

Short Communications

A Re-Analysis of Some Conductance Data

B. A. AKRAWI, W. H. LEE and R. J. WHEATON

Department of Chemistry, University of Surrey,
Guildford, Surrey, England

Recently P. Beronius has published the result of conductance studies of some salts in non-aqueous solvents; these include lithium bromide and sodium iodide in 1-octanol^{1,2} ($\epsilon=9.85$), rubidium iodide in 1-butanol³ ($\epsilon=17.5$), and the alkali metal iodides

in ethanol ($\epsilon=24.30$) and methanol⁴ ($\epsilon=32.63$). The conductance data were analysed to obtain parameters Λ_∞ , K_A (the ion-pair association constant) and a , the distance of closest approach of the ions; the equations used were those of Pitts,⁵ Fuoss-Hsia,⁶ Fuoss-Onsager (1957)⁷ and Fuoss (1975).⁸ For the solvents 1-octanol and 1-butanol, the distance parameter was set equal to the appropriate Bjerrum distance,⁹ 28.45 and 16.02 Å respectively, and the ranges of concentration analysed were limited, so that the formation of triple ions in these solvents could be neglected.

We have re-analysed these experimental conductances, along with results obtained by Wikander and Isaacson¹⁰ for alkali metal iodides in 1-propanol, using an equation recently developed here;^{11–14} in this analysis, the R -parameter, defined as the distance of separation within which all pairs of ions have lost their relative translational motion

Table 1. Conductance data for some salts at 25 °C.

	$R/\text{Å}$	K_A	Λ_∞	$\sigma(\Lambda)^a$	q	Ref.
Methanol						
NaI	6.0	12.8	108.51	0.053	8.6	4
KI	5.5	13.2	115.51	0.053	8.6	4
RbI	6.5	18.0	119.68	0.050	8.6	4
CsI	7.7	23.1	124.22	0.041	8.6	4
Ethanol						
NaI	9.1	55.8	47.57	0.009	11.5	4
KI	9.1	81.9	50.70	0.008	11.5	4
RbI	8.6	105.4	52.18	0.012	11.5	4
CsI	10.3	140.5	53.63	0.030	11.5	4
1-Propanol						
NaI	11.3	191.9	24.38	0.011	13.7	14
KI	11.1	350.2	26.31	0.009	13.7	14
RbI	8.6	472.0	26.99	0.006	13.7	14
CsI	8.4	646.4	27.72	0.007	13.7	14
1-Butanol						
RbI	18.4	1698	18.40	0.007	16.0	3
1-Octanol						
NaI	28.5	40118	4.49	0.000	28.4	2
LiBr	28.5	56444	3.93	0.000	28.4	1

^a Standard deviation from experimental data.

(and thus make no contribution to electrical conductance), is made a variable. Details of the method used to analyse the experimental data are given elsewhere.¹³ The results obtained are shown in Table 1.

It will be seen that the R values obtained correspond to the Bjerrum distance, very closely for the two salts in 1-octanol, and approximately, for RbI in 1-butanol. From these and similar results¹⁰ we infer that in the limit of low dielectric constant ($\epsilon \rightarrow 1$) the distance parameter R corresponds to the Bjerrum distance q . This is in contrast to the situation in solvents of high dielectric constant such as water, where R is strongly dependent upon short-range forces, representing the distance between the ions at which a stable ion-pair, either contact or solvent-separated, is first formed.¹³

With regard to conductances in methanol and ethanol, as was pointed out by Beronius *et al.*,⁴ and as discussed by Lee and Wheaton,¹³ if only contact ion-pairs are formed, the association constant would be expected to increase with decreasing cation size, *i.e.* in the order CsI < RbI < KI < NaI. The values of K_A in Table 1 show the reverse dependence. As discussed elsewhere¹³ this can only be explained by assuming the formation of solvent-separated ion-pairs. Unlike the a values obtained previously,⁴ the R values shown in Table 1 are entirely consistent with this assumption. With the Fuoss-Onsager, Fuoss-Hsia and Pitts equations, all of which are based on the primitive (charged sphere) model, ion-association only has meaning in terms of contact ion-pairs; the concept of ion-solvation is in fact meaningless with the primitive model, where ion-dipole forces are, by definition, neglected and the solvent is assumed to have no structure.

In conclusion, therefore, we feel that the Lee-Wheaton equation is particularly suitable for use in the analysis of conductance data for systems of the type discussed here, in which ion-association occurs to a significant extent and solvent separated ion-pairs may be found.

Acknowledgement. RJW wishes to thank the Royal Commission for the Exhibition of 1851 for their financial support.

1. Beronius, P. and Lindback, T. *Acta Chem. Scand. A* 32 (1978) 423.
2. Beronius, P. *Acta Chem. Scand. A* 32 (1978) 469.
3. Beronius, P. *Acta Chem. Scand. A* 32 (1978) 467.
4. Beronius, P., Wikander, R. and Nilsson, A.-M. *Z. Phys. Chem. Abt. A* 70 (1970) 52.
5. Pitts, E. *Proc. R. Soc. London A* 217 (1953) 43.
6. Fuoss, R. M. and Hsia, K.-L. *Proc. Natl. Acad. Sci. U.S.A.* 58 (1968) 1818.
7. Fuoss, R. M. and Onsager, L. *J. Phys. Chem.* 61 (1957) 668.
8. Fuoss, R. M. *J. Phys. Chem.* 79 (1975) 525; 1983.
9. Bjerrum, N. *K. Dan. Vidensk. Selsk., Mat.-Fys. Medd.* 7 (1926) No. 9.
10. Wikander, G. and Isacson, U. *Z. Phys. Chem. Abt. A* 81 (1972) 57.
11. Wheaton, R. J. *Ph. D. Thesis*, University of Surrey, Guildford 1978.
12. Lee, W. H. and Wheaton, R. J. *J. Chem. Soc. Faraday Trans. 2*, 74 (1978) 743.
13. Lee, W. H. and Wheaton, R. J. *J. Chem. Soc. Faraday Trans. 2*, 74 (1978) 1456.
14. Lee, W. H. and Wheaton, R. J. *J. Chem. Soc. Faraday Trans. 2*, 75 (1979) 1128.

Received January 7, 1980