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Comparison of the Conductance Equations of Fuoss-Onsager, Fuoss-Hsia and Pitts with the Data of Bis(2,9-dimethyl-1,10-phenanthroline)Cu(I) Perchlorate

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Conductance equations derived by Fuoss-Onsager (1965), Fuoss-Hsia (1967) and Pitts (1953) were compared using the conductance data of bis(2,9-dimethyl-1,10-phenanthroline)Cu(I) perchlorate in acetonitrile, nitrobenzene and nitromethane at 25°C, which have relatively high dielectric constant. The chelate salt was found to be completely dissociated in these solvents. Though the Pitts equation was found to reproduce the data more satisfactorily than the Fuoss-Onsager (F–O) and the Fuoss-Hsia (F–H) equations, the derived distance of the closest approach *a* from the Pitts equation was unrealistically small for the bulky complex salt. It was shown that the F–H equation is preferable for the analysis of conductance data for both associated and unassociated electrolytes.

Theoretical comparison of the conductance theories established by Fuoss and Onsager,[1,2] and Pitts[3] was made recently by Pitts *et al.*[4] They pointed out that though both theories were nominally based on the same model of "a charged sphere in a continuum" there were differences in formulation and procedure, and they criticised the boundary conditions used in the F–O theory. Fuoss and Onsager assumed that only the radial component of the vector velocity vanishes at contact and that the potential and field should be continuous when the distance between two ionic centers is equal to a. On the other hand, Pitts required the conditions that the asymmetric (perturbed) part of the potential must vanish at $r=a$ and the velocity vector vanish on the surface of the ion. They emphasized the superiority of the Pitts theory by comparing the extent of fitting of both theories to experimental data.

Stokes[5] was the first to compare these theories ex-

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

[2] R. M. Fuoss, L. Onsager and J. F. Skinner, *ibid.*, **69**, 2581 (1965).

[3] E. Pitts, *Proc. Roy. Soc. Ser. A*, **217**, 43 (1953).

[4] E. Pitts, B. E. Tabor and J. Daly, *Trans. Faraday Soc.*, **65**, 849 (1969), *ibid.*, **66**, 693 (1970).

[5] R. H. Stokes, *J. Phys. Chem.*, **65**, 1242 (1961).

perimentally and reported that the F–O equation reproduced the conductance data of hydrochloric acid in water at 25°C only up to 0.004 N, whereas the Pitts equation could be applied to 0.02 N. Fernandez-Prini and Prue[6] also compared these equations using high precision data of inorganic salts composed of monoatomic ions in water, methanol and dimethyl formamide all of which are hydrogen-bonded solvents and solvate strongly to ions, especially small ions. They found that the Pitts equation accounts satisfactorily for the experimental data and the derived parameters are reasonable except in methanol, in which the distance of the closest approach calculated by the Pitts equation was found to be smaller than that by the F–O equation by about 1 Å. However, it is ambiguous whether the derived *a*-value corresponds to the contact or the solvent-separated contact distance of an ion pair, since both types of ion pairs may exist in the hydrogen-bonded solvents such as water and methanol. A reasonable value of *a* can therefore have some arbitrariness.

Thus, measurements with bulky electrolytes in some aprotic organic solvents which do not seem to solvate ions strongly are expected to clarify whether *a*-values obtained are reasonable or not, since *a*-values in this case will correspond to the contact distances. Bis(2,9-dimethyl-1,10-phenanthroline)Cu(I) perchlorate was chosen because of its stability in solution and symmetry, thus being suitable as a model electrolyte for conductance measurement. Since the chelate cation is surrounded by bulky aromatic groups, the association constants are expected to be smaller than those of the hydrodynamically corresponding tetrabutylammonium salt in which the positive charge is located predominantly on the nitrogen atom.[7]

Experimental

Materials. Bis(2,9-dimethyl-1,10-phenanthroline)Cu(I) perchlorate (Dojin Chemicals Ltd.) was recrystallized from acetone solution. Its purity was checked by analysis. The analytical data were as follows. Found: C, 58.05; H, 4.11; N, 9.67%. Calcd for $C_{28}H_{24}N_4O_4ClCu$: C, 58.03; H, 4.17; N, 9.67%. The stability of the chelate cation in each solvent was confirmed by the absorption spectrum in the visible region. Nitrobenzene was washed three times with conductivity water, kept over anhydrous calcium chloride for several days and filtered off. The filtrate was passed through a molecular sieve and fractionated under reduced pressure (below 10 mmHg). The product was still slightly yellow, its specific conductance being negligibly small. Reagent grade acetonitrile was kept over potassium hydroxide pellets for 24 hr and distilled over phosphorus pentoxide, followed by fractionation. Its specific conductance was 3.3×10^{-8} ohm^{-1}cm^{-1}. Reagent grade nitromethane was dried with anhydrous calcium chloride and distilled over drierite under reduced pressure. A middle fraction was collected. Its specific conductance was 6.0×10^{-8} ohm^{-1}cm^{-1}. Purity of the solvents was checked by measuring their densities. Observed values were 1.1986 and 0.7766 for $PhNO_2$ and CH_3CN, respectively, which were in good agreement with the values in literature, viz., 1.1977[8] and 0.7767,[9] respectively. The density of CH_3NO_2 was 1.1298, slightly lower than the value 1.1312 reported by Kay *et al.*[10] They purified CH_3NO_2 by distillation at reduced pressure followed by fractional crystallization, which, however, was found to increase the water content. Water content of the solvents used was examined by titration with the Karl Fischer reagent and found to be less than 0.01 wt% in CH_3NO_2 and CH_3CN and 0.001wt% in $PhNO_2$. Other physical properties of the solvents were taken from literature.[8,9,10]

Apparatus and Procedure. Conductance measurements were carried out with a conductometer, type MY-7 (Yanagimoto Mfg. Co., Ltd.) with a Wheatstone bridge (800 c/s). All the resistances were calibrated with a resistance box (Yokogawa Electric Works Ltd.) standardized by Shinkawa Electric Co. Pyrex conductance cells were of Erlenmeyer type with lightly platinized electrodes, containing about 200 ml of solution, and were standardized with aqueous KCl solutions, using the Lind, Zwolenik and Fuoss constants.[11] Potassium chloride was recrystallized three times from conductivity water and dried at 500°C. Cells were washed with nitric acid and steam before each run. Cell solutions were thermostated to 25±0.01°C in a double water bath with a mercury-in-glass thermoregulator. In order to attain temperature equilibrium rapidly and avoid the polarization effect during measurements, the solution in the cell was stirred by a magnetic stirrer. All solutions were prepared gravimetrically since the molecular weight of the complex salt is very high (579.522). For each run, a sample of 100—110 mg was directly added to the solvent of known conductivity in the cell. After a constant value of resistance was attained, 30 ml of solution was siphoned out and an equal volume of the solvent was added to the cell. The procedure was continued until an appropriate concentration was attained. Concentration range was $\kappa a<0.2$ within which the approximations used to establish the conductance equations are valid. CH_3CN and CH_3NO_2 are so volatile and hygroscopic that a drybox was used for preparation of the solutions.

Results and Discussion

The measured equivalent conductance Λ and the corresponding concentration C in equivalents per liter are given in Table 1. These data were analyzed by means of the following three equations for unassociated electrolytes.

Fuoss-Onsager equation (1965)[2]:

$$\Lambda = \Lambda_0 - SC^{1/2} + E'C\ln(6E_1'C) + LC \tag{1}$$

$$S = \alpha\Lambda_0 + \beta_0,\ E' = E_1'\Lambda_0 - E_2',$$

$$E_1' = 2.942\times10^{12}/(DT)^3,$$

$$E_2' = 0.4333\times10^8/\eta(DT)^2,\ L = L_1 + L_2(b),$$

$$ab = \beta = e^2/DkT$$

$$L_1 = 3.202E_1'\Lambda_0 - 3.420\,E_2' + \alpha\beta_0$$

$$L_2(b) = 2E_1'\Lambda_0 h(b) + 44E_2'/3b - 2E'\ln b$$

$$h(b) = (2b^2+2b-1)/b^3$$

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6) R. Fernandez-Prini and J. E. Prue, *Z. Phys. Chem.* (Leipzig), **228**, 373 (1965).

7) K. Miyoshi, *J. Phys. Chem.*, **76**, 3029 (1972).

8) E. Hirsch and R. M. Fuoss, *J. Amer. Chem. Soc.*, **82**, 1018 (1960).

9) D. F. Evans, C. Zawoyski, and R. L. Kay, *J. Phys. Chem.* **69**, 3878 (1965).

10) R. L. Kay, S. C. Blum, and H. I. Schiff, *ibid.*, **67**, 1223 (1963).

11) J. Lind, J. Zwolenik, and R. M. Fuoss, *J. Amer. Chem. Soc.*, **81**, 1557 (1959).

Fuoss-Hsia equation (1967)[12] modified by Fernandez-Prini (1969)[13]:

$$\Lambda = \Lambda_0 - SC^{1/2} + EC\log C + J_1C - J_2C^{3/2} \qquad (2)$$

$$E = E_1\Lambda_0 - E_2,\ E_1 = 2.3026(\kappa^2a^2b^2/24C),$$

$$E_2 = 2.3026(\kappa ab\beta_0/16C^{1/2}),\ J_1 = \delta_1\Lambda_0 + \delta_2$$

$$J_2 = \delta_3\Lambda_0 + \delta_4$$

$$\delta_1 = [(\kappa ab)^2/24C][1.8147 + 2\ln(ka/C^{1/2}) + 2h(b)]$$

$$\delta_2 = \alpha\beta_0 + \beta_0(\kappa a/C^{1/2}) - \beta_0[(\kappa ab)/16C^{1/2}] \times[1.5337 + (4/3b) + 2\ln(\kappa a/C^{1/2})]$$

$$\delta_3 = [b^2(\kappa a)^3/24C^{3/2}][0.6094 + (4.4748/b) + (3.8284/b^2)]$$

$$\delta_4 = [\beta_0(\kappa ab)^2/24C][2h(b) - 1.9384] + \alpha\beta_0(\kappa a/C^{1/2}) + [\beta_0(\kappa a)^2/C] - [\beta_0b(\kappa a)^2/16C][1.5405 + (2.2761/b)] - (\beta_0{}^2\kappa ab/16\Lambda_0C^{1/2})[(4/3b) - 2.2194]$$

Pitts equation (1953)[3] modified by Fernandez-Prini and Prue (1965)[6,14]:

$$\Lambda = \Lambda_0 - SC^{1/2} + EC\log C + J_1C - J_2C^{3/2} \qquad (3)$$

$$\delta_1 = (\kappa ab)^2[\ln(\kappa a/C^{1/2}) + 2/b + 1.7718]/12C$$

$$\delta_2 = \beta_0\kappa a/C^{1/2} + \beta_0\kappa ab[0.01387 - \ln(\kappa a/C^{1/2})]/8C^{1\ 2}$$

$$\delta_3 = (\kappa ab)^3[1.2929/b^2 + 1.5732/b]/6C^{3/2}$$

$$\delta_4 = \beta_0(\kappa a)^2/C + 0.23484\beta_0b(\kappa a)^2/3C$$

All calculations were performed on a TOSBAC 3400 digital computer using the least squares method proposed by Kay.[15] The following equation was used.

$$\Delta\Lambda = \Lambda(\text{obsd}) - \Lambda(\text{calcd}) = \Delta\Lambda_0 + (C\partial J_1/\partial a - C^{3/2}\partial J_2/\partial a)\Delta a$$

(In Fernandez-Prini and Prue's paper, equation (8) is misprinted.) In order to bring the data into conformity with Fernandez-Prini's treatment, the data weighted by concentration were also analysed. No viscosity correction was made. Parameters obtained are given in Tables 2 and 3, where σ is a standard deviation. The complex salt was found to be completely dissociated in these solvents, since when the data were treated with a three-parameter equation involving the association constant K_A, a negative K_A with a larger standard deviation was derived. The magnitude of standard deviations in Tables 2 and 3 clearly indicates that the Pitts equation is preferable to the F–O and F–H equations.

TABLE 1.

CH_3CN		CH_3NO_2		$PhNO_2$	
$C\times10^4$	Λ	$C\times10^4$	Λ	$C\times10^4$	Λ
36.367	139.98	26.769	87.090	29.691	28.509
29.958	141.55	24.159	87.503	27.078	28.656
25.535	142.76	21.995	87.873	24.583	28.795
22.232	143.76	20.206	88.186	22.064	28.945
18.444	145.02	16.957	88.818	19.784	29.096
16.519	145.66	15.238	89.176	17.539	29.249
14.663	146.38	13.812	89.497	15.523	29.401
12.198	147.45	12.132	89.894	11.972	29.700
9.9121	148.52	10.875	90.206	9.3770	29.957
8.5128	149.27	9.4738	90.592	8.1487	30.085
				6.9359	30.224

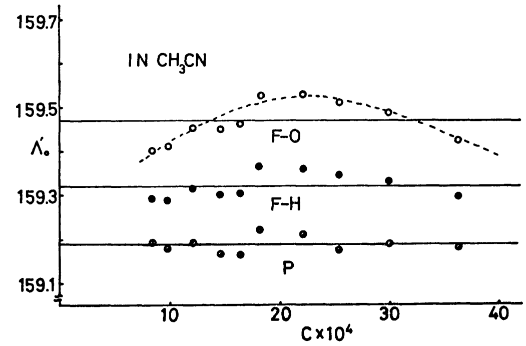

Fig. 1. Λ_0' plots in CH_3CN.

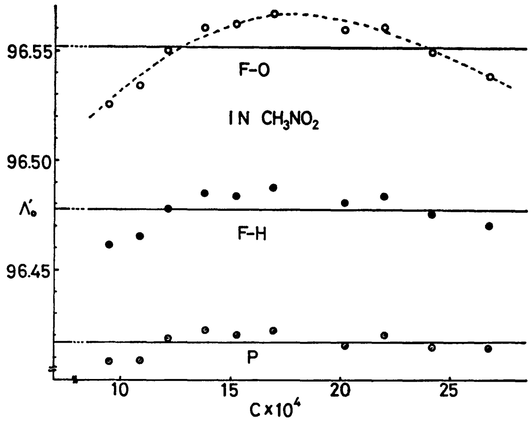

Fig. 2. Λ_0' plots in CH_3NO_2.

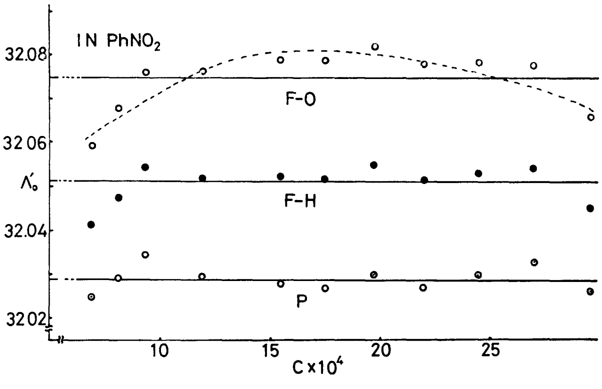

Fig. 3. Λ_0' plots in $PhNO_2$.

As is suggested by Fernandez-Prini and Prue,[6] it is useful to introduce Λ_0' to examine the fitting,

$$\Lambda_0' = \Lambda(\text{obsd}) - \Lambda(\text{calcd}) + \Lambda_0$$

Λ_0' calculated from the observed conductance weighted by concentration is plotted against concentration in Figures 1, 2 and 3. We see that the Pitts equation

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[12] R. M. Fuoss and K-L. Hsia, *Proc. Nat. Acad. Sci.*, **57**, 1550 (1967).

[13] R. Fernandez-Prini, *Trans. Faraday Soc.*, **65**, 3311 (1969).

[14] According to the modification by Pitts in 1969, the numerical constant 0.23484 in δ_4 is reported to become 0.52772. E. Baumgartner, M. Busch, and R. Fernandez-Prini, *J. Phys. Chem.*, **74**, 1821 (1970).

[15] R. L. Kay, *J. Amer. Chem. Soc.*, **82**, 2099 (1960).

Table 2. Derived parameters (unweighted)

		CH_3CN	CH_3NO_2	$PhNO_2$
Fuoss-Onsager	Λ_0	159.44	96.540	32.069
	a(Å)	4.22±0.04	4.54±0.04	4.35±0.03
	L	1247±16	777.3±7.8	266.4±2.7
	σ	0.046	0.014	0.007
Fuoss-Hsia	Λ_0	159.30	96.470	32.048
	a(Å)	4.64±0.02	5.01±0.40	4.73±0.01
	J_1	2169±8	1320±80	482.3±1.0
	J_2	3000±60	2000±1300	657.2±3.9
	σ	0.030	0.010	0.0046
Pitts	Λ_0	159.19	96.413	32.029
	a(Å)	3.46±0.02	3.85±0.24	3.47±0.01
	J_1	2347±5	1418±48	519.4±0.7
	J_2	5610±40	3600±800	1259±3
	σ	0.020	0.006	0.0032

Table 3. Derived parameters (weighted by concentration)

		CH_3CN	CH_3NO_2	$PhNO_2$
Fuoss-Onsager	Λ_0	159.47	96.552	32.075
	a(Å)	4.17±0.04	4.51±0.04	4.31±0.03
	L	1230±16	771.5±7.3	263.5±2.7
	σ	0.015	0.0042	0.0019
Fuoss-Hsia	Λ_0	159.32	96.478	32.051
	a(Å)	4.60±0.02	4.99±0.38	4.71±0.01
	J_1	2156±8	1320±80	480.4±0.8
	J_2	2950±50	2000±1200	649.5±2.3
	σ	0.010	0.0028	0.0013
Pitts	Λ_0	159.19	96.417	32.029
	a(Å)	3.45±0.01	3.84±0·22	3.47±0.01
	J_1	2344±5	1416±45	519.2±0.6
	J_2	5592±33	3600±700	1258±2
	σ	0.006	0.0016	0.0009

shows the best performance in every case. The plots of Λ_0' from the F–O equation have a curvature, meaning a deficiency of the concentration dependent terms in the equation. Similar results were obtained for hydrogen chloride in water and alkali metal halides in water, methanol and dimethyl formamide by Fernandez-Prini and Prue and for alkali metal halides in water by Pitts *et al.*[4] The plot from the F–H equation which contains $C^{3/2}$ term also seems to be curved, but the curvature is not so noticeable as that from the F–O equation. On the other hand, Tables 2 and 3 show that *a*-values obtained with the Pitts equation are considerably smaller than those with the F–O and F–H equations. This trend is also found by Fernandez-Prini and Prue.

Perchlorate ion is known to be one of the least solvated ions and it may be assumed that a large cation such as this chelate is not solvated, since the positive charge on the cation is screened by the bulky aromatic ligands. Thus *a*-values in this case will correspond to the contact distance between the cation and the anion.

It may thus be concluded that *a*-values from the Pitts equation are unrealistically small because the sum of the crystallographic radius of ClO_4^- and that of the chelate cation estimated from the bond lengths significantly exceeds 3.5 Å obtained with the Pitts equation. (The crystallographic radius of the chelate cation is not found in literature to the author's knowledge). It is also seen from Tables 2 and 3 that *a*-values derived with the F–O and F–H equations seem to be small for the bulky complex perchlorate. However, it should be noted that *a*-values generally show a considerable dependence upon the dielectric constant of the medium,[2,16] and that those obtained with tetraalkylammonium halides and picrates in CH_3NO_2, MeOH and CH_3CN are almost constant irrespective of a considerable variation in crystallographic radius and smaller than those expected from their ionic radii, viz., the derived *a*-values are 3.9±0.3 Å,[10] 3.6±0.2 Å,[17] and 3.6±0.2 Å[9] for all the halides and picrates investigated in CH_3NO_2, MeOH and CH_3CN, respectively. Of course a viscosity correction affecting *a*-values to some extent[9] was made in

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[16] J. Lind and R. M. Fuoss, *J. Phys. Chem.*, **65**, 999, 1414 (1961), *ibid.*, **66**, 1727 (1962).

[17] R. L. Kay, C. Zawoyski, and D. F. Evans, *ibid.*, **69**, 4208 (1965).

these cases. Evans and Gardam[18] found that when the F–H equation was applied to several tetraalkylammonium salts in alcohols, small but constant a-values were obtained which were independent of the dielectric constant. It is seen from Tables 2 and 3 that a-values from the F–H equation are slightly larger than those from the F–O equation. Though the continuum theory is adequate to describe the concentration dependence of the conductance, the size dependence in the F–O theory appears to need revision.[17]

The reason why the Pitts equation in general gives smaller values of a has been discussed by Fernandez-Prini and Prue[6,13] in outline and by Pitts[4] in detail. The main differences between these theories lie in the boundary conditions used to solve the equation of continuity. Pitts neglected the Brownian terms in the velocity of the ion from the viewpoint of the model his theory was based on. The Pitts equation does not allow for the kinetic (osmotic) term which contributes to the increase in the velocity of the ion in the F–O theory. Valleau[19] pointed out that this term should be regarded as completely unrealistic and should be dropped. Recently Carman[4,20] has stated from the consideration of the cancellation of terms in the F–O theory that the E value in the F–O theory should be $(E_1\Lambda_0-2E_2)$[21] but not $(E_1\Lambda_0-E_2)$. He emphasized that the F–O and Pitts theories are not mutually exclusive since they are based on the same model.

As Pitts *et al.*[4] pointed out, it is too complicated to discuss the two theories term by term and it is more useful to compare the resulting parameters. When the data of the complex salt in CH_3CN–CCl_4 and $PhNO_2$–CCl_4 mixtures with dielectric constants less than 15 were analyzed with the Pitts equation involving the association constant K_A term, no convergence was obtained whereas the F–O and the F–H equations gave reasonable parameters.[22]

From the present discussions, it is concluded that the F–H equation is recommended for the analysis of the conductance data of both unassociated and associated electrolytes also in these aprotic solvents.[13]

The author wishes to express his deep gratitude to Professor Yuroku Yamamoto, Hiroshima University, and to Mr. Toshihiro Tominaga for their valuable discussions and directions in the course of this study.

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[18] D. F. Evans and P. Gardam, *J. Phys. Chem.*, **72**, 3281 (1968).

[19] J. P. Valleau, *ibid.*, **69**, 1745 (1965).

[20] P. C. Carman, *ibid.*, **74**, 1653 (1970).

[21] A. D'Aprano, *ibid.*, **75**, 3290 (1971).

[22] K. Miyoshi and T. Tominaga, to be submitted in *J. Phys. Chem.*