The Conductance of n-Butylammonium Picrate in Alcohols at 25°

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Summary The ion-pairing of n-butylammonium picrate in aliphatic alcohols has about the same value as that of tetra-alkyl ammonium picrates: solvation effects on the hydrogen-bonded solvent molecules on the cation increase dissociation of the primary ammonium salt.

THE extensive literature in the field of acid–base equilibria in aprotic organic solvents has recently been reviewed.[1] Use of conductance determinations to obtain ion-pair association data for ionophores is quite general. Comparison of the ion-pairing of substituted ammonium picrates in some aprotic solvents is then possible. Ion-pair association constants of completely alkylated cations are much lower than those of partially substituted ammonium picrates, but an exception to this rule is found in pyridine solvent.

Numerous conductance studies have been reported on tetra-alkylammonium salts in various solvents,[2] though the use of hydrogen bonded solvents is limited.[3] We therefore report the conductance behaviour of the n-butylammonium picrate in several alcohol solvent systems.

We measured the conductance of n-butylammonium picrate solutions in aliphatic alcohols with a Wayne–Kerr B 221 A Universal a.c. bridge. Dielectric-constant measurements were performed with a WTW Dipolmeter D.01, having a beat frequency of 2 MHz. Viscosities were measured with a Ubelhode Viscosimeter. Details of the experimental procedures will be described elsewhere.[4]

The experimental data were analysed with the Fuoss–Onsager equations[5] in the form:

$$\Lambda = \Lambda_0 - S(c\gamma)^{1/2} + Ec\gamma \log c\gamma + Jc\gamma - K_A c\gamma \Lambda f^2 \quad (1)$$

for associated electrolytes. It can be expressed by

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec \log c + Jc \quad (2)$$

for unassociated electrolytes.

These are the general conductance equations for 1 : 1 electrolytes at concentration at which κa does not exceed 0·2 and for solvents in which higher clusters than pairs do not form.

κ is the Debye–Hückel parameter;

a should be the centre to centre distance between anion and cation at contact in a pair.

S and E are theoretically predictable constants (given a preliminary value of Λ_0), J and K_A are, from the mathematical point of view, arbitrary constants to be computed from the conductance data.

γ is the fraction of salt present as free ions. The association constant K_A describes the association of ions to non-conducting pairs:

$$K_A = \frac{1-\gamma}{c\gamma^2 f^2} = \frac{4Na^3}{3000} \exp \frac{e^2}{a\,D\,kT}$$

The mean ion activity coefficient f was computed from the iterated a obtained from the J coefficient. No viscosity correction was applied. The usual correction does not alter the value of Λ_0 and K_A, it changes only slightly the value of J and consequently of a.

The conductance parameters can be obtained from least-squares analyses. The computer programs have been described by Kay.[6]

TABLE 1

Conductance parameters for n-butylammonium picrate solutions at 25°

Solvent	Λ_0 (ohm^{-1}cm^{2}mole^{-1})	a (Å)	K_A (l mole^{-1})	$\sigma\Lambda$
MeOH	99·40 ± 0·16	1·3 ± 0·1	—	0·26
	98·78 ± 0·30	3·17 ± 0·70	18 ± 6	0·33
EtOH	44·88 ± 0·11	2·84 ± 0·30	83 ± 9	0·11
$\mathrm{Pr^nOH}$	23·28 ± 0·05	4·04 ± 0·14	403 ± 9	0·05
$\mathrm{Bu^nOH}$	15·81 ± 0·05	4·42 ± 0·20	1062 ± 23	0·06
$\mathrm{Bu^sOH}$	13·11 ± 0·04	6·56 ± 0·16	4036 ± 40	0·02

The parameters obtained are given in Table 1, σ_Λ is the standard deviation of the individual points. For the methanol solutions the first entry refers to equation (1) and the second to equation (2). For the higher alcohols, results from the associated electrolyte conductance equation are alone listed, owing to the fact that the σ_Λ agreement was much better.

Small values of K_A should be interpreted with reserve; the results obtained in methanol are not quite decisive with respect to the amount of association in this solvent. In the higher alcohols the n-butylammonium picrate is definitely associated. The slope of a plot of log K_A against $1/D$ is constant; its value predicted by the theory[7] should be proportional to $1/a$.

From the slope of the plot, a value of a = 3·1 Å is obtained, and from the intercept a value of a = 2·8 Å is obtained (eq. 3).

The distance parameters deduced from the J coefficient of the conductance equations are, however, different, increasing with the J value. This has long been recognized[8] and has prompted various re-investigations[9] of the model and of the formulations used in deriving the conductance equations.

Comparison of the conductance parameters for the n-butylammonium picrate with those obtained in the same solvents for tetramethylammonium picrate (see Table 2). The two salts have the same molecular weight) shows no definite difference in the association constants in methanol or ethanol solvent. It was previously shown that in methanol all of the tetra-alkylammonium picrates are associated to the same degree.[3b]

Yet in general, the ion-pair dissociation constants of tetrasubstituted ammonium picrates are much greater than those of incompletely substituted picrates, not only in low-dielectric-constant solvents (benzene, chlorobenzene, ethylene chloride) but also in nitrobenzene ($D = 34{\cdot}82$).

Solvation effects of the hydrogen-bonded solvent molecules on the monosubstituted cations should increase dissociation of the salt pair. Interaction of the alcohol solvent molecules with the hydrogens of the partially substituted alkylammonium picrates should likewise weaken the bond energy of the salt. Both effects increase free ion concentrations.

The distance parameter of about 3 Å is, however, low and computing the infinite dielectric constant ion-pair association constant, neglecting hydrogen-bond effects, should give about the same value as the experimental one.

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TABLE 2

Ion-pair association constants of tetramethylammonium and n-butylammonium picrates at 25°

Solvent (D)		Salt	K_A
Nitrobenzene	(34·82)	Me_4NPi	25[a]
		$BuNH_3Pi$	6·450[b]
			6·620[c]
MeOH	(32·63)	Me_4NPi	13 ± 2[d]
			11 ± 2[e]
			10·5 ± 0·6[e]
			13·6[f]
		$BuNH_3Pi$	18 ± 6
EtOH	(24·30)	Me_4NPi	110 ± 40[g]
		$BuNH_3Pi$	83 ± 9

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