Acta Chemica Scandinavica A 30 (1976) 115—120

Remarks on the Problem of Finding Best Set Conductance Parameters for Electrolyte Solutions

PER BERONIUS

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

Three conductance equations in current use, the expanded forms of the Fuoss-Hsia and Pitts equations and a recent equation of Fuoss including the Chen effect, have been used to analyze conductance data for several univalent electrolytes in pure solvents and binary solvent mixtures. The method of handling the conductance data is based on determination of the values of the limiting molar conductivity and the ion-pair association constant which minimize $\sigma(\Lambda)$, the standard deviation between experimental and computed Λ values, for a range of values of the distance parameter, R, the maximum centre-to-centre distance between the ions in the ion-pair. For each equation the graph of $\sigma(\Lambda)$ *vs.* R is frequently observed to exhibit two minima with almost equal $\sigma(\Lambda)$'s, one minimum often appearing at a value of R close to the Bjerrum radius, q, the other minimum deviating considerably from the Bjerrum q value. Though not in obvious contradiction with the position taken by Justice that the distance parameter should be numerically identified with the Bjerrum radius, the present observations suggest that the Justice point of view might be questioned.

The dependence of the molar conductivity, Λ, on electrolyte concentration, c, for electrolytes which are subject to ion-pair formation may be described by means of equations of the type,

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

where α is the degree of dissociation of the ion-pairs and Λ_∞ is the molar conductivity at infinite dilution. The other symbols in eqn. (1) will be defined below. Let us merely remark here that the J coefficients depend upon, among other factors, a distance parameter, R, the maximum centre-to-centre distance between the ions in the ion-pair.

From eqn. (1), combined with the mass action law for the equilibrium between unpaired and paired ions (ion-pair association constant, K_A), and the Debye-Hückel equation [1]

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

for the mean molar activity coefficient, γ, of free ions, the parameters Λ_∞, K_A, and R may be iteratively computed, *cf.* Ref. 2. That combination of Λ_∞, K_A, and R which minimizes $\sigma(\Lambda)$, the standard deviation between observed and computed Λ values, is usually adopted as the "best set".

In a preceding investigation [3] conductance data for numerous univalent electrolytes in pure and mixed solvents were analyzed by means of the Fuoss-Hsia conductance equation [4,5] in the form developed by Fernandez-Prini [6] ("FHFP" equation). The method of calculation used involves iterative determination of those values of Λ_∞ and K_A which minimize $\sigma(\Lambda)$ for selected values of the distance parameter, R, over a range of the latter (usually from 1 to 25 Å); *cf.* Ref. 7.

Very frequently the $\sigma(\Lambda) - R$ curve was found to exhibit two minima with almost identical $\sigma(\Lambda)$'s, one minimum appearing rather close to the Bjerrum radius,[8] q, the other minimum appearing at a value of $R \ll q$. This indicates that the Justice point of view that R should be numerically identified with the Bjerrum radius, *cf.* Refs. 9 and 10, may be questioned. Compare the conflicting positions concerning the physical interpretation of the distance parameter taken by Fuoss [11] and Justice.[12]

The preceding investigation [3] of non-unique sets of conductance parameters, restricted to

the FHFP equation, has been now extended to two other important conductance equations, *viz.* the Pitts equation [13] in the expanded form of Fernandez-Prini and Prue,[14] ("PFPP" equation) and a recent equation of Fuoss as developed by Justice [15] ("FJ" equation) in which the so-called Chen effect [16] is taken into account. Some typical results for univalent electrolytes in pure solvents and binary solvent mixtures will be discussed in the present paper.

CALCULATIONS

The three conductance equations studied in the present investigation are all of the form given in eqn. (1) in which S is the Onsager limiting law coefficient.[17] In the FHFP and PFPP equations $E = E_1\Lambda_\infty - E_2$, while in the FJ equation $E = E_1\Lambda_\infty - 2E_2$. The coefficients E_1 and E_2 are given in Ref. 17. The σ coefficients appearing in the J terms of eqn. (1), in which $J_1 = \sigma_1\Lambda_\infty + \sigma_2$ and $J_2 = \sigma_3\Lambda_\infty + \sigma_4$, were taken from Ref. 6 for the FHFP equation, from Ref. 14 for the PFPP equation, and from Ref. 15 for the FJ equation.

Solvent permittivities, ε, and viscosities, η, used in the calculations are the same as in the original investigations.[18-22]

A detailed account of the method of computation developed to find the values of Λ_∞ and K_A which minimize $\sigma(\Lambda)$ for some assigned value of the distance parameter in the conductance equation, eqn. (1), and in the Debye-Hückel equation, eqn. (2), has been previously given.[3,7]

The calculations of Λ_∞, K_A, and $\sigma(\Lambda)$ were repeated by means of a CDC 3300 computer for a selected range of R values and a graph of the conditional minimum $\sigma(\Lambda)$ as a function of association distance prepared. The R value of the minimum * (or minima) of the $\sigma(\Lambda) - R$ curve was established with an uncertainty of less than 0.02 Å by repeated calculations around the minimum using successively smaller increments in R.

* Throughout the text the association constant, K_A, is given on the molar scale. The units of Λ_∞ and $\sigma(\Lambda)$ are $cm^2\ \Omega^{-1}\ mol^{-1}$.

DISCUSSION

Conductance parameters derived according to the FHFP and FJ equations are almost identical. This statement may be illustrated by means of Fig. 1 in which Λ_∞, K_A, and $\sigma(\Lambda)$ have been plotted *vs.* R for cesium iodide in a dioxane-water mixture [18] ($\varepsilon = 12.81$) at 25 °C for the three equations concerned. For the FHFP and FJ equations the curves representing the dependence of Λ_∞ and of K_A on R practically overlap and the shapes of the $\sigma(\Lambda) - R$ curves are very similar in character.

Conductance data at 25 °C for cesium iodide in seven different dioxane-water mixtures with permittivities in the range $12.81 \leq \varepsilon \leq 60.18$ are reported by Lind and Fuoss.[18] Graphs of $\sigma(\Lambda)$ *vs.* R according to the PFPP and FJ equations for these systems are shown in Figs. 1 and 2. Because of the close resemblance of the $\sigma(\Lambda) - R$ curve according to the FHFP equation with that of the FJ equation any graphical representation for the FHFP equation is omitted in Fig. 2.

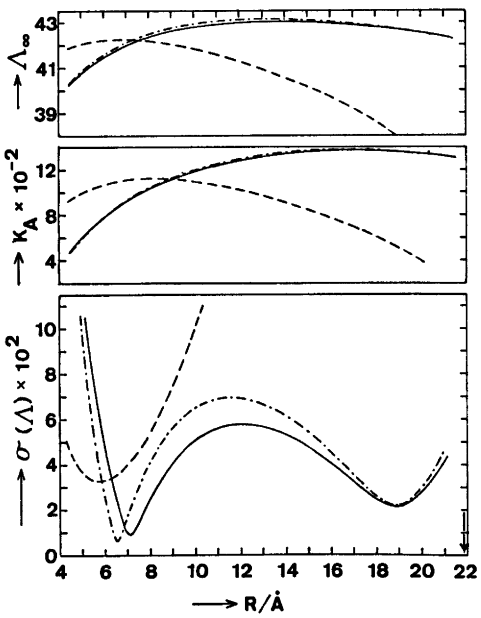

Fig. 1. Graphs of Λ_∞, K_A, and $\sigma(\Lambda)$ *vs.* R for CsI in a dioxane–water mixture [18] ($\varepsilon = 12.81$) at 25 °C for PFPP equation (- - -), FHFP equation (- · -), and FJ equation (———), *cf.* Table 1. The arrow indicates the Bjerrum radius, q.

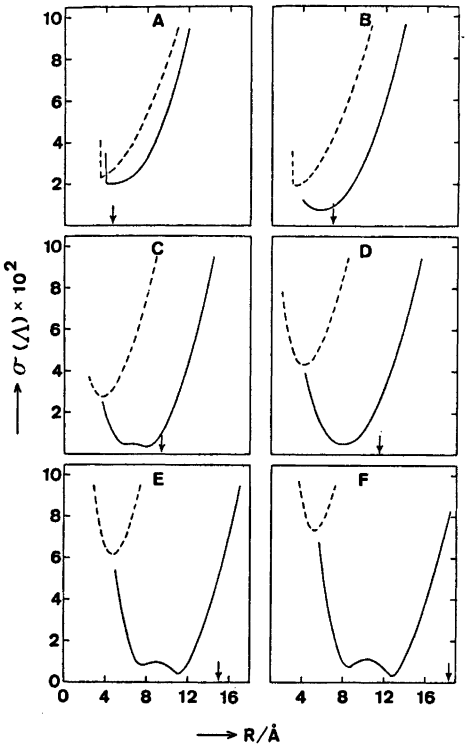

Fig. 2. Graphs of $\sigma(\Lambda)$ *vs.* R for CsI in dioxane – water mixtures [18] at 25 °C for PFPP equation (- - -) and FJ equation (———). The diagrams A – F refer to solvent mixtures with permittivities equal to 60.18, 40.57, 29.79, 24.44, 18.68, and 15.29, respectively, *cf.* Table 1. The arrows indicate the Bjerrum radius.

Given in Table 1 is a compilation of the conductance parameters corresponding to the minima of the $\sigma(\Lambda) - R$ curves (*cf.* Figs. 1 and 2) according to the PFPP and FJ equations for the cesium iodide dioxane – water systems. Since the FJ and FHFP equations yield almost identical values of the conductance parameters no results for the FHFP equation are tabulated. Two sets of values for Λ_∞, K_A, R, and $\sigma(\Lambda)$ are listed for those $\sigma(\Lambda) - R$ curves exhibiting double minima. Included in this table are also the values of the Bjerrum radius [8]

$$q = |z_+ z_-| e^2/(2\varepsilon \mathbf{k} T) \qquad (3)$$

where z_+ and z_- are the valencies of the ions, e is the electronic charge, $\mathbf{k}$ is Boltzmann's constant, and T is the absolute temperature.

For these systems it is found that the PFPP equation yields $\sigma(\Lambda) - R$ curves with a single minimum, *cf.* Figs. 1 and 2, while the FJ and FHFP equations, in most instances, yield curves with two minima (Table 1).

Hughes and Price [19] report conductance data for several quaternary ammonium bromides in ethyl methyl ketone at 25 °C. In general curves with two minima are obtained according to all three equations studied (Table 2).

Hughes and White [20] report conductance data at 25 °C for potassium iodide in seven different acetone – water mixtures. With the exception of that solvent mixture containing 3.304 per cent of water, the graphs of $\sigma(\Lambda)$ *vs.* R exhibit double minima for all three conductance equations investigated (Table 3).

Table 1. Parameters for CsI in dioxane-water mixtures at 25 °C derived from conductance data in Ref. 18.

Diox. wt %	ε	η/cP	Λ_∞/cm² Ω^{-1} mol^{-1} PFPP	FJ	K_A/M^{-1} PFPP	FJ	R/Å PFPP	FJ	q/Å	$\sigma(\Lambda)$/cm² Ω^{-1} mol^{-1} PFPP	FJ
22.1	60.18	1.328	99.39	99.40	0.00	0.5	3.49	4.52	4.66	0.023	0.020
44.6	40.57	1.820	66.82	66.86	0.5	3.9	3.24	5.84	6.91	0.019	0.008
57.1	29.79	1.982	56.38	56.51	8.0	20.8	3.69	8.03	9.41	0.027	0.003
				56.49		13.8		5.99			0.005
63.7	24.44	1.986	52.13	52.32	29.0	47.8	4.16	8.10	11.46	0.043	0.005
70.7	18.68	1.922	48.06	48.49	119	187	4.71	11.16	15.00	0.061	0.004
				48.39		145		7.63			0.008
75.2	15.29	1.839	45.30	45.97	384	533	5.22	12.85	18.33	0.073	0.003
				45.76		439		8.50			0.008
78.5	12.81	1.754	42.19	42.02	1054	937	5.73	7.11	21.87	0.033	0.009
				42.69		1362		18.86			0.022

Table 2. Parameters for electrolytes in ethyl methyl ketone at 25 °C derived from conductance data in Ref. 19. $\varepsilon = 18.014$; $\eta = 0.3774$ cP; $q = 15.55$ Å.

Salt[a]	Λ_0/cm² Ω^{-1} mol^{-1}		K_A/M^{-1}		R/Å		$\sigma(\Lambda)$/cm² Ω^{-1} mol^{-1}	
	PFPP	FJ	PFPP	FJ	PFPP	FJ	PFPP	FJ
Et_4NBr	158.24	158.25	976	1006	5.81	11.60	0.032	0.026
Pr_4NBr	146.60	146.53	965	976	3.32	6.39	0.012	0.010
	146.89	146.83	1048	1089	8.55	16.81	0.023	0.020
Bu_4NBr	139.79	139.67	826	831	4.02	7.02	0.009	0.008
	140.02	140.00	878	927	7.08	15.50	0.012	0.011
Pe_4NBr	135.09	134.94	813	810	4.94	7.70	0.011	0.010
		135.28		886		13.98		0.011
Hex_4NBr	131.19	131.14	684	694	3.05	5.58	0.013	0.012
	131.44	131.41	777	825	9.34	18.00	0.024	0.023
$Hept_4NBr$	128.42	128.37	678	689	3.32	6.00	0.009	0.008
	128.65	128.62	761	810	8.96	17.56	0.016	0.015
Oct_4NBr	126.26	126.19	678	687	3.57	6.29	0.008	0.008
	126.47	126.45	751	800	8.43	17.02	0.011	0.011

[a] For Me_4NBr no reevaluation of the conductance data was undertaken because of the narrow concentration range investigated (from 0.01791 to 0.03993 mM).

Table 3. Parameters for KI in acetone-water mixtures at 25 °C derived from conductance data in Ref. 20.

H_2O wt %	ε	η/cP	Λ_0/cm² Ω^{-1} mol^{-1}		K_A/M^{-1}		R/Å		q/Å	$\sigma(\Lambda)$/cm² Ω^{-1} mol^{-1}	
			PFPP	FJ	PFPP	FJ	PFPP	FJ		PFPP	FJ
0.179	20.23	0.301	197.20	197.17	61.8	67.5	1.67	2.98	13.85	0.14	0.14
			197.35	197.34	163	198	13.39	21.28		0.15	0.14
0.291	20.29	0.302	195.85	195.83	67.3	74.4	1.43	2.63	13.81	0.14	0.14
			195.97	195.96	178	212	15.02	22.63		0.15	0.15
1.175	20.76	0.309	190.54	190.51	62.9	68.7	1.60	2.87	13.50	0.081	0.079
			190.69	190.68	158	191	13.39	21.02		0.097	0.096
2.012	21.21	0.316	185.60	185.56	83.7	87.1	2.66	4.34	13.21	0.083	0.081
			185.74	185.74	140	173	9.49	17.45		0.095	0.096
2.817	21.64	0.324	180.54	180.51	75.3	79.3	2.53	4.20	12.95	0.027	0.027
			180.67	180.67	133	164	10.34	17.93		0.028	0.028
3.304	21.90	0.329	177.20	177.26	117	139	5.94	10.85	12.79	0.14	0.12
3.574	22.04	0.332	171.59	171.57	115	142	14.58	21.45	12.71	0.050	0.051
			171.37	171.33	14.7	20.6	0.98	1.75		0.057	0.057

Table 4. Parameters for LiBr in acetone-methanol mixtures at 25 °C derived from conductance data in Ref. 21.

MeOH wt %	ε	η/cP	Λ_0/cm² Ω^{-1} mol^{-1}		K_A/M^{-1}		R/Å		q/Å	$\sigma(\Lambda)$/cm² Ω^{-1} mol^{-1}	
			PFPP	FJ	PFPP	FJ	PFPP	FJ		PFPP	FJ
0.1	20.6	0.300	193.56	193.01	3467	3441	5.11	10.41	13.60	0.12	0.15
0.3	20.6	0.300	190.88	190.68	2648	2660	3.98	10.01	13.60	0.15	0.15
1.0	20.7	0.301	185.72	185.90	1571	1649	2.85	13.58	13.54	0.057	0.057
			186.10	185.63	1636	1583	7.18	6.17		0.065	0.061
2.0	20.8	0.301	181.57	181.52	1087	1098	2.71	5.50	13.47	0.16	0.15
			181.87	181.78	1149	1171	7.03	13.86		0.19	0.17
5.0	21.1	0.301	174.45	174.42	663	695	5.64	12.85	13.28	0.073	0.071
			174.26	174.12	631	632	3.30	5.54		0.078	0.095
10.0	21.6	0.304	166.43	166.65	354	397	4.35	11.47	12.97	0.099	0.065
				166.42		353		6.01			0.11
20.0	22.7	0.314	154.00	154.02	132	131	3.93	5.11	12.34	0.14	0.078
				154.27		175		11.06			0.087
50.0	26.3	0.370	128.56	128.80	18.1	40.9	3.88	8.73	10.65	0.18	0.087

Table 5. Parameters for electrolytes in ethylene glycol at 25 °C derived from conductance data in Ref. 22. $\varepsilon = 37.70$; $\eta = 0.1619$ P; $q = 7.43$ Å.

Salt[a]	Λ_∞/cm² Ω⁻¹ mol⁻¹		K_A/M⁻¹		R/Å		$\sigma(\Lambda)$/cm² Ω⁻¹ mol⁻¹	
	PFPP	FJ	PFPP	FJ	PFPP	FJ	PFPP	FJ
Me_4NBr	7.954	7.960	4.0	11.8	3.35	8.31	0.0044	0.0039
		7.954		1.5		3.33		0.0046
Et_4NBr	7.172	7.174	2.5	9.8	3.90	8.88	0.0039	0.0038
		7.173		1.1		4.16		0.0039
Pr_4NBr	6.718	6.722	3.6	8.1	3.49	6.39	0.0036	0.0027
Bu_4NBr	6.488	6.493	2.4	7.4	3.43	6.49	0.0042	0.0036
Me_4NI	7.578	7.579	8.0	14.2	5.16	9.85	0.0053	0.0053
	7.575	7.574	0.0	0.0	1.81	2.69	0.0054	0.0054
Et_4NI	6.798	6.797	10.5	15.5	9.41	13.24	0.0025	0.0025
	6.808	6.807	0.0	0.0	1.94	2.81	0.0046	0.0046
Pr_4NI	6.347	6.345	14.3	0.0	8.22	1.78	0.0044	0.0041
	6.348	6.347	0.0	19.6	1.16	12.29	0.0043	0.0044
Bu_4NI[a]	6.060	6.059	14.6	19.4	11.04	14.55	0.0041	0.0040
	6.071	6.069	0.0	0.0	1.18	1.80	0.0060	0.0056

[a] The point at $c = 2.3781$ mM was omitted because it deviated by -1 % from the curve fitted according to eqn. (1) to the remaining points.

Similar results are obtained for lithium bromide in eight different acetone-methanol mixtures [21] (Table 4).

Conductance data referring to four quaternary ammonium bromides and the corresponding iodides in ethylene glycol at 25 °C are reported.[22] With some exceptions (Me_4NBr and Et_4NBr according to FJ and FHFP equations) the present analysis results in $\sigma(\Lambda) - R$ curves with a single minimum for the bromides (Table 5). For the iodides two minima are obtained for all three conductance equations. One minimum, appearing for some value of R within the 1 – 3 Å range, which is in fact less than the sum of the crystallographic radii for the iodide ion and quaternary ammonium ions concerned,[23]

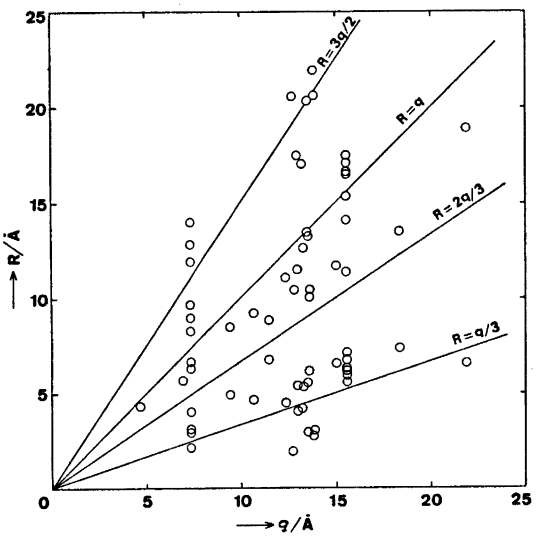

Fig. 3. Association distance, according to FHFP equation, *vs.* Bjerrum radius for the electrolyte systems listed in Tables 1 – 5. For the $\sigma(\Lambda) - R$ curves exhibiting two minima, *cf.* Figs. 1 and 2, the R values of both have been plotted.

corresponds to $K_A = 0$ (no association to ion-pairs). The other minimum, appearing within the 5 – 15 Å range (Table 5), corresponds to small positive values of K_A. These results do not seem to indicate that the quaternary ammonium halides discussed behave like strong electrolytes [22] in ethylene glycol. Compare the discussions [24,25] concerning the difficulty of establishing association constants uniquely from electrical conductance data for only slightly associated electrolytes.

The examples given in the present paper show conclusively that for the PFPP equation as well as for the FJ and FHFP equations the goodness of the fit of the conductance equation to the experimental points is of little help in determining the "exact" value of the distance parameter. This is so not only for highly dissociated salts, *cf.* Ref. 24, but also for electrolytes showing considerable association to ion-pairs, *e.g.* lithium bromide with $K_A = 1.6 \times 10^3$ in the acetone-methanol mixture with $\varepsilon = 20.7$, *cf.* Table 4. There is an obvious demand for supplementary methods to establish the value of the distance parameter.

In Fig. 3 the values of the association distance according to the FHFP equation for the systems listed in Tables 1 – 5 have been plotted *vs.* Bjerrum radius. For the systems giving $\sigma(\Lambda) - R$ curves with two minima the R values of both have been plotted. From this graph it is found that some sets of data may be represented by $R = q$, which is in accord with the Justice point of view.[9,10] However, other sets may be represented by $R = q/3$, $R = 2q/3$, $R = 3q/2$ *etc.* Similar graphs of R *vs.* q are obtained for the PFPP and FJ equations.

Although these results do not disprove that the distance parameter should be numerically identified with the Bjerrum radius [9,10] it is obvious that such a point of view cannot be accepted without reservation.

Acknowledgement. Financial support from the Swedish Natural Science Research Council is gratefully acknowledged.

REFERENCES

1. Robinson, R. A. and Stokes, R. H. *Electrolyte Solutions*, Butterworths, London 1965, pp. 229 – 230.
2. Kay, R. L. *J. Amer. Chem. Soc. 82* (1960) 2099.
3. Beronius, P. *Acta Chem. Scand. A 29* (1975) 289.
4. Fuoss, R. M. and Hsia, K.-L. *Proc. Nat. Acad. Sci. U. S. 57* (1967) 1550.
5. Fuoss, R. M. and Hsia, K.-L. *Proc. Nat. Acad. Sci. U. S. 58* (1968) 1818.
6. Fernández-Prini, R. *Trans. Faraday Soc. 65* (1969) 3311.
7. Beronius, P. *Acta Chem. Scand. A 28* (1974) 77.
8. Bjerrum, N. *Kgl. Dan. Vidensk. Selsk. Mat. Fys. Medd. 7* (1926) No 9.
9. Justice, J.-C. *Electrochim. Acta 16* (1971) 701.
10. Renard, E. and Justice, J.-C. *J. Solution Chem. 3* (1974) 633.
11. Fuoss, R. M. *J. Phys. Chem. 78* (1974) 1383.
12. Justice, J.-C. *J. Phys. Chem. 79* (1975) 454.
13. Pitts, E. *Proc. Roy. Soc. London A 217* (1953) 43.
14. Fernández-Prini, R. and Prue, J. E. *Z. Phys. Chem. (Leipzig) 228* (1965) 373.
15. Barthel, J., Justice, J.-C. and Wachter, R. *Z. Phys. Chem. (Frankfurt am Main) 84* (1973) 100.
16. Chen, M. S. *Thesis*, Yale University 1969.
17. Fuoss, R. M. and Accascina, F. *Electrolytic Conductance*, Interscience, New York 1959, Chap. XV.
18. Lind, Jr., J. E. and Fuoss, R. M. *J. Phys. Chem. 65* (1961) 1414.
19. Hughes, S. R. C. and Price, D. H. *J. Chem. Soc. A* (1967) 1093.
20. Hughes, S. R. C. and White, S. H. *J. Chem. Soc. A* (1966) 1216.
21. Nilsson, A.-M. *Acta Chem. Scand. 27* (1973) 2722.
22. DeSieno, R. P., Greco, P. W. and Mamajek, R. C. *J. Phys. Chem. 75* (1971) 1722.
23. Robinson, R. A. and Stokes, R. H. *Electrolyte Solutions*, Butterworths, London 1965, pp. 125 and 461.
24. Duer, W. C., Robinson, R. A. and Bates, R. G. *J. Chem. Soc. Faraday Trans. 1* (1972) 716.
25. Barker, B. J., Huffman, Jr., H. L. and Sears, P. G. *J. Phys. Chem. 78* (1974) 2689.

Received August 13, 1975.