

Short Communications

The Ion Pair – Triple Ion Borderland of Sodium Iodide in 1-Butanol at 25 °C

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The present study of the aggregation of sodium iodide in 1-butanol by means of the conductimetric method constitutes part of a programme the intention of which is to identify aggregates formed by electrolytes in organic solvent media and to establish their structures.

Experimental. The solvent (Merck, *p.a.*) and the salt (Merck, *suprapur*) were pretreated according to Ref. 1. A Daggett-Bair-Kraus type conductivity cell² of 1300 ml capacity was used. By means of a calibrated precision buret (Metrohm Herisau, Dosimat E 535) kept in an air thermostat at 25 °C portions of a stock sodium iodide solution were added to the cell initially containing a known quantity of the pure solvent. After each addition the cell resistance at 25.00 ± 0.02 °C was measured as previously outlined.¹

Results and conclusions. In Table 1 the experimentally established molar conductivity, $\Lambda(\text{exp})$, is given at different analytical concentrations, c , of the salt.

The FHFP conductance equation^{3–5} for associated symmetrical electrolytes,

$$\Lambda = \Lambda_{\infty} - Sc_i^{1/2} + Ec_i^{10} \log c_i + J_1 c_i - J_2 c_i^{3/2} - K_A c_i \gamma^2 \Lambda \quad (1)$$

was fitted⁶ by means of a Cyber 172 computer to the four lowest concentration points (Table 1) using $\eta = 0.0246$ P for the viscosity⁷ and $\epsilon = 17.51$ for the relative permittivity⁸ of the solvent, and $R = 16$ Å (Bjerrum radius) for the maximum distance^{9–11} between centers of charge in the ion pair.

In eqn. (1) Λ is the molar conductivity at the concentration c_i of free ions, Λ_{∞} is that at infinite dilution, S and E are defined in Ref. 12, and J_1 and J_2 in Ref. 5, K_A is the ion pair association constant, and γ is the mean molar activity coefficient of free

Table 1. Data for NaI in 1-butanol at 25 °C.

$c \times 10^4$ M	$\Lambda(\text{exp})$ $\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$	$\Delta\Lambda$ $\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$
3.1860	13.841	0.000
3.2155	13.824	–0.002
5.2622	12.983	0.007
5.3108	12.962	0.003
7.3011	12.340	0.002
7.3688	12.317	–0.002
9.3042	11.831	–0.002
9.3904	11.808	–0.005
11.272	11.415	–0.002
11.377	11.390	–0.006
13.205	11.064	–0.001
13.328	11.039	–0.005
15.105	10.762	0.002
15.246	10.738	–0.001
16.973	10.498	0.006
17.132	10.475	0.005
18.809	10.266	0.013
18.985	10.242	0.010
20.614	10.058	0.019
20.807	10.034	0.017
22.389	9.8710	0.027
22.599	9.8471	0.025
24.135	9.7015	0.035
24.362	9.6778	0.033
25.852	9.5468	0.043
26.095	9.5231	0.042
27.541	9.4046	0.052
27.800	9.3812	0.051
30.838	9.1523	0.070
31.129	9.1293	0.070
34.031	8.9349	0.090
34.354	8.9115	0.089

ions which was calculated from the Debye-Hückel equation,¹³

$$^{10} \log \gamma \simeq ^{10} \log f = -Ac_i^{1/2} / [1 + BRc_i^{1/2}] \quad (2)$$

where f is the mean rational activity coefficient.

The curve fitting outlined above was repeated upon increasing the concentration range to the five, six, etc. lowest concentration points. By this means

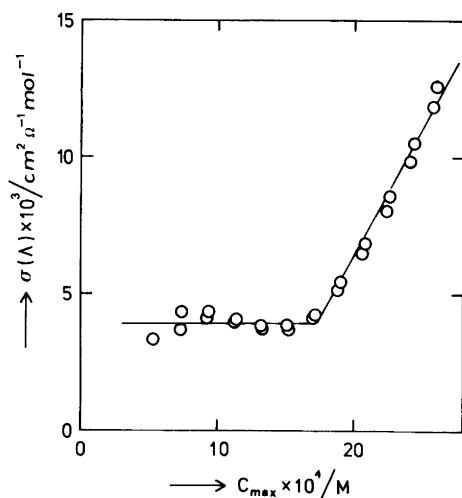


Fig. 1. Dependence of $\sigma(\Lambda)$ on maximum electrolyte concentration for application of the FHFP equation, eqn. (1), to conductivity data of NaI in 1-butanol at 25 °C.

$\sigma(\Lambda)$, i.e. the standard deviation between experimental and calculated Λ values, was obtained as a function of the upper limit of the concentration interval studied, see Fig. 1 according to which the fit of eqn. (1) to the experimental points deteriorates markedly at salt concentrations above $c = 17 \times 10^{-4}$ M. This effect may be taken as evidence of the formation of higher aggregates than ion pairs at concentrations above this value.

According to theory¹² the maximum concentration of negligible triple ion formation for 1:1-electrolytes in a solvent of relative permittivity, ϵ , at 25 °C is,

$$c_{\max} = 3.2 \times 10^{-7} \epsilon^3 \quad (3)$$

which for the system under investigation yields, $c_{\max} = 17.2 \times 10^{-4}$ M. The prediction according to eqn. (3) and the experimentally established concentration limit, cf. Fig. 1, are thus in complete agreement.

Application of eqn. (1) to the points within the free ion-ion pair range ($c \leq 17.132 \times 10^{-4}$ M; cf. Table 1) yielded: $\Lambda_{\infty} = 16.739 \pm 0.007 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$; $S = 82.82$; $E = 648.2$; $J_1 = 3413$; $J_2 = 20\,670$; and $K_A = 602 \pm 1 \text{ (M}^{-1}\text{)}$ where the errors quoted are standard deviations. Using these values of the constants eqn. (1) was extrapolated to the higher concentrations investigated ($c \geq 18.809 \times 10^{-4}$ M) to obtain the difference,

$$\Delta\Lambda = \Lambda(\text{exp}) - \Lambda(\text{calc}) \quad (4)$$

between experimental and calculated Λ values. The results in the last column of Table 1 reveal that for electrolyte concentrations above $c = 17 \times 10^{-4}$ M the difference $\Delta\Lambda$ is positive and increases with increasing concentration. An effect of this kind is to be expected in case of triple ion formation, cf. Refs. 13 and 14.

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