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Short Communications

Ion Pair Formation of Rubidium Iodide in 1-Butanol at 25 °C

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As part of a study of the structure of univalent electrolytes in n-alcohols the association constant for ion pair formation of rubidium iodide in 1-butanol at 25 °C was determined by electrical conductance measurements. A survey of the literature reveals that precise conductance data referring to this solvent are available for only a few salts, see, *e.g.*, Ref. 1.

Experimental. The solvent (Merck, *pro analysi*) was dried using a molecular sieve (Fischer, type 4A) and fractionally distilled; electrolytic conductivity, $\kappa = 2.5 \times 10^{-9}$ S cm^{-1}; $d = 0.80601$ g cm^{-3} (lit.[2] 0.8060 g cm^{-3}). The values, $\eta = 0.0246$ P and $\varepsilon = 17.51$, for the viscosity[1] and relative permittivity,[2] respectively, were used in the calculations. Rubidium iodide (Merck, *suprapur*) was dried for 4 h at 110 °C.

The two conductivity cells used, each of 300 cm^3 capacity, were of the Daggett-Bair-Kraus type.[3] They were fitted with bright platinum electrodes. The cell constants were 0.055727 and 0.056040 cm^{-1}. Conductivity measurements were performed at 25.00±0.03 °C and different frequencies between 2 and 5 kHz using a Leeds and Northrup conductivity bridge and extrapolated to infinite frequency.

Table 1. Dependence of molar conductivity on concentration of rubidium iodide in 1-butanol at 25 °C.

Run A $c \times 10^4$ M	Λ S cm^2 mol^{-1}	Run B $c \times 10^4$ M	Λ S cm^2 mol^{-1}
1.9994	14.298	1.9213	14.405
3.9532	12.619	3.9274	12.629
6.0083	11.484	5.9695	11.506
8.0462	10.649	7.9974	10.668
10.053	10.041	10.055	10.041
12.033	9.5517	11.989	9.5684

Calculations and results. Molar conductivities, Λ, for different rubidium iodide concentrations, c, are given in Table 1. To avoid disturbances due to formation of higher aggregates than ion pairs the measurements were confined to concentrations below 1.7 mM. This concentration limit was derived from the condition,[4]

$$c \leq 3.2 \times 10^{-7}\, \varepsilon^3 \qquad (1)$$

New expressions for the relaxation and electrophoretic terms, $\Delta X/X$ and $\Delta\Lambda_e$, in the conductance equation for pairwise associated symmetrical electrolytes,

$$\Lambda = \alpha[\Lambda_\infty(1 - \Delta X/X) - \Delta\Lambda_e] \qquad (2)$$

where α is the degree of dissociation and Λ_∞ is the limiting molar conductivity, have recently been derived by Fuoss.[5,6]

The association constant, K_A, Λ_∞, and $\sigma(\Lambda)$, *i.e.* the standard deviation between experimental and computed Λ values, were calculated from eqn. (2) and the law of mass action for the equilibrium between free and paired ions,

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

using a computer programme[7] similar to that outlined in Ref. 8. In eqn. (3) γ is the mean molar activity coefficient of free ions. The maximum center-to-center distance, R, between the ions in the ion pair was set equal to the Bjerrum radius.[9] The results of these calculations are given in Table 2 where "F75" refers to eqn. (2), *i.e.* the Fuoss equation[5,6] from 1975. For comparison the values of K_A and Λ_∞ according to the modified Fuoss-Hsia ("FHFP") and Pitts' ("PFPP") conductance equations[10,11] are included. Errors quoted are standard deviations.

Eqns. (2) and (3) may be combined to yield,

$$(\Lambda - HY)/(1 + RX) = \Lambda_\infty - K_A c\alpha\gamma^2\Lambda/(1 + RX) \qquad (4)$$

where $RX = -\Delta X/X$, and $HY = -\Delta\Lambda_e$. A graph according to eqn. (4) is shown in Fig. 1.

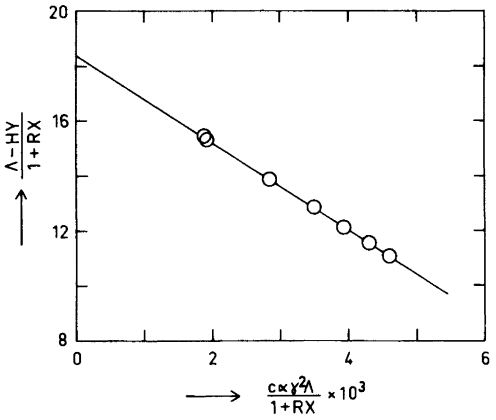

Fig. 1. Graph corresponding to eqn. (4) for rubidium iodide in 1-butanol at 25 °C.

Table 2. Data for rubidium iodide in 1-butanol at 25 °C.

Conductance equation	K_A M^{-1}	Λ_∞ S cm^2 mol^{-1}	$\sigma(\Lambda)$ S cm^2 mol^{-1}
F75	1593± 6	18.40±0.02	0.01
FHFP	1743± 7	18.48±0.02	0.01
PFPP	1663±13	18.32±0.04	0.02

An estimate of the distance of closest approach, a, of the ions in the ion pair may be obtained from the Bjerrum theory.[9] Using the value of K_A derived from the F75 equation (Table 2) one arrives at $a=3.0$ Å, which is close to the crystal radii sum for Rb^+ and I^-.

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