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On the Interpretation of Conductance Data for Electrolyte Solutions

PER BERONIUS

Division of Physical Chemistry, University of Umeå, S-901 87 Umeå Sweden

For electrolytes subject to ion-pair formation the limiting molar conductivity, Λ_∞, the association constant, K_A, and the association distance, R, may be derived from conductance equations involving these quantities as adjustable parameters. Ordinarily that set of conductance parameters, Λ_∞, K_A, and R which minimizes $\sigma(\Lambda)$, the standard deviation between observed and computed Λ values, is adopted as the "best set".

In this investigation the equation of Fuoss and Hsia, in the form of Fernandez-Prini, has been applied to conductance data for numerous 1:1-electrolytes in pure and mixed solvents. By employing calculational methods involving the determination of those values of Λ_∞ and K_A which minimize $\sigma(\Lambda)$ for selected values of the distance parameter, R, it is shown that the "best set" of conductance parameters is frequently non-unique; almost equally good fits of the conductance equation to the experimental points are obtained for two significantly different values of the distance parameter.

By measurements of electrical conductance, Masterton and Bierly [1] investigated the 2:2-electrolyte, $[Co(NH_3)_5NO_2]SO_4$ in aqueous solution at 25 °C with respect to the equilibrium between free ions and ion-pairs. Their conductance data were subsequently reanalyzed by Hanna, Pethybridge, and Prue [2] using the conductance equation of Fuoss, Hsia, and Fernandez-Prini [3–5] ("FHFP" equation) in its form for associated electrolytes,

$$\Lambda = \alpha[\Lambda_\infty - S(c\alpha)^{1/2} + Ec\alpha\,{}^{10}\log(c\alpha) + J_1 c\alpha - J_2(c\alpha)^{3/2}] \quad (1)$$

together with the law of mass action for the equilibrium between free ions and ion-pairs and the Debye-Hückel equation for the mean activity coefficient of free ions.

In eqn. (1) Λ is the molar conductivity at the analytical concentration, c, of the electrolyte, α is the degree of dissociation of the ion-pairs, S and E are coefficients [6] which depend upon Λ_∞, ε, the permittivity of solvent, η, the viscosity of solvent, and T, the absolute temperature, while J_1 and J_2, according to Ref. 5, are also dependent upon the association distance, R. The last quantity is defined as the furthest distance of separation of the ions in the ion-pair; compare for instance Ref. 7.

One result of the aforementioned reanalysis [2] of the conductance data for the $[Co(NH_3)_5NO_2]SO_4$ system was that the "best set" of conductance parameters, *viz.* $\Lambda_\infty = 289.52$ cm^2 Ω^{-1} mol^{-1}, $K_A = 367$ M^{-1}, and $R = 12.5$ Å, giving a standard deviation, $\sigma(\Lambda) = 0.12$ cm^2 Ω^{-1} mol^{-1}, between experimental and calculated Λ values was not unique.* The insignificantly larger $\sigma(\Lambda) = 0.13$ was obtained for the set, $\Lambda_\infty = 289.42$, $K_A = 320$, and $R = 7.2$ Å.

Upon reanalyzing conductance data by means of the FHFP equation for numerous 1:1 electrolytes in pure and mixed solvents the present author observed similar behaviour for a not insignificant proportion of systems examined. The object of the present paper is to document and discuss some typical results for electrolyte systems showing behaviour of this kind.

CALCULATIONAL METHODS

Two calculational methods, the first according to Ref. 2, the second according to Ref. 8, were used to investigate the existence of non-unique

* These units are implied throughout the remaining text.

sets of conductance parameters. The first method permits $\sigma(\Lambda)$ to be determined for arbitrary combinations of Λ_∞ and R provided that these quantities do not differ too much from the "best set" parameters. In the second method one restricts oneself to establish the conditional minimum $\sigma(\Lambda)$ as a function of R (*i.e.* with implicit variation of Λ_∞ and K_A). Hence, the second method requires less computer time.

The values of ε and η used in the calculations are the same as adopted in the original publications.[9-15]

The computer programmes, which were prepared for use with a CDC 3300 computer, operate essentially as follows.

Method 1. For a selected pair of values of Λ_∞ and R, α values are iteratively calculated for all concentrations under investigation starting with $\alpha = \Lambda/\Lambda_\infty$ as a first approximation. Eqn. (1) is then repeatedly applied in the usual manner, *cf.* Ref. 16, until for all points the difference between successive α values falls below a predetermined limit, which was set equal to 1×10^{-7} in the present study. (Increasing this limit to 1×10^{-6} yielded practically identical results).

For each experimental point (c/Λ), an association constant is then calculated using the expression,

$$K_A = \frac{\Lambda_\infty - S(c\alpha)^{1/2} + Ec\alpha\,{}^{10}\log(c\alpha) + J_1 c\alpha - J_2(c\alpha)^{3/2} - \Lambda}{c\alpha\gamma^2\Lambda} \quad (2)$$

obtained from eqn. (1) and the law of mass action,

$$K_A = (1-\alpha)/(c\gamma^2\alpha^2) \quad (3)$$

for the equilibrium between free ions and ion-pairs.

In eqn. (3) γ is the mean molar activity coefficient of free ions, which is calculated from the Debye-Hückel equation,

$$^{10}\log\gamma \simeq -A(c\alpha)^{\frac{1}{2}}/[1 + BR(c\alpha)^{\frac{1}{2}}] \quad (4)$$

where A and B depend upon the solvent.[17]

The average value of K_A for the N experimental points is then computed and used together with the selected Λ_∞ and R to obtain calculated Λ values for the different concentrations investigated. The standard deviation between experimental and calculated Λ values is computed from the expression,

$$\sigma(\Lambda) = \left(\frac{\sum[\Lambda(\text{exp}) - \Lambda(\text{calc})]^2}{N-3}\right)^{\frac{1}{2}} \quad (5)$$

The calculations are repeated, as demonstrated below, for different combinations of Λ_∞ and R to establish the dependence of $\sigma(\Lambda)$ on these quantities.

Method 2. Preliminary figures for Λ_∞ and K_A are used, together with a pre-selected value of R, to start the calculations. Values of α are computed as above. For each experimental point the difference,

$$\Delta\Lambda = \Lambda(\text{exp}) - \Lambda(\text{calc}) \quad (6)$$

is then established.

The preliminary figures for Λ_∞ and K_A are improved by adding the $\Delta\Lambda_\infty$ and ΔK_A obtained upon solving the set of normal equations [8] derived from the expression,

$$\Delta\Lambda = \frac{\partial\Lambda}{\partial\Lambda_\infty}\Delta\Lambda_\infty + \frac{\partial\Lambda}{\partial K_A}\Delta K_A \quad (7)$$

cf. Ref. 16 and references therein. The improved values of Λ_∞ and K_A are used to start a second round of computation (with unchanged R value). This procedure is repeated until $\Delta\Lambda_\infty$ falls below a pre-selected limit, which was set equal to 1×10^{-7} in this study. The final Λ_∞ and K_A are used together with the selected R in calculating, according to eqn. (5), the standard deviation between experimental and computed Λ values, *i.e.* the conditional minimum $\sigma(\Lambda)$ for the R value chosen.

The calculational procedure outlined is repeated for several different values of R to establish the dependence of the conditional minimum $\sigma(\Lambda)$ on R over the desired range of the latter. In the present study the range $1-25$ Å was investigated using 0.2 Å increments in R. Repeated calculations with successively smaller increments were then performed near each minimum of the $\sigma(\Lambda) - R$ curve to determine the R value of the minimum with less than 0.01 Å uncertainty.

Applications. The use of the two calculational methods outlined will be demonstrated by their application to the conductance data of Evans and Gardam [9] for Bu_4NClO_4 in propanol at 25 °C.

Using Method 1 the dependence of $\sigma(\Lambda)$ on Λ_∞ was established for selected values of the distance parameter, R. Results for a few R values are shown graphically in Fig. 1.

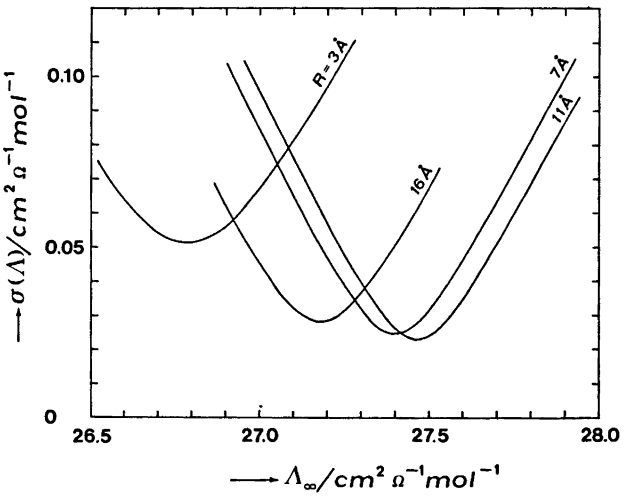


Fig. 1. Standard deviation of single Λ-value as a function of Λ_∞ (implicit variation of K_A) at different values of the distance parameter, R, for Bu_4NClO_4 in propanol [9] at 25 °C.

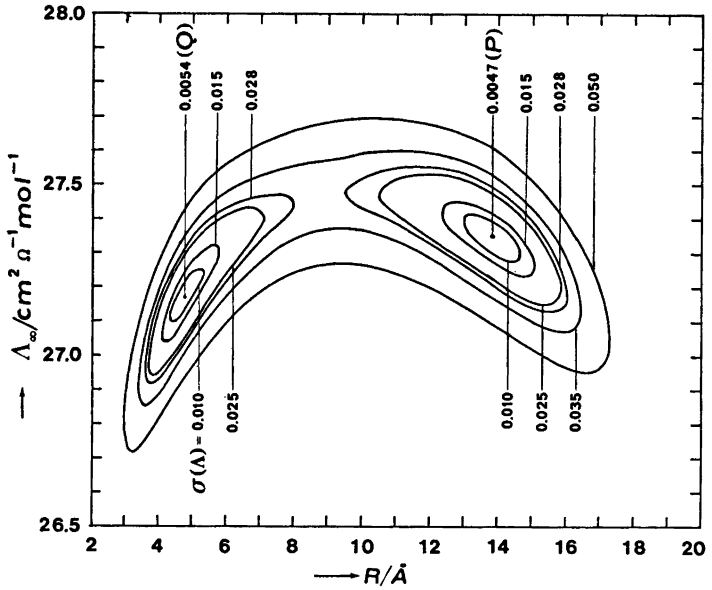
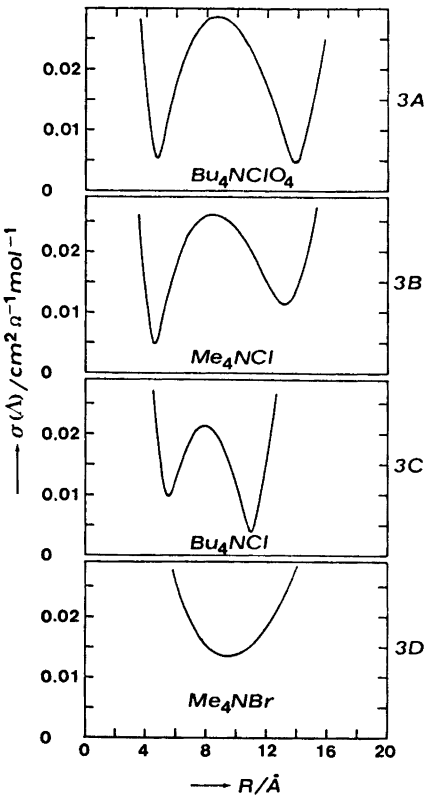


Fig. 2. Contour diagram for the same system as in Fig. 1. The contour lines, representing the different values of $\sigma(\Lambda)$ quoted in the diagram, illustrate how $\sigma(\Lambda)$ depends on different combinations of Λ_∞ and R. The points P and Q indicate minima.

By employing a large number of curves of the kind shown in Fig. 1 the contour diagram, Fig. 2, was constructed. The contour lines represent different values of $\sigma(\Lambda)$. Pertinent values of $\sigma(\Lambda)$ are attached to the contour lines.

The contour diagram for the system concerned exhibits two minima, in Fig. 2 denoted P and Q, respectively. The minimum at P, with $\sigma(\Lambda) = 0.0047$ cm² Ω^{-1} mol^{-1}, corresponds to the "best set" parameters, $\Lambda_\infty = 27.35$, $K_A = 905$, $R = 13.86$ Å, while the minimum at Q, with the insignificantly larger $\sigma(\Lambda) = 0.0054$, refers to



Figs. 3 A–D. Conditional minimum $\sigma(\Lambda)$ as a function of the distance parameter, R (implicit variation of Λ_∞ and K_A) for electrolytes in propanol [9] at 25 °C.

the set, $\Lambda_\infty = 27.17$, $K_A = 789$, $R = 4.75$ Å. The two minima, with almost identical values of $\sigma(\Lambda)$, appear thus at two significantly different association distances.

The contour diagram representation of $\sigma(\Lambda)$ in Fig. 2 for the Bu_4NClO_4–propanol system may be compared with the alternative representation in Fig. 3A in which the conditional minimum $\sigma(\Lambda)$, obtained by means of Method 2, has been plotted *vs.* association distance.

Three additional examples of $\sigma(\Lambda) - R$ curves, derived from the conductance data in Ref. 9 for quaternary ammonium salts in propanol, have been included in Fig. 3 to demonstrate a few different shapes of such curves.

RESULTS AND DISCUSSION

Evans and Gardam [9] report conductance data for twelve tetraalkylammonium salts in propanol at 25 °C. For ten* of these systems the present reanalysis (Method 2) yielded $\sigma(\Lambda) - R$ curves with double minima, *cf.* Figs. 3 A–C. A compilation of the values of Λ_∞, K_A, R, and $\sigma(\Lambda)$ corresponding to these minima is given in Table 1 ("FHFP" equation). For comparison the corresponding values derived in the original investigation [9] from the Fuoss-Onsager equation of 1957 ("FO-57" equation) have been included in this table. The considerably better fit of the FHFP equation to the experimental data as compared with the FO-57 equation is apparent from the $\sigma(\Lambda)$'s listed in the last column.

I has been claimed [7] that the distance parameter, R, should be identified with Bjerrum's critical distance,[18] $q = |z_+ z_-| e^2/(2\varepsilon kT)$, where z_+ and z_- are the valencies of the ions, e is the electronic charge, and k is Boltzmann's constant. Hence, it may be of interest to compare the association distances according to the FHFP equation in Table 1 with this critical distance, which for 1:1 salts in propanol ($\varepsilon = 20.45$) amounts to 13.70 Å. With the exception of Me_4NCl the association distance of the "best set" for each salt listed in this table is rather close to the critical Bjerrum distance though, as pointed out in a previous section, the $\sigma(\Lambda)$'s for Bu_4NClO_4 at 4.75 and 13.86 Å are almost identical.

The conductance data for two of the salts listed in Table 1 (Me_4NCl and He_4NI) have been previously treated in a different manner by Justice [7] using eqns. (1), (3), and (4). In his method the R parameter of the J_1 term in the FHFP equation and in the Debye-Hückel expression is set equal to Bjerrum's critical distance. The value of R in the J_2 term of the FHFP equation which minimizes $\sigma(\Lambda)$ is then evaluated. For comparison with the values of the parameters derived in the present study for these two salts in propanol the corresponding figures according to the Justice method, as reported in Ref. 7, are included in Table 1, in which the notation "FHFP-Bj" is used to denote that special case of the FHFP equation in which R in the J_1 term is set equal to the critical Bjerrum distance.

Reynolds and Kraus [10] report conductance data for fourteen salts in acetone at 25 °C. The

* For the remaining two salts, Et_4NI and Me_4NBr, $\sigma(\Lambda) - R$ curves with a single minimum, at 8.95 and 9.41 Å, respectively, were obtained.

Table 1. Conductance parameters for electrolytes in propanol [a] at 25 °C derived from conductance data of Evans and Gardam.[9] The two sets of Λ_∞, K_A, R, and $\sigma(\Lambda)$ quoted for each salt according to the FHFP equation correspond to the two minima in the $\sigma(\Lambda)-R$ curve, *cf.* Figs. 3 A–C. N = number of points (c,Λ).

Salt	N	Cond. equation	Λ_∞ cm² Ω⁻¹ mol⁻¹	K_A M⁻¹	R Å	$\sigma(\Lambda)$ cm² Ω⁻¹ mol⁻¹
Me_4NCl	7	FHFP	25.28	583	13.15	0.011
		FHFP	25.06	470	4.59	0.005
		FO-57	25.05	456	4.2	0.01
		FHFP-Bj	25.29	587	13.4	0.01
Bu_4NCl	8	FHFP	21.26	237	10.96	0.004
		FHFP	21.19	173	5.52	0.010
		FO-57	21.16	149	4.4	0.02
Et_4NBr	8	FHFP	27.30	436	9.28	0.0017
		FHFP	27.27	419	7.76	0.0021
		FO-57	27.19	373	5.0	0.01
Pr_4NBr	8	FHFP	24.66	369	10.35	0.0010
		FHFP	24.51	301	5.54	0.0079
		FO-57	24.42	270	4.4	0.02
Bu_4NBr	8	FHFP	23.06	355	10.88	0.0014
		FHFP	22.97	294	5.89	0.0068
		FO-57	22.92	266	4.6	0.01
Pr_4NI	8	FHFP	26.31	490	10.80	0.0013
		FHFP	26.17	423	5.81	0.0073
		FO-57	26.08	391	4.5	0.02
Bu_4NI	8	FHFP	24.76	510	11.21	0.0010
		FHFP	24.66	445	6.00	0.0055
		FO-57	24.60	415	4.7	0.01
i-Am_3BuNI	8	FHFP	24.12	552	11.87	0.0021
		FHFP	24.06	493	6.37	0.0061
		FO-57	24.02	462	4.9	0.01
He_4NI	8	FHFP	22.27	536	12.37	0.0025
		FHFP	22.21	469	6.16	0.0065
		FO-57	22.18	442	4.8	0.01
		FHFP-Bj	22.281	547	13.1	0.002
Bu_4NClO_4	8	FHFP	27.35	905	13.86	0.0047
		FHFP	27.17	789	4.75	0.0054
		FO-57	27.13	769	4.2	0.01

[a] $\eta = 1.952$ cP; $\varepsilon = 20.45$; Bjerrum's critical distance, $q = 13.70$ Å.

present reanalysis of their data yielded $\sigma(\Lambda)-R$ curves with double minima for eleven* systems, see Table 2.

* Two salts, Bu_4NI and Et_4NPi, yielded $\sigma(\Lambda)-R$ curves with a single minimum, at 7.00 and 9.11 Å, respectively. For Me_4NF no minimum was obtained in the 1–25 Å range. Calculations outside this range revealed one minimum at 0.44 Å (Λ_∞ = 182.43; $K_A = 1093$; $\sigma(\Lambda) = 0.15$) and another minimum at 32.70 Å ($\Lambda_\infty = 182.51$; $K_A = 1334$; $\sigma(\Lambda) = 0.17$).

Inspection of this table reveals that for all salts listed, with the exception of LiPi, one of the two minima in the $\sigma(\Lambda)-R$ curve appears close to Bjerrum's critical distance, which for 1:1-electrolytes in acetone at 25 °C ($\varepsilon = 20.47$) amounts to 13.69 Å, while the other minimum appears for association distances in the 4.8–7.5 Å range. It is noteworthy that for a large proportion of the salts listed in Table 2, *viz.* Bu_4NFBPh_3, Bu_4NPi, Bu_4NClO_4, Bu_4NBr,

Table 2. Conductance parameters for electrolytes in acetone [a] at 25 °C calculated by means of the FHFP equation from data of Reynolds and Kraus.[10] N = number of points (c,Λ).

Salt	N	Λ_∞ cm² Ω⁻¹ mol⁻¹	K_A M⁻¹	R Å	$\sigma(\Lambda)$ cm² Ω⁻¹ mol⁻¹
Bu_4NFBPh_3	6	134.35	107	14.20	0.047
		134.28	39	5.98	0.048
Bu_4NPi	6	152.43	104	15.68	0.12
		152.31	15	4.78	0.09
Bu_4NClO_4	6	182.93	128	11.85	0.15
		182.86	91	7.34	0.14
Bu_4NNO_3	6	187.31	217	13.65	0.074
		187.17	150	5.72	0.017
Bu_4NBr	6	183.42	328	12.62	0.0976
		183.35	285	7.26	0.0971
Me_4NFBPh_3	6	165.26	182	13.05	0.061
		165.18	131	6.80	0.046
LiPi	6	158.12	1023	24.92	0.025
		157.94	830	1.47	0.078
NaPi	6	163.85	763	13.54	0.043
		163.78	714	7.52	0.061
KPi	6	166.34	320	13.07	0.027
		166.28	270	6.90	0.073
KI	6	193.01	163	13.05	0.18
		192.83	100	5.81	0.11
KCNS	5	201.83	281	13.00	0.062
		201.77	235	7.15	0.022

[a] $\eta = 0.304$ cP; $\varepsilon = 20.47$; Bjerrum's critical distance, $q = 13.69$ Å.

Me_4NFBPh_3, and NaPi, almost equally good fits of the conductance equation to the experimental points are obtained for two quite different values of the association distance, *viz.* for $R \simeq q$ and $R \ll q$.

The series of conductance data according to Graham, Kell, and Gordon [11] for LiCl, NaCl, and KCl in ethanol at 25 °C, and according to Hawes and Kay [12] for CsCl in this solvent yielded all $\sigma(\Lambda) - R$ curves with double minima, *cf.* Table 3 in which data according to the Justice treatment [7] are included. For all these systems one minimum appears close to Bjerrum's critical distance, which for this solvent at 25 °C ($\varepsilon = 24.3$) and the charge type of salt concerned is equal to 11.53 Å. However, better fits are in fact obtained for R values of the order 4 – 5 Å, *i.e.* considerably below the Bjerrum distance. Noteworthy is also the better fit of the FHFP equation as compared with the FHFP-Bj equation.

Banewicz, Maguire, and Shih [13] report conductance data for Et_4NClO_4 in valeronitrile at four temperatures. Reanalysis of their data results in a similar pattern to that above, *i.e.* one minimum in the $\sigma(\Lambda) - R$ curve appears close to the Bjerrum q value, which for this solvent ($18.06 \leq \varepsilon \leq 20.03$) at the temperatures concerned varies from 13.99 to 14.31 Å, while another minimum, with approximately the same $\sigma(\Lambda)$, appears at $R = 3.9$ Å, see Table 4. Included in this table is also the set of conductance parameters at 25 °C evaluated according to the Justice method in Ref. 7.

Table 3. Parameters for electrolytes in anhydrous ethanol [a] at 25 °C calculated from conductance data of Graham, Kell, and Gordon [11] (LiCl, NaCl, KCl), and Hawes and Kay [12] (CsCl). N = number of points (c,Λ).

Salt	N	Cond. equation	Λ_∞ cm² Ω⁻¹ mol⁻¹	K_A M⁻¹	R Å	$\sigma(\Lambda)$ cm² Ω⁻¹ mol⁻¹
LiCl	6	FHFP	38.96	77	12.83	0.018
		FHFP	38.93	29	4.67	0.012
		FHFP-Bj	38.95	68	11.9	0.02
NaCl	6	FHFP	42.19	102	13.99	0.023
		FHFP	42.16	44	4.04	0.017
		FHFP-Bj	42.18	87	12.4	0.03
KCl	6	FHFP	45.43	142	12.80	0.018
		FHFP	45.41	98	5.05	0.012
		FHFP-Bj	45.43	134	11.8	0.02
CsCl	5	FHFP	48.54	205	9.71	0.0051
		FHFP	48.39	170	5.27	0.0021
		FHFP-Bj	48.58	215	10.7	0.008

[a] $\eta = 1.084$ cP; $\varepsilon = 24.3$; Bjerrum's critical distance, $q = 11.53$ Å.

Table 4. Conductance parameters for Et_4NClO_4 in valeronitrile [a] calculated from data reported by Banewicz, Maguire, and Shih.[13] N = number of points (c,Λ).

t °C	N	Cond. equation	Λ_∞ cm² Ω⁻¹ mol⁻¹	K_A M⁻¹	R Å	$\sigma(\Lambda)$ cm² Ω⁻¹ mol⁻¹	q Å
25	19	FHFP	88.64	310	14.16	0.14	13.99
		FHFP	88.11	189	3.89	0.17	13.99
		FHFP-Bj	88.49	302	14.0	0.15	13.99
30	16	FHFP	94.56	319	13.64	0.15	14.03
		FHFP	93.73	192	3.89	0.14	14.03
40	15	FHFP	106.81	336	14.15	0.19	14.18
		FHFP	106.08	206	3.90	0.18	14.18
50	17	FHFP	119.66	359	14.38	0.225	14.31
		FHFP	118.81	225	3.92	0.222	14.31

[a] $\eta = 0.6928$, 0.6485, 0.5719, and 0.5084 cP and $\varepsilon = 20.03$, 19.64, 18.81, and 18.06 at 25, 30, 40, and 50 °C, respectively.

For three * of the twelve salts in sulfolane at 30 °C ($\varepsilon = 43.33$; $q = 6.36$ Å) investigated by Fernandez-Prini and Prue [14] double minima with nearly identical $\sigma(\Lambda)$'s were obtained at two different values of the distance parameter, R, as can be seen from Table 5 in which the conductance parameters, evaluated in the original investigation from the Pitts' equation ("P" equation), are also listed.

Of the five series of conductance data for NaCl in propanol-water mixtures at 15 °C reported by Goffredi and Shedlovsky [15] three series yielded $\sigma(\Lambda) - R$ curves with double minima. Again, nearly identical $\sigma(\Lambda)$'s are observed at two quite different association distances, one of which appears at $R \simeq q$, see Table 6 which for comparison includes the values of the conductance parameters evaluated in the

* The remaining nine salts yielded $\sigma(\Lambda) - R$ curves with a single minimum at the following values of the association distance: $LiClO_4$, 5.87 Å; $NaClO_4$, 5.53 Å; $KClO_4$, 5.47 Å; $RbClO_4$, 10.49 Å; $CsClO_4$, 5.20 Å; LiI, 5.85 Å; Et_4NI, 3.35 Å; LiCl, 6.66 Å; KPF_6, 8.71 Å.

Table 5. Parameters for sulfolane [a] as solvent at 30 °C calculated from conductance data of Fernandez-Prini and Prue.[14] N = number of points (c,Λ).

Salt	N	Cond. equation	Λ_∞ cm² Ω⁻¹ mol⁻¹	K_A M⁻¹	R Å	$\sigma(\Lambda)$ cm² Ω⁻¹ mol⁻¹
NaI	14	FHFP	10.868	7.77	8.30	0.0031
		FHFP	10.867	0.34	3.12	0.0034
		P	10.865	4.7	5[b]	0.003
KI	12	FHFP	11.255	9.6	8.33	0.0062
		FHFP	11.253	1.3	2.74	0.0061
		P	11.253	6.5	5[b]	0.005
LiBr	13	FHFP	13.237	279	9.13	0.0063
		FHFP	13.235	270	2.95	0.0062
		P	13.250	278	5[b]	0.010

[a] $\eta = 10.29$ cP; $\varepsilon = 43.33$; Bjerrum's critical distance, $q = 6.36$ Å. [b] Arbitrarily chosen value for the distance parameter.[14]

Table 6. Conductance parameters for sodium chloride in aqueous propanol at 15 °C calculated from data of Goffredi and Shedlovsky.[15] N = number of points (c,Λ).

N	η cP	ε	Cond. equation	Λ_∞ cm² Ω⁻¹ mol⁻¹	K_A M⁻¹	R Å	$\sigma(\Lambda)$ cm² Ω⁻¹ mol⁻¹	q Å
6	3.805	38.60	FHFP	25.906	14.9	6.99	0.0025	7.51
			FHFP	25.899	9.7	4.65	0.0022	7.51
			FOS	25.894	6	3.1	0.002	7.51
5	3.310	28.19	FHFP	21.199	65	9.47	0.0013	10.28
			FHFP	21.159	40	4.52	0.0014	10.28
			FOS	21.144	31	3.19	0.003	10.28
6	2.881	24.50	FHFP	20.212	148	15.55	0.0054	11.83
			FHFP	20.196	83	4.08	0.0053	11.83
			FOS	20.19	76	3.2	0.006	11.83

original research from the Fuoss-Onsager-Skinner ("FOS") equation.

Several further examples of 1:1-electrolyte systems for which sets of conductance parameters with almost equal $\sigma(\Lambda)$'s are observed at two different values of the distance parameter might be listed. As stated in the introduction, however, the purpose of this paper is to cite only some typical examples. The examples here accounted for would suffice to give an idea of the frequent appearance of such non-unique sets of conductance parameters.

CONCLUSIONS

From the present reevaluation, by means of the FHFP equation, of a large body of conductance data for 1:1-electrolytes in pure and mixed solvents it follows that the "best set" of conductance parameters frequently refers to a value of the association distance coinciding within experimental errors with Bjerrum's critical distance, a result in accord with observations of Justice.[7] However, these observations provide no unequivocal support for a conclusion that the distance parameter, R, should be numerically identified with the Bjerrum q value because of the frequent observations that, for a given system, an equally good fit as for $R = q$ may be obtained for a value of the association distance deviating considerably from Bjerrum's critical distance.

In calculating activity coefficients for non-associated ions using the Debye-Hückel ap-

proximation, eqn. (4), the use of R values less than the Bjerrum q value is in poor consistency with approximations made in deriving the activity coefficient expression, *cf.* Ref. 19. Yet, the present treatment of experimental data reveals that an equally good fit as for $R=q$, or even a better fit, is frequently observed for an association distance value considerably less than Bjerrum's critical distance.

An extension of the present investigation to include other conductance equations, in particular the Pitts equation, *cf.* Ref. 20, is a matter for further research.

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