

Comments on the Note "A Re-Analysis of Some Conductance Data" by B. A. Akrawi, W. H. Lee and R. J. Wheaton

PER BERONIUS

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

In the Akrawi *et al.* contribution¹ to the interpretation of the distance parameter²⁻²⁷ in electrolytic conductance theory, a problem which has for a long time past been subject to much controversy, it is claimed that the distance parameter, *R*, approaches the Bjerrum radius, *q*, in low dielectric constant solvents. The evidence of this conclusion, which is based on calculations using a conductance equation derived in a series of papers by Lee and Wheaton,²⁸⁻³⁰ is not convincing. This conductance equation, the derivation of which starts from a model almost identical to that proposed by Fuoss,¹⁹⁻²⁰ will be referred to as the Fuoss-Lee-Wheaton (FLW) equation.

In general, it is not possible to obtain a unique value of the distance parameter from electrical conductance data, *cf.* Refs. 31-33. The experimental points (*c*, Λ) may be equally well reproduced over a range of *R* values. In other words the goodness of fit is frequently quite insensitive to the value of the distance parameter. In this respect the FLW equation³⁰ appears to be no exception to other conductance equations, *e.g.* the extended Fuoss-Hsia³⁴⁻³⁶ and Pitts^{37,38} equations, and the Fuoss 1978 equation.²⁷

The model on which the FLW equation is based allows for solvent separated as well as contact ion pairs. It may be noted that this equation and the extended Fuoss-Hsia (FHFP) equation,³⁴⁻³⁶ which

is based on the hard spheres model, yield almost identical association constants (K_A) for values of K_A exceeding about 15. A few examples are given in Table 1.

1. Akrawi, B. A., Lee, W. H. and Wheaton, R. J. *Acta Chem. Scand. A* 34 (1980) 307.
2. Fuoss, R. M. *J. Am. Chem. Soc.* 81 (1959) 2659.
3. Kay, R. L. *J. Am. Chem. Soc.* 82 (1960) 2099.
4. Justice, J.-C. and Fuoss, R. M. *J. Phys. Chem.* 67 (1963) 1707.
5. Fernandez-Prini, R. and Prue, J. E. *Trans. Faraday Soc.* 62 (1966) 1257.
6. Janz, G. J. and Tait, M. J. *Can. J. Chem.* 45 (1967) 1101.
7. Fernandez-Prini, R. *Trans. Faraday Soc.* 64 (1968) 2146.
8. Justice, J.-C., Bury, R. and Treiner, C. *J. Chim. Phys. Phys.-Chim. Biol.* 65 (1968) 1708.
9. Justice, J.-C. *J. Chim. Phys. Phys.-Chim. Biol.* 66 (1969) 1193.
10. Pitts, E., Tabor, B. E. and Daly, J. *Trans. Faraday Soc.* 65 (1969) 849.
11. Pitts, E., Tabor, B. E. and Daly, J. *Trans. Faraday Soc.* 66 (1970) 693.
12. Matesich, M. A., Nadas, J. A. and Evans, D. F. *J. Phys. Chem.* 74 (1970) 4568.
13. Hanna, E. M., Pethybridge, A. D. and Prue, J. E. *Electrochim. Acta* 16 (1971) 677.
14. Hanna, E. M., Pethybridge, A. D. and Prue, J. E. *J. Phys. Chem.* 75 (1971) 291.
15. Justice, J.-C. *Electrochim. Acta* 16 (1971) 701.
16. DeRossi, C., Sesta, B., Battistini, M. and Petrucci, S. *J. Am. Chem. Soc.* 94 (1972) 2961.
17. Barthel, J., Justice, J.-C. and Wachter, R. *Z. Phys. Chem. (Frankfurt am Main)* 84 (1973) 100.
18. Fuoss, R. M. *J. Phys. Chem.* 78 (1974) 1383.
19. Fuoss, R. M. *Proc. Natl. Acad. Sci. USA* 71 (1974) 4491.
20. Fuoss, R. M. *J. Phys. Chem.* 79 (1975) 525.
21. Justice, J.-C. *J. Phys. Chem.* 79 (1975) 454.
22. Mattina, C. F. and Fuoss, R. M. *J. Phys. Chem.* 79 (1975) 1604.
23. Yeager, H. L. and Kratochvil, B. *Can. J. Chem.* 53 (1975) 3448.
24. Fuoss, R. M. *J. Phys. Chem.* 80 (1976) 2091.
25. Pethybridge, A. D. and Spiers, D. J. *J. Chem. Soc. Faraday Trans. 1*, 73 (1977) 768.
26. Fuoss, R. M. *J. Solution Chem.* 7 (1978) 771.
27. Fuoss, R. M. *J. Phys. Chem.* 82 (1978) 2427.
28. Lee, W. H. and Wheaton, R. J. *J. Chem. Soc. Faraday Trans. 2*, 74 (1978) 743.
29. Lee, W. H. and Wheaton, R. J. *J. Chem. Soc. Faraday Trans. 2*, 74 (1978) 1456.
30. Lee, W. H. and Wheaton, R. J. *J. Chem. Soc. Faraday Trans. 2*, 75 (1979) 1128.

Table 1. Comparison of ion pair association constants (molarity scale) according to FLW and FHFP conductance equations at 25 °C.

Solvent	Salt	<i>R</i> Å	$K_A \times 10^{-3}$	
			FLW	FHFP
Ethanol ³⁹	NaI	9.1	0.0558	0.0506
	KI	9.1	0.0819	0.0767
	RbI	8.6	0.1054	0.0980
	CsI	10.3	0.1405	0.1410
1-Butanol ⁴⁰	RbI	18.4	1.70	1.74
1-Octanol ⁴¹	NaI	28.5	40.1	39.8
1-Octanol ⁴²	LiBr	28.5	56.4	57.1

31. Beronius, P. *Acta Chem. Scand. A* 28 (1974) 77.
32. Beronius, P. *Acta Chem. Scand. A* 29 (1975) 289.
33. Beronius, P. *Acta Chem. Scand. A* 30 (1976) 115.
34. Fuoss, R. M. and Hsia, K.-L. *Proc. Natl. Acad. Sci. U.S.A.* 57 (1967) 1550.
35. Fuoss, R. M. and Hsia, K.-L. *Proc. Natl. Acad. Sci. U.S.A.* 58 (1968) 1818.
36. Fernandez-Prini, R. *Trans. Faraday Soc.* 65 (1969) 3311.
37. Pitts, E. *Proc. R. Soc. London A* 217 (1953) 43.
38. Fernandez-Prini, R. and Prue, J. E. *Z. Phys. Chem. (Leipzig)* 228 (1965) 373.
39. Beronius, P., Wikander, G. and Nilsson, A.-M. *Z. Phys. Chem. (Frankfurt am Main)* 70 (1970) 52.
40. Beronius, P. *Acta Chem. Scand. A* 32 (1978) 467.
41. Beronius, P. *Acta Chem. Scand. A* 32 (1978) 469.
42. Beronius, P. and Lindbäck, T. *Acta Chem. Scand. A* 32 (1978) 423.

Received March 4, 1980.