ibid.*, **62**, 1339 (1958); R. M. Fuoss, *ibid.*, **63**, 633 (1959).

(4) R. M. Fuoss, *THIS JOURNAL*, **80**, 3163 (1958); **81**, 2659 (1959).

(5) F. Accascina, A. D'Aprano and R. M. Fuoss, *ibid.*, **81**, 1058 (1959); F. Accascina, S. Petrucci and R. M. Fuoss, *ibid.*, **81**, 1301 (1959).

(6) R. M. Fuoss, *ibid.*, **79**, 3301 (1957).

tained generally by a Shedlovsky extrapolation and a Fuoss-Shedlovsky plot, respectively, were found satisfactory as initial values. An initial value of J was calculated from a guess at a reasonable value for a . A calculated value of the equivalent conductance, $\Lambda_{\text{calc.}}$, was obtained by substitution of these initial values in equation 1 and $\Delta\Lambda$ was set equal to the difference between the measured Λ and this calculated value. To a good approximation, eq. 2 can be replaced by

$$\Lambda - \Lambda_{\text{calc.}} = \Delta\Lambda_0 + c\gamma\partial J/\partial a\Delta a - \Delta f^2 c\gamma\Delta K_A \quad (3)$$

All coefficients in this equation were known or could be calculated from the initial values of Λ_0 , a and K_A . A least square solution of the three normal equations derived from equation 3 gave the best values of the unknowns which minimized $\Sigma(\Delta\Lambda)^2$. These changes in the unknowns were added to the initial values and the whole calculation repeated including the calculation of all constants involving Λ_0 . When Δa converged to less than 5×10^{-11} cm. the iteration was stopped and the standard deviation in each unknown, $\sigma(\Lambda_0)$, $\sigma(a)$ and $\sigma(K_A)$, as well as the standard deviation of the individual points $\sigma(\Lambda)$, were calculated.

Before $\Lambda_{\text{calc.}}$ could be calculated as outlined above, it was necessary to have values for γ , the degree of dissociation, and f^2 , the mean ion activity coefficient. The method outlined by Fuoss⁶ was used for this purpose with one difference. Initial values of the degree of dissociation, obtained from $\gamma_0 = \Lambda/(\Lambda_0 - Sc^{1/2}\Lambda^{1/2}/\Lambda_0^{1/2})$ were substituted, along with the initial values of Λ_0 and J , directly into $\gamma = \Lambda/(\Lambda_0 - Sc^{1/2}\gamma_0^{1/2} + Ec\gamma_0 \log c\gamma_0 + Jc\gamma_0)$ to obtain γ for the first iteration. The γ_0 approximation, of course, was used only in the first iteration. Possibly a more consistent method of evaluating γ would have been to calculate it from the K_A obtained in the preceding iteration. f^2 was obtained from the Debye-Hückel second approximation with a set equal to some reasonable value.

In all cases studied, the final values of the unknowns were found to be independent of the choice made for the initial values of the unknowns. Convergence was found to be almost complete after one iteration. To take an extreme case, when the initial values used for Λ_0 , a and K_A were 34.6, 6.5 Å. and 0.00, respectively, the values after the first least squares treatment were 35.276, 7.23 Å. and 447, respectively. The final values obtained were 35.273, 7.38 Å. and 456 with standard deviations of 0.001, 0.05 Å. and 1.3, respectively.

When an unassociated electrolyte was under investigation, equation 1 in the form

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

was used directly to determine Λ_0 and J by least squares. Once J was determined the best value of a was obtained by an iteration procedure involving $\partial J/\partial a$. Convergence was very rapid in most cases since J is close to being linear in a in the working range 2-8 Å.

It must be remembered that, if this simplified form of the conductance equation is employed in cases where ion association is not negligible, the negative term involving K_A will be included in the Jc term and low values for J , and consequently for a , will result.

One complication that arises in using a computer for this type of analysis concerns what should be done about points that are off the curve by a considerable amount. In a graphical analysis such points can be ignored but a least squares calculation gives equal weight to all points. Moreover most of the conductance data in the literature were designed for extrapolation purposes and consequently include an abnormally large number of points in the dilute range where the precision is poorest. In order to avoid the necessity of making several arbitrary decisions as to what data to include or reject, it was decided that each conductance value should be properly weighted.

That some decision had to be made as to weighting can be seen by expressing equation 4 in terms of L , which is 1000 times the specific conductance

$$L = \Lambda_0 c - Sc^{3/2} + Ec^2 \log c + Jc^2 \quad (5)$$

Although the calculation of the unknowns using this equation is just as valid as the use of equation 4, the results would not agree exactly since they are weighted differently. Equation 4 gives equal weight to each value of Λ whereas equation 5 gives equal weight to each value of L . If equal weight is given to each value of L , it is equivalent to assuming a constant random error in the measurement of L . Conse-

quently, since $\Delta\Lambda = \Delta L/c$, the corresponding error in Λ would be proportional to $1/c$ and each value of Λ must be weighted by c^2 . If equation 4 is multiplied by the square root of this weighting factor, it can be seen that the two equations become identical in all respects.

It was felt that c^2 was somewhat too drastic a weighting factor and a value of c was decided on ($c\gamma$ in the case of equation 1). This is equivalent to assuming a random error in the specific conductance which is proportional to $c^{1/2}$.

The complete computation took about 5 minutes for equation 1 and one minute for equation 4 for a set of data consisting of conductances at six concentrations. The program had a two-minute loading time.

Results

All conductances were corrected to agree with the Jones and Bradshaw standards if this was not already the case. No attempt was made at correcting the molecular weights of the various salts to agree with the latest accepted values. Data at the actual measured concentrations were used, if reported, in place of values at rounded concentrations. With one limitation on concentration range, all data as reported in the literature were used in the calculations unless otherwise noted. The highest concentrations used in each set of data conformed to that for which $ka < 0.2$. This limitation on concentration range has been demonstrated¹⁰ recently and was particularly important here due to the manner in which the data were weighted.

The latest values of the various universal constants were used to compute S , E and J . The necessary equations and constants have been summarized elsewhere.⁷ The values of the dielectric constants and the viscosities of the various solvents investigated are given in Table I. Included in the table are approximate values for the coefficients in equation 1 computed for KCl at 25° unless otherwise noted. The values of $\partial J/\partial a$ have been included to facilitate conversion of $\sigma(a)$ to conductance units.

TABLE I
SOLVENT PROPERTIES AND THEORETICAL CONSTANTS

	D	100 η	S	E	J	10^{-8} $\partial J/\partial a$
H ₂ O (5°) ^a	86.12	1.5188	56	35	117	39
(25°) ^a	78.54	0.8949	95	59	200	65
(55°) ^a	68.53	0.5072	168	108	360	117
CH ₃ OH-H ₂ O ^b	49.84	1.326	85	121	304	87
CH ₃ OH ^c	32.64 ^h	0.5445	243	576	1270	340
C ₂ H ₅ OH ^d	24.3	1.084	150	634	1700	250
<i>n</i> -C ₄ H ₉ OH ^e	20.4	1.93	98 ^g	634 ^g	1360 ^g	250 ^g
NH ₃ (-34°) ^f	22.0	0.2558	1200	14800	41200	3400

^a B. B. Owen and H. Zeldes, *J. Chem. Phys.*, **18**, 1083 (1950). ^b 50 mole %. H. I. Schiff and A. R. Gordon, *ibid.*, **16**, 336 (1948). ^c J. P. Butler, H. I. Schiff and A. R. Gordon, *ibid.*, **19**, 752 (1951). ^d J. R. Graham, G. S. Kell and A. R. Gordon, *THIS JOURNAL*, **79**, 2352 (1957). ^e T. A. Gover and P. G. Sears, *J. Phys. Chem.*, **60**, 330 (1956). ^f V. F. Hnizda and C. A. Kraus, *THIS JOURNAL*, **71**, 1565 (1949). ^g Calculated from the Λ_0 and a for KI. ^h All methanol data were analyzed using this value of D from Gosting and Albright, *ibid.*, **68**, 1061 (1946), and Jones and Davies, *Phil. Mag.*, **28**, 307 (1939) in place of the value referred to in ref. *c*.

In Table II are given the results of the computations using equation 4, for water, 50 mole % methanol-water and methanol solutions at various temperatures. The values of the standard deviation of the individual points are not recorded since they

(10) F. Accascina, R. L. Kay and C. A. Kraus, *Proc. Natl. Acad. Sci.*, **45**, 804 (1959).

TABLE II
SUMMARY OF THE RESULTS OF CALCULATIONS BASED ON
EQUATION 4

Ref.	Salt	Δ_0	$\sigma(\Delta_0)$	$10^3 a$	$10^3 \sigma(a)$	J^{∞} S^i	AgClO ₃ AgNO ₃	126.31 133.39	.05 .02	0.9 2.1	.1 .2	
							H ₂ O, 35°					
							BG ^j	KCl	180.53	0.03	3.20	0.05
							BG ^j	KBr	182.39	.04	3.45	.06
JB ^{dd}	KBr	83.38	0.01	3.41	0.06	OZ ^a	KI	180.76	.02	3.51	.03	
							T ^{ee}	LiCl	140.22	.01	3.19	.02
							BG ^j	NaCl	153.86	.03	3.37	.06
OZ ^a	KCl	94.270	0.004	3.15	0.02	V ⁱ	RbCl	185.58	.01	2.93	.02	
OZ ^a	KBr	96.025	.005	3.25	.02	V ⁱ	CsCl	184.35	.01	2.71	.01	
OZ ^a	KI	95.341	.005	3.51	.02							
T ^{ee}	LiCl	70.33	.01	3.25	.07	H ₂ O, 45°						
T ^{ee}	NaCl	77.90	.01	3.00	.06	BG ^j	KCl	212.57	0.05	3.19	0.06	
V ⁱ	RbCl	97.90	.01	3.02	.06	BG ^j	KBr	214.34	.05	3.36	.06	
V ⁱ	CsCl	97.58	.01	2.67	.04	OZ ^a	KI	212.32	.03	3.52	.04	
							T ^{ee}	LiCl	166.98	.01	3.24	.03
							BG ^j	NaCl	182.79	.04	3.33	.05
BG ^j	KCl	121.01	0.02	3.28	0.04	V ⁱ	RbCl	217.98	.01	2.97	.01	
BG ^j	KBr	122.89	.02	3.56	.06	V ⁱ	CsCl	216.52	.02	2.80	.04	
OZ ^a	KI	121.91	.01	3.49	.03	H ₂ O, 55°						
T ^{ee}	LiCl	91.67	.01	3.27	.06	OZ ^a	KCl	245.96	0.07	3.14	0.10	
BG ^j	NaCl	101.12	.02	3.26	.06	OZ ^a	KBr	247.35	.02	3.24	.03	
V ⁱ	RbCl	125.18	.01	2.97	.03	OZ ^a	KI	244.96	.05	3.53	.07	
V ⁱ	CsCl	124.63	.02	2.60	.07	T ^{ee}	LiCl	195.24	.03	3.19	.06	
							T ^{ee}	NaCl	213.43	.03	3.06	.04
T ^{ee}	LiCl	115.03	0.01	3.30	0.03	V ⁱ	RbCl	251.48	.01	2.89	.01	
JG ^k	LiCl	.08	.02	3.25	.08	V ⁱ	CsCl	250.10	.01	2.73	.01	
S ⁱ	LiCl	.13	.02	3.14	.06	50 mole % CH ₃ OH-H ₂ O, 25°						
KK ^m	LiCl	.03	.03	3.39	.08	SG ^b	NaCl	66.67	0.01	3.15	0.03	
SL ⁿ	NaCl	126.59	.01	3.19	.02	SG ^b	KCl	75.06	0.01	2.66	0.02	
T ^{ee}	NaCl	.59	.02	3.20	.04	CH ₃ OH, 25°						
BG ^j	NaCl	.54	.02	3.30	.05	BSG ^o	KCl	104.80	0.02	3.29	0.02	
SM ^o	NaCl	.57	.02	3.22	.04	EK ^z	KCl	104.88	.03	3.28	.03	
S ⁱ	NaCl	.50	.03	3.5	.2	FH ^v	KCl	105.00	.04	2.9	.1	
OZ ^a	KCl	149.94	.01	3.10	.02	JG ^k	KBr	108.88	.01	3.45	.01	
SM ^o	KCl	.94	.01	3.11	.01	FH ^v	KBr	109.31	.04	3.3	.1	
BG ^j	KCl	.91	.02	3.16	.03	JG ^k	KI	115.22	.03	3.78	.03	
B ^p	KCl	.98	.01	3.12	.06	FH ^v	KI	114.89	.04	3.7	.1	
D ^q	KCl	.98	.02	2.99	.07	JG ^k	LiCl	92.05	.05	3.73	.04	
S ⁱ	KCl	.99	.02	2.90	.15	FH ^v	LiCl	91.17	.04	3.8	.1	
V ⁱ	RbCl	154.54	.01	2.90	.02	BSG ^o	NaCl	97.53	.02	3.73	.02	
V ⁱ	CsCl	153.68	.02	2.61	.04	EK ^z	NaCl	97.30	.01	3.72	.02	
JG ^k	NaBr	128.24	.01	3.45	.05	FH ^v	NaCl	97.22	.06	3.9	.2	
OZ ^a	KBr	151.767	.004	3.26	.01	FH ^v	RbCl	108.28	.07	2.4	.2	
BG ^j	KBr	.76	.03	3.36	.06	FH ^v	CsCl	113.22	.04	2.0	.1	
JB ^{dd}	KBr	.77	.03	3.28	.06	JG ^k	NaBr	101.64	.05	3.79	.04	
B ^p	NaI	127.28	.01	4.07	.03	ⁱ W. E. Voisenet, Thesis, Yale University (1951). ^j G. C. Benson and A. R. Gordon, <i>J. Chem. Phys.</i> , 13 , 473 (1945). ^k R. E. Jervis, D. R. Muir and A. R. Gordon, <i>THIS JOURNAL</i> , 75 , 2855 (1953). ^l T. Shedlovsky, <i>ibid.</i> , 54 , 1411 (1932). ^m K. A. Krieger and M. Kilpatrick, <i>ibid.</i> , 59 , 1878 (1937). ⁿ B. Saxton and T. W. Langer, <i>ibid.</i> , 55 , 3638 (1933). ^o T. Shedlovsky, A. S. Brown and D. A. MacInnes, <i>Trans. Electrochem. Soc.</i> , 66 , 165 (1934). ^p E. G. Baker, Thesis, Brown University, 1951. ^q C. W. Davies, <i>J. Chem. Soc.</i> , 432 (1937). ^r R. W. Martel and C. A. Kraus, <i>Proc. Natl. Acad. Sci.</i> , 41 , 9 (1955). ^s J. H. Jones, <i>THIS JOURNAL</i> , 66 , 1115 (1944). ^t K. A. Krieger and M. Kilpatrick, <i>ibid.</i> , 64 , 7 (1942). ^u C. B. Monk, <i>ibid.</i> , 70 , 3281 (1948). ^v R. A. Robinson and C. W. Davies, <i>J. Chem. Soc.</i> , 574 (1937). ^w E. L. Swarts, Thesis, Brown University, 1954. ^x E. C. Evers and A. G. Knox, <i>THIS JOURNAL</i> , 73 , 1739 (1951). ^y J. E. Frazer and H. Hartley, <i>Proc. Roy. Soc. (London)</i> , A109 , 351 (1925). ^z P. A. Lasselle and J. G. Aston, <i>THIS JOURNAL</i> , 55 , 3067 (1933). ^{aa} J. H. Jones, <i>ibid.</i> , 67 , 855 (1945). ^{bb} J. H. Jones, <i>ibid.</i> , 68 , 240 (1946). ^{cc} J. H. Jones, <i>ibid.</i> , 69 , 2065 (1947). ^{dd} G. Jones and C. F. Bickford, <i>ibid.</i> , 56 , 602 (1934). ^{ee} F. W. Tober, Dissertation, Yale University (1948).						
LA ^e	NaI	127.12	.13	3.56	.3							
JG ^k	KI	150.53	.01	3.86	.05							
OZ ^a	KI	.50	.03	3.53	.07							
B ^p	KI	.57	.03	3.67	.06							
MK ^r	NaBrO ₃	105.76	.01	2.76	.04							
J ^s	NaBrO ₃	105.97	.02	2.9	.1							
J ^s	KBrO ₃	129.31	.02	2.2	.1							
B ^p	KBrO ₃	129.04	.02	2.5	.2							
KK ^t	KIO ₃	114.15	.02	2.11	.04							
M ^u	KIO ₃	114.20	.03	1.7	.2							
J ^{aa}	LiClO ₄	106.06	.02	3.5	.1							
J ^{aa}	NaClO ₄	117.56	.04	3.0	.1							
J ^{aa}	KClO ₄	140.84	.02	1.64	.03							
RD ^v	TiClO ₄	142.56	.06	1.8	.2							
J ^{bb}	KIO ₄	127.71	.04	2.0	.1							
SK ^w	NaNO ₃	121.67	.01	2.77	.02							
SK ^w	KNO ₃	145.16	.01	1.90	.02							
B ^p	KNO ₃	145.08	.01	2.40	.04							
S ⁱ	KNO ₃	144.87	.03	1.9	.2							
J ^{bb}	KReO ₄	127.85	.05	2.2	.2							

are approximated very closely by $\sigma(\Lambda_0)$. The highest concentration used in these calculations was 0.01 mole/l. for aqueous solutions, 0.007 for 50 mole % methanol-water solutions and 0.005 for methanol solutions. The corresponding concentrations at 25° for which $\kappa a = 0.2$ for an ion size of 5Å. were 0.023, 0.015 and 0.01 mole/l., respectively. Included in Table II are results for several alkali metal salts with oxyanions and a few miscellaneous salts. These have been added for comparison purposes since they have been of interest in the conductance field for some time. Some of the values for the parameters listed in the table are the result of averaging more than one set of data by the same workers. In these cases the best values of the unknowns were obtained by the averaging procedure outlined below.

At 25° for both aqueous and methanol solutions, it can be seen that many sets of data by different workers were available for the same salt. In order to study a as a function of solvent and temperature, it was necessary to have a single value of this parameter for each salt in any one solvent and at any one temperature. A simple average gave too much weight at those values of a which had a high $\sigma(a)$. Instead of discarding data when $\sigma(a)$ was higher than some arbitrary value, each value of a was weighted by the inverse square of its standard deviation and an average value, \bar{a} , was obtained from

$$\bar{a} = \Sigma a \sigma^{-2}(a) / \Sigma \sigma^{-2}(a)$$

The standard deviation associated with this average value of a was computed from

$$\sigma^2(\bar{a}) = \Sigma (a - \bar{a})^2 \sigma^{-2}(a) / \Sigma \sigma^{-2}(a)$$

The values obtained for \bar{a} and $\sigma(\bar{a})$ in aqueous and methanol solutions at 25° are given in Table III.

TABLE III
VALUES OF \bar{a} AT 25°

		$10^3 \bar{a}$	$10^3 \sigma(\bar{a})$
H ₂ O	LiCl	3.29	0.07
	NaCl	3.23	.05
	KCl	3.11	.02
	KBr	3.28	.02
	KI	3.69	.15
	NaI	4.07	.05
CH ₃ OH	KCl	3.26	0.06
	KBr	3.45	.02
	KI	3.78	.03
	NaCl	3.73	.01

The $(\bar{a})_T$ values given in Table IV were obtained by taking a weighted average of the a values at the various temperatures between 5 and 55° for each alkali halide. The low $\sigma(\bar{a})_T$ values in all cases, with the possible exception of NaCl, indicate little if any dependence of a on temperature.

In a number of solvents the alkali halides and the nitrates were appreciably associated. An analysis, using equation 1, gave the results shown in Table V for 50 mole % methanol-water, methanol, ethanol, propanol-1 and liquid ammonia solutions. The highest concentrations used in the solvents in the order listed above were 7, 5, 2, 2 and 2.5×10^{-3} , respectively, each of which was below the concentration corresponding to $\kappa a = 0.2$.

TABLE IV
VALUES OF $(\bar{a})_T$ FOR AQUEOUS SOLUTIONS FROM 5-55°

	$10^3(\bar{a})_T$	$10^3\sigma(\bar{a})_T$
LiCl	3.21	0.03
NaCl	3.19	.13
KCl	3.17	.05
RbCl	2.93	.04
CsCl	2.72	.03
KBr	3.28	.07
KI	3.51	.02

Not all of the data listed by HK for liquid ammonia solutions were included in the calculations. Only those sets of data were analyzed that covered a concentration range extending beyond $10^{-3}N$ and contained measurements at more than five concentrations. This restriction was necessary due to the extreme dilution to which the measurements were carried in some cases.

TABLE V
SUMMARY OF THE RESULTS OF CALCULATIONS BASED ON EQUATION 1

Ref.	Salt	Λ_0	$\sigma(\Lambda_0)$	$10^3 a$	$10^3 \sigma(a)$	K_A	$\sigma(K_A)$
		50 mole % CH ₃ OH-H ₂ O, 25°					
SG ^b	KCl	75.10	0.01	3.2	0.2	1.2	0.3
		CH ₃ OH, 25°					
FH ^v	CsCl	113.42	0.08	4.5	1.5	15	7
FH ^v	LiNO ₃	100.21	.03	5.2	0.8	10	4
FH ^v	NaNO ₃	106.29	.04	4.9	0.7	19	4
FH ^v	KNO ₃	113.80	.05	7.1	1.9	39	7
FH ^v	RbNO ₃	117.21	.03	2.2	0.5	18	3
		C ₂ H ₅ OH, 25°					
GKG ^d	LiCl	38.94	0.02	4.4	0.3	27	4
GKG ^d	NaCl	42.17	.02	4.0	.2	44	3
GKG ^d	KCl	45.42	.02	4.6	.2	95	3
		<i>n</i> -C ₂ H ₅ OH, 25°					
GS ^e	NaI	23.87	0.08	4.2	0.8	100	20
GS ^e	KI	25.69	0.04	3.6	0.7	230	20
		NH ₃ , -34°					
HK ^f	KCl ^{ff}	348.0	0.1	6.7	0.2	1060	6
HK ^f	KBr	346.8	.2	7.8	.3	453	8
HK ^f	KI	345.1	.1	6.6	.3	183	7
HK ^f	NaBr	314.3	.3	5.9	.2	263	7

^{ff} Λ at $C = 3.3413 \times 10^{-4}$ was not used in the calculation.

Discussion

A comparison of the Λ_0 values, listed in Table II, with the values obtained by a Shedlovsky type extrapolation illustrates the effect of the log term in the conductance equation. Fuoss and Onsager² have shown that the inclusion of this term should result in higher values for Λ_0 . If the data for KCl at 25° on aqueous solutions are taken as an example, the increase in Λ_0 over the literature value is about 0.06 Λ -unit whereas $\sigma(\Lambda_0)$ has a maximum value of 0.02. The results for methanol solutions are not as consistent in this respect since the minimum in a Λ vs. $C^{1/2}$ plot occurred in the measurable concentration range and Λ_0 was obtained in different ways by the various workers. JG and BSG used an empirical log term to extrapolate their data and consequently their values of Λ_0 show both positive and negative deviations from the values in Table II. This same effect was found

with the data of FH, although they used a simple $C^{1/2}$ plot to extrapolate their data. This is not surprising in view of the rather low precision of their measurements. It is interesting to note that the values of Λ_0 obtained from the data of FH and EK are in better agreement with the more precise measurements of JG and BSG after this Fuoss-Onsager type of extrapolation than before.

The agreement of the Λ_0 values with the law of independent limiting ionic mobilities can be checked with the aid of known transference numbers. In aqueous solution at 25° there is reasonable agreement, within the precision of the transference numbers,¹¹ between the limiting conductances for chloride ion obtained from the lithium, sodium and potassium salts. However, the bromide and iodide ion limiting conductances obtained from the sodium and potassium salts differ by 0.10 and 0.23 conductance unit, respectively. Since the limiting conductance of the potassium ion in the different halides was found constant, it would appear that the above discrepancy can be attributed to the NaBr and NaI data and not necessarily to the method of extrapolation. In 50 mole % methanol-water, methanol and ethanol solutions transference numbers are available¹² for both NaCl and KCl and, in each of these cases, the limiting conductances of the chloride ion agree within the uncertainties in the measurement of the transference numbers.

The number of data is far too extensive to show plots for the differences between measured and calculated values of Λ . The value of $\sigma(\Lambda_0)$ is a good indication of how well the calculated values of Λ agree with the experimental. It can be seen that in aqueous solutions of the alkali halides, the agreement amounts to 0.02 Λ unit, or better than 0.02% in most cases. In those cases where $\sigma(\Lambda_0)$ is higher, the deviations were found to be random with few exceptions. The data of SM and BG show deviations with a systematic curvature which, however, are not significantly greater than experimental error except at higher temperatures and lower concentrations. The data of OZ for KI show this same curvature particularly at 55°.

The values of \bar{a} for the alkali halides in aqueous and methanol solutions, listed in Table III, are all of the correct order of magnitude. $\sigma(\bar{a})$ is quite low in most cases indicating that there is reasonable agreement in the concentration dependence of Λ for data from the various workers. The results for KI in water at 25° are a notable exception. The rather high $\sigma(\bar{a})$ indicates that although a could be determined with high precision in each of the three sets of data used to calculate \bar{a} , there was poor agreement in the value of a obtained. Using the data in Table I it can be seen that an uncertainty of 0.15 Å. in a corresponds to almost 0.1 Λ unit or 0.07% at $c = 0.01$.

The main effect of the Fuoss⁴ revision of the conductance equation is shown in Table VI. Here

(11) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., A.C.S. Monograph No. 137, Reinhold Publishing Corporation, New York, N. Y., 1958, p. 699.

(12) L. W. Shemilt, J. A. Davies and A. R. Gordon, *J. Chem. Phys.*, **16**, 340 (1948); J. A. Davies, R. L. Kay and A. R. Gordon, *ibid.*, **19**, 749 (1951); J. R. Graham and A. R. Gordon, *THIS JOURNAL*, **79**, 2350 (1957).

the a values obtained from the data of OZ are compared to those reported by Fuoss and Onsager² in their original paper. It can be seen that the Fuoss revision has resulted in consistently lower a values that show much less spread over a range of temperature. However, some of the credit for the constant a values must be given to the method of weighted least squares which, it would appear, has successfully ignored the larger variations at low concentrations in contrast to the graphical method.

TABLE VI
A COMPARISON OF THE ORIGINAL WITH THE REVISED a VALUES

t , °C.	$10^3 a$ (ref. 2)	$10^3 a$ (Table II)	t , °C.	$10^3 a$ (ref. 2)	$10^3 a$ (Table II)
	KCl			KI	
5	3.29	3.15	5	3.94	3.51
25	3.50	3.10	15	3.95	3.49
55	3.39	3.14	25	3.90	3.53
			35	4.01	3.51
	KBr		45	3.98	3.52
5	3.58	3.25	55	4.15	3.53
25	3.57	3.26			
55	3.61	3.24			

The results listed in Table IV and VI indicate that a single value of a can describe the conductance of free ions over a considerable temperature range. With the exception of NaCl, the $\sigma(\bar{a})_T$ values are small. Consequently, to a very good approximation, Λ_0 can be obtained at any temperature from a single conductance measurement at a concentration where the solvent conductance is practically negligible. Also, this temperature independence adds considerably to the reliance one can put on the physical interpretation of a .

For comparison purposes the various a values for the alkali halides at 25° along with the crystallographic radii¹³ have been plotted for aqueous solutions in Fig. 1 and for methanol and 50 mole% methanol-water in Fig. 2. It can be seen in both figures that the ion size parameter increases $\text{Cl} < \text{Br} < \text{I}$. The most significant feature of these results is, however, the decrease in a from lithium through to cesium for any one halide in both water and methanol. The extended Debye-Hückel equation for activity coefficients gave higher a values,¹⁴ but they showed the same ordered arrangement as is reported here from conductance measurements. This variation in ion size is in qualitative agreement with the hydrodynamic radii to be expected from mobility data but this explanation cannot account for a values which are lower than the crystallographic radii. Fuoss⁴ has noted that the revised equation gave a values for the potassium halides that agreed with the corresponding crystallographic radii.

The values of a lower than the corresponding crystallographic radii could possibly be explained by the viscosity correction that Fuoss⁶ has shown must be applied when large ions are involved. This can be disproved by a simple calculation. The viscosity correction amounts to subtracting the

(13) L. Pauling, "Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1948, Chapter X.

(14) R. A. Robinson and H. S. Harned, *Chem. Revs.*, **28**, 419 (1941).

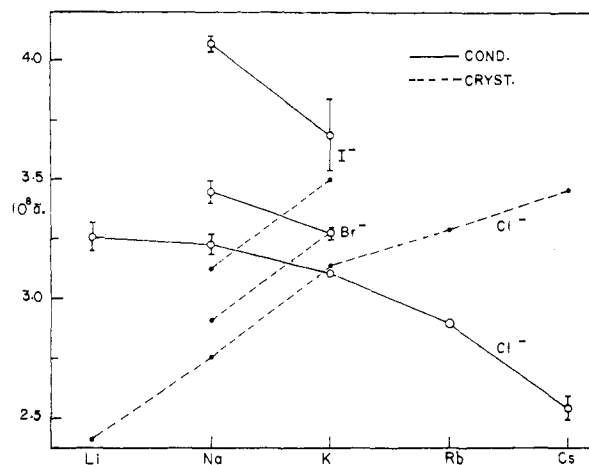


Fig. 1.—Average values of the ion size parameter, \bar{a} , for the alkali halides in aqueous solution at 25°. The solid lines join the \bar{a} values while the broken lines join the crystallographic radii.

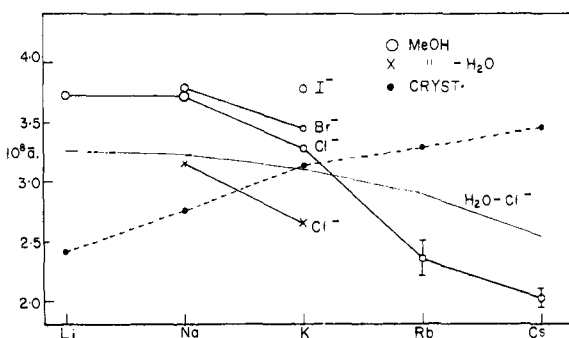


Fig. 2.—Average values of the ion size parameter, \bar{a} , for the alkali halides in methanol and 50 mole % methanol-water solutions at 25°. The \bar{a} values for aqueous solution are included as given by the lighter solid line.

Einstein viscosity term $\pi N_0 \Delta_0 R^3 c / 300$ from the R.H.S. of equation 4 for each ion of radius R . If we take the rather high value of 3 Å. for the size of both the cesium and chloride ions (crystallographic radii are 1.66 and 1.81 Å., respectively) and set $R^3 = 2 \times 3^3$, this viscosity correction increases the coefficient J by approximately 8 in aqueous solution. From the data in Table I it can be seen this would increase a by 0.12 Å. at most and thus cannot explain the extremely low a for CsCl. In methanol solution this correction is completely negligible due to the larger value of $\partial J / \partial a$ and the lower Δ_0 .

The decrease in a values can be explained satisfactorily if the assumption is made that the alkali halides are slightly associated into ion pairs even in aqueous and methanol solutions and that the degree of association increases $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$. As has already been pointed out any association will result in low a values when equation 4 is used. Eigen and Wicke¹⁵ have been able to explain the concentration dependence of activity coefficients, heats of dilution and apparent molar heat capacities of the alkali halides at higher concentration in aqueous solution by association con-

(15) M. Eigen and E. Wicke, *J. Phys. Chem.*, **58**, 702 (1954).

stants that follow the same order postulated here (with the exception of CsBr).

The data for aqueous and methanol solutions were analyzed using equation 1 in an attempt to detect the postulated association. Except for CsCl in methanol negative values for K_A and exceedingly low a values were obtained as expected. An inspection of equation 1 shows that as K_A approaches the value of one, the association term, $K_A \Delta f^2 c \gamma$, can be separated completely from the linear term, $J c \gamma$, only if the data have almost unattainable precision. Δf^2 does not change appreciably with concentration in solvents of higher dielectric constant if the degree of association is small. In these cases, the association term, to a first approximation, is linear in $c \gamma$ and cannot be distinguished from the linear term $J c \gamma$.

However, the association behavior of the alkali halides was studied in a number of solvents in which the degree of association is large. These results from Table V are plotted in Fig. 3. It can

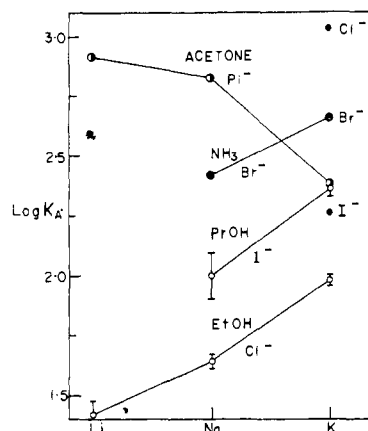


Fig. 3.—Association constants for some of the alkali halides in various solvents.

be seen quite clearly that for each solvent the association constants increase in the same manner as postulated for aqueous solution. Furthermore, the data for KCl in 50 mole% methanol-water was of such high precision that a reasonable association constant could be calculated directly. At the same time the a value increased from 2.66 to 3.2 Å., which is in much better agreement with what would be expected from the crystallographic radius.

As can be seen in Fig. 3, the association constants for the potassium salts of the halides in liquid ammonia increase $\text{I} < \text{Br} < \text{Cl}$. Sufficient data were not available in the other associating solvents to demonstrate this, but it is possible that the lower a values for chloride and bromide compared with iodide salts in aqueous and methanol solutions could indicate that this same association pattern is present. In any case it is interesting to note that, in liquid ammonia, the change in association constant with change in cation is in the direction predicted by polarizabilities whereas the reverse is true for a change in anion.

The order of magnitude of the association constants, that would have to be postulated to account for the low values of a in aqueous solution, can be obtained if a reasonable assumption is made as to

the solvated radii. The ion "cavity" values, r' , of Latimer, Pitzer and Slansky,¹⁶ which are 0.95 Å. greater than the crystallographic radii, were used for this purpose. In Table VII are shown the association constants obtained from

$$(r' - a)\partial J/\partial a = K_A \Lambda_0$$

where the approximations $f^2 = 1$ and $\Lambda = \Lambda_0$ have been made. They are compared to the values reported by Eigen and Wicke mentioned above. The excellent agreement must be considered only as agreement in order of magnitude due to the many assumptions made in obtaining both sets of association constants. It should be noted that the ordered arrangement is as postulated for both anions and cations.

TABLE VII

APPROXIMATE ASSOCIATION CONSTANTS FOR THE ALKALI HALIDES IN AQUEOUS SOLUTION AT 25°

	K_A	K_A (EW ¹⁸)		K_A	K_A (EW ¹⁸)
LiCl	0.0	0.0	NaBr	0.2	
NaCl	.2	.2	NaI	.0	
KCl	.4	.4	KBr	.4	0.4
RbCl	.6		KI	.3	
CsCl	.8	.5			

Some attempt was made to obtain data for the alkali halides in solvents which are not similar to water. Due to solubility limitations not many data are available with the precision required. The alkali picrates in acetone¹⁷ were investigated and it was found that the association order was reversed, that is, the association constants increased $K < Na < Li$. However, this difference in associating behavior could be attributed to differences in the picrate ion-cation interaction in comparison to the halide ion-cation interaction and should not necessarily be attributed to a specific solvent effect.

A number of salts that have been of interest in the conductance field for some time are included in Table II with the results for aqueous solution at 25°. The a values are all unreasonably low indicating considerable ion pairing in the bromates, nitrates and perchlorates. These salts have been suspected of being associated for some time but

(16) W. M. Latimer, *J. Chem. Phys.*, **23**, 90 (1955).

(17) M. B. Reynolds and C. A. Kraus, *THIS JOURNAL*, **70**, 1709 (1948).

attempts at obtaining an association constant independent of concentration have not been too successful. Fuoss and Kraus¹⁸ have shown that it can be done if data in mixed solvents are available. They obtained a value of 0.5 for K_A for NaBrO₃ using the data of M.K. The alkali nitrates in methanol are associated to such an extent that the data of FH could be analyzed successfully as is shown in Table V. Again the association constants increased significantly on going from lithium to potassium. The value of K_A for RbNO₃ seems to contradict this sequence, but it should be noted that the a value is quite low indicating, possibly, that a satisfactory partition of terms has not been accomplished due to lack of precision. The data for CsNO₃ did not have the precision necessary for this type of analysis.

As a check on the method of weighting employed, the data for the alkali halides in aqueous solution at 25° were analyzed using equation 4 unweighted. The results when averaged agreed with the values given in Table III within a standard deviation in all cases, but the uncertainties associated with the parameters in some cases became quite large due to poor precision in the dilute concentration range.

In conclusion it should be pointed out that it is always tempting to try to give a parameter, such as the ion size parameter a , a rigid physical significance. What these calculations were designed to show is that the a values obtained from the Fuoss-Onsager equation can be explained in a reasonable manner and are consistent with a set pattern much in contrast to the various ion size parameters that have been proposed in the past.¹⁹

The computer programs that have been outlined above can be used on any 650 computer and possibly on others. Any person interested in using the programs may obtain a complete listing of them by writing to the author.

The author wishes to acknowledge the donation of computer time from the Applied Mathematics Department of Brown University and to express his appreciation for their cooperation in preparing the programs.

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(18) R. M. Fuoss and C. A. Kraus, *ibid.*, **79**, 3304 (1957).

(19) K. H. Stern and E. S. Amis, *Chem. Revs.*, **59**, 1 (1959), have summarized the various methods which have been used to calculate ion size parameters.