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Structure of Ion Pairs. Rubidium Iodide in n-Alcohols at 25 °C

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Recently improved conductance theory (Fuoss 1975) has been used to interpret conductance data for rubidium iodide in the four lowest n-alcohols at 25 °C. The experimental association constant and the Bjerrum theory were combined to determine the minimum distance between centres of charge in the ion pair. It is concluded that the character of the ion pair gradually changes from loose to tight with increasing length of the carbon chain in the solvent molecule. Evidence for the existence of contact ion pairs in butanol are presented. The method of Robinson and Stokes is used to introduce a correction factor into Stokes' law in estimating, by means of mobility data for tetra-substituted ammonium ions, the radii of the solvated rubidium and iodide ions. Empirical linear relationships between the crystallographic radius of the tetra-substituted ammonium ion and the Stokes' law radius are presented. The solvation numbers of the free rubidium and iodide ions decrease from about 3–4 for methanol as solvent to about 2 for butanol.

During investigations of the effect of ion agglomeration on the kinetics of nucleophilic displacement reactions, *cf.* Ref. 1, a large body of conductance data for alkali iodides in n-alcohols have accumulated. This collection of data may be used to derive comprehensive information regarding various interactions in these solutions. The present study, in which electrical conductance data for rubidium iodide in the four lowest n-alcohols at 25 °C are interpreted in terms of modern conductance theory,[2,3] was primarily undertaken to investigate how the structure of the ion pairs is affected by the character of the solvent.

CONDUCTANCE THEORY

As pointed out by Fuoss,[2] who has recently developed a new theory for the conductance of symmetrical associated electrolytes, at most three parameters may be provided by conductance data for a given system. Two of these parameters, *viz.* Λ_∞ (limiting molar conductivity) and K_A (ion pair association constant) depend directly on molecular parameters while the third parameter, R, is a distance. This parameter comes in through the boundary conditions used in evaluating the constants of integration in the treatment of long-range effects (relaxation field and electrophoretic countercurrent). In earlier more primitive models, $R=a$, *i.e.* R is identified as the center-to-center distance at contact of cation and anion. In the Fuoss revised model R is uncoupled from short-range effects through a theory for the long-range effects in which the boundary conditions are independent of details of molecular structure. The distance parameter, R, is defined as the distance, r, from a reference ion beyond which continuum theory may be applied. Those ions which fulfil the condition, $a \leq r \leq R$, and for which unique partners can be statistically defined, are defined as paired.

In its most compressed form the Fuoss conductance equation from 1975 ("F75" equation) is,[2,3]

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

where Λ and Λ_∞ are the molar conductivities at concentration, c, and at infinite dilution, respectively, α is the degree of dissociation, ΔX is the relaxation field, X is the external field, and $\Delta\Lambda_e$ is the decrease in molar conductivity due to the electrophoretic countercurrent. For 1:1-electrolytes we have,

$$\frac{\Delta X}{X} = \frac{2\tau[e^{(1-q)t}-1]}{3t(1+t)} - \frac{\tau^2 \ln t}{3\mu^2} - \frac{\beta^2 t^2 F_2}{R^2} - \frac{\beta^3 t^2 F_3}{R^3} \qquad (2)$$

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$$\Delta\Lambda_e = \beta_0(c\alpha)^{\frac{1}{2}}\left[\frac{1}{1+t} + \frac{\tau(1+\mu)\ln t}{4\mu^2} + tH_1 + \frac{t\beta H_2}{R}\right] \quad (3)$$

where, $\tau = \beta\varkappa/2$, $\beta = e^2/\varepsilon kT$, where e = protonic charge, ε = relative permittivity of the solvent, k = Boltzmann's constant, and T = absolute temperature, $\varkappa^2 = 8\pi n_0\alpha e^2/\varepsilon kT$, where n_0 = number of ions of a given sign per unit volume, $q^2 = 1/2$, $t = \varkappa R$, $\mu = (1+\varkappa R)\exp(-\varkappa R)$, and $\beta_0 = 82.50/\eta(\varepsilon T)^{\frac{1}{2}}$, where η is the viscosity of the solvent. F_2, F_3, H_1, and H_2 are functions of $\varkappa R$ which, as regards F_3 and H_2, are of different forms for different intervals of $\varkappa R$.

CALCULATIONS

The parameters Λ_∞ and K_A were derived from eqn. (1) combined with the mass action law for the equilibrium between free and paired ions,

$$K_A = (1-\alpha)/c\gamma^2\alpha^2 \quad (4)$$

and the Debye-Hückel equation for the mean activity coefficient of free ions,

$$\ln\gamma \simeq \ln f = -\beta\varkappa/2(1+\varkappa R) \quad (5)$$

where γ and f denote the mean molar and rational activity coefficients, respectively.

The distance parameter, R, was set equal to the Bjerrum radius, $\beta/2$; *cf.* Ref. 2.

A computer programme was developed to determine, by means of a Cyber 172 computer, the values of Λ_∞ and K_A which minimize $\sigma(\Lambda)$, the standard deviation between measured and calculated Λ values. The programme is similar to the second of those outlined in Ref. 4.

The calculations are based on electrical conductance data at 25 °C for rubidium iodide in methanol and ethanol according to Ref. 5, and in 1-propanol and 1-butanol according to Refs. 6 and 7, respectively.

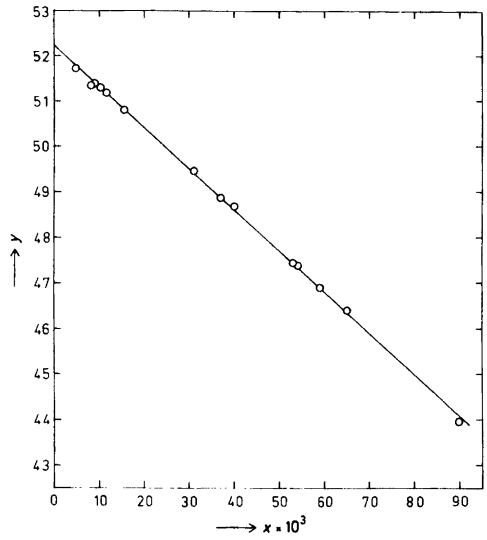

Fig. 1. Graph according to eqn. (6) for RbI in ethanol at 25 °C.

The values, $\varepsilon = 32.70$, 24.55, 20.33, and 17.51 for the relative permittivity[8] and $\eta = 0.005445$, 0.01078, 0.01952, and 0.0246 P for the viscosity of methanol, ethanol,[8] 1-propanol,[9] and 1-butanol,[10] respectively, were used in the calculations.

Eqns. (1) and (4) may be combined to yield a linear relationship,

$$y = \Lambda_\infty - K_A x \quad (6)$$

where,

$$y = (\Lambda + \Delta\Lambda_e)/(1 - \Delta X/X) \quad (7)$$

$$x = c\alpha\gamma^2\Lambda/(1 - \Delta X/X) \quad (8)$$

Estimates of the standard deviations in Λ_∞ and K_A were obtained by application of eqn. (6) to the final y and x values computed using the method of

Table 1. Data for RbI in n-alcohols at 25 °C derived using the F75 equation.[2]

Solvent	$\beta/2$ Å	K_A M^{-1}	Λ_∞ S cm^2 mol^{-1}	$\sigma(\Lambda)$ S cm^2 mol^{-1}
MeOH	8.57	12±0.3	119.73±0.04	0.09
EtOH	11.41	91±1	52.23±0.03	0.06
PrOH	13.78	424±2	26.96±0.02	0.02
BuOH	16.00	1593±6	18.40±0.02	0.01

least squares. A graph according to eqn. (6) for ethanol as solvent medium is shown in Fig. 1.

A summary of the results of these calculations is given in Table 1.

DISCUSSION

Revised values of Λ_∞. In the following discussion values of Λ_∞, reevaluated by means of the F75 equation from literature data for several univalent electrolyte systems at 25 °C, will be used. These systems include potassium chloride[11] and iodide[5] in methanol, sodium chloride[12] and iodide[5] in ethanol, sodium iodide in 1-propanol,[6] and tetra-substituted ammonium iodides in methanol,[13] ethanol, 1-propanol,[9] and 1-butanol.[14] The computation of Λ_∞ was performed as outlined above using $R=\beta/2$ for the distance parameter.

Ionic conductances. For methanol as solvent at 25 °C $\Lambda_\infty(\mathrm{KCl})=104.90$ S cm^2 mol^{-1} and the cation limiting transport number, $t_\infty^+(\mathrm{KCl})=0.5001$ according to Ref. 15, yielced $\lambda_\infty(\mathrm{K}^+)=52.46$, which combined with $\Lambda_\infty(\mathrm{KI})=115.58$ gave $\lambda_\infty(\mathrm{I}^-)=63.12$. A similar procedure for ethanol as solvent using $\Lambda_\infty(\mathrm{NaCl})=42.25$, $t_\infty^+(\mathrm{NaCl})=0.4813$ according to Ref. 16, and $\Lambda_\infty(\mathrm{NaI})=47.69$ gave $\lambda_\infty(\mathrm{I}^-)=27.36$. The value, $\lambda_\infty(\mathrm{I}^-)=13.87$, referring to 1-propanol, was calculated from $\Lambda_\infty(\mathrm{NaI})=24.47$ and the transport number,[17] $t_\infty^-(\mathrm{NaI})=0.567$. For 1-butanol the value, $\lambda_\infty(\mathrm{I}^-)=9.66$ has been reported.[18]

These results, combined with the Λ_∞'s for rubidium iodide in Table 1, gave the limiting molar conductivities of the rubidium ion in the alcohols concerned; see Table 2 in which the radii of the iodide and rubidium ions according to Stokes' law,[19]

$$r_s = |z|F^2/(6\pi L\eta\lambda_\infty) \qquad (9)$$

are included. In eqn. (9) z is the valency of the ion, F is the Faraday constant, and L is the Avogadro constant.

Solvation of unpaired ions. Robinson and Stokes[19] have proposed a method of estimating the radii of solvated ions using a modified form of Stokes' law. In this method correction factors to Stokes' law are calculated on basis of mobility data for tetra-substituted ammonium ions (Q_4N^+), the size of which may be estimated, *e.g.* from bond-lengths and angles. These large ions, which are of low surface charge density, would interact only weakly with the solvent molecules. A method of this kind will be used below to estimate the sizes of solvated rubidium and iodide ions in the alcohols under investigation.

Limiting molar conductivities, $\lambda_\infty(Q_4N^+)$, of tetra-substituted ammonium ions were calculated

Table 2. Limiting ionic conductivities and Stokes' radii in n-alcohols at 25 °C.

Solvent	$\lambda_\infty(\mathrm{I}^-)$ S cm^2 mol^{-1}	$\lambda_\infty(\mathrm{Rb}^+)$ S cm^2 mol^{-1}	$r_s(\mathrm{I}^-)$ Å	$r_s(\mathrm{Rb}^+)$ Å
MeOH	63.12	56.61	2.39	2.66
EtOH	27.36	24.87	2.78	3.06
PrOH	13.87	13.09	3.03	3.21
BuOH	9.66	8.74	3.45	3.81

Table 3. Limiting molar conductivities at 25 °C derived from literature data[9,13,14] using the F75 equation.[2] Am = n-C_5H_{11}.

$\Lambda_\infty(Q_4NI)$ S cm^2 mol^{-1}	MeOH	EtOH	PrOH	BuOH
Me_4NI	131.83	–	–	–
Et_4NI	–	56.45	29.02	19.56
Pr_4NI	109.10	50.21	26.34	18.20
Bu_4NI	101.97	46.92	24.79	17.24
Am_4NI	97.99	–	–	–

Table 4. Limiting ionic conductivities and Stokes' radii in n-alcohols at 25 °C.

Solvent	Ion	$\lambda_\infty(Q_4N^+)$ S cm^2 mol^{-1}	r_s Å
MeOH	Me_4N^+	68.71	2.19
	Pr_4N^+	45.98	3.28
	Bu_4N^+	38.85	3.88
	Am_4N^+	34.87	4.32
EtOH	Et_4N^+	29.09	2.61
	Pr_4N^+	22.85	3.33
	Bu_4N^+	19.56	3.89
PrOH	Et_4N^+	15.15	2.77
	Pr_4N^+	12.47	3.37
	Bu_4N^+	10.92	3.85
BuOH	Et_4N^+	9.90	3.37
	Pr_4N^+	8.54	3.90
	Bu_4N^+	7.58	4.40

Table 5. Estimates[19] of the crystallographic radii of tetra-substituted ammonium ions.

Ion	Me_4N^+	Et_4N^+	Pr_4N^+	Bu_4N^+	Am_4N^+
r/Å	3.47	4.00	4.52	4.94	5.29

using the data for $\lambda_\infty(I^-)$ in Table 2 and $\Lambda_\infty(Q_4NI)$ in Table 3. The values obtained are given in Table 4 together with Stokes' law radii, r_s, derived from eqn. (9).

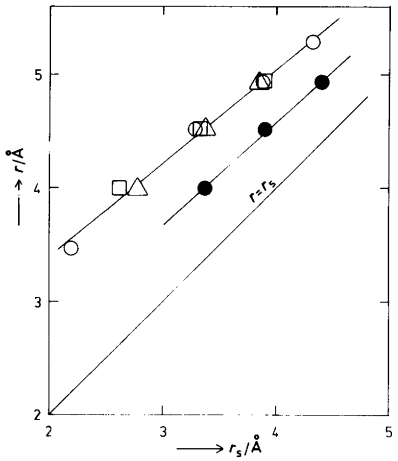

Fig. 2. Dependence of crystal radius on Stokes' radius for tetra-substituted ammonium ions in methanol (open circles), ethanol (squares), 1-propanol (triangles), and 1-butanol (full circles) at 25 °C.

The crystallographic radii estimates, r, of tetra-substituted ammonium ions in Table 5 were taken from the monograph of Robinson and Stokes.[19]

Graphs of the dependence of r on r_s are shown in Fig. 2. Linear relationships between these quantities were observed. Application of the method of least squares to the points referring to methanol, ethanol, and 1-propanol yielded the following relationship between r and r_s,

$$r = 1.741 + 0.828 r_s \qquad (10)$$

which is valid in the interval, $2.2 < r_s < 4.5$ Å, while the relation,

$$r = 0.934 + 0.913 r_s \qquad (11)$$

which may be used in the interval, $3.3 < r_s < 4.5$ Å, was obtained for 1-butanol as solvent medium.

We may now employ the r_s values in Table 2 and eqns. (10)–(11) to estimate the sizes of the solvated entities. The results in Table 6 indicate that the "radii" of the solvated rubidium and iodide ions increase with increasing length of the carbon chain in the solvent molecule.

The average number, n, of alcohol molecules involved in the solvated entity was estimated on the basis of its volume neglecting the volume of the bare ion itself and ascribing the solvating alcohol molecules their ordinary liquid volumes, *i.e.* neglecting electrostriction. The solvation numbers derived by this means for the rubidium and iodide ions are quoted in Table 6.

For the rubidium ion the solvation number decreases from about 4 for methanol to about 2 for butanol. The same tendency of decreasing solvation number with increasing length of the carbon chain in the solvent molecule is observed for the iodide ion for which the solvation numbers are slightly less than those of the rubidium ion.

Table 6. Corrected Stokes' law radii and solvation numbers in n-alcohols at 25 °C.

Solvent	$r(I^-)$ Å	$r(Rb^+)$ Å	$n(I^-)$	$n(Rb^+)$
MeOH	3.72	3.94	3.2	3.8
EtOH	4.04	4.27	2.8	3.3
PrOH	4.25	4.40	2.6	2.9
BuOH	4.08	4.41	1.9	2.4

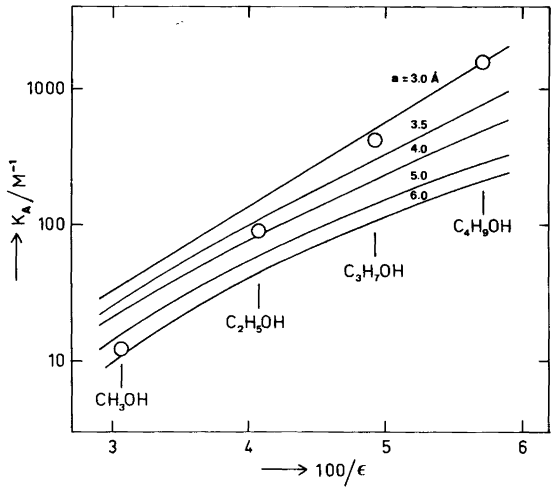

Fig. 3. Dependence of ion pair association constant on relative permittivity of the solvent for univalent electrolytes at 25 °C. The fulldrawn curves are based on eqn. (12). The circles represent experimental values for RbI.

Ion pair structure. According to Bjerrum[20] two oppositely charged ions of valencies z_1 and z_2 constitute an ion pair if the distance, r, between their charges is less than a critical distance, $|z_1 z_2|\beta/2$, which is the distance at which their mutual electrical potential energy is equal to $2kT$.

The minimum distance, a, between the charges in the ion pair may be calculated by equating the measured K_A value and the theoretical value,[20]

$$K_A = \frac{4\pi L}{1000} \int_a^{\beta/2} r^2 e^{\beta/r} dr \qquad (12)$$

referring to univalent electrolytes. By this means we may now investigate how the minimum distance depends on the character of the solvent.

Graphical representations of the dependence of the theoretical K_A according to eqn. (12) on the relative permittivity of the solvent are shown in Fig. 3 for different (constant) values of the minimum ion-ion distance, a, in the ion pair. The experimental K_A's are denoted by circles.

Table 7. Minimum center-to-center distance for RbI in n-alcohols at 25 °C according to eqn. (12).

Solvent	MeOH	EtOH	PrOH	BuOH
a/Å	5.8	3.9	3.1	3.0

From this graph it can be immediately seen that the minimum distance, a, is by no means independent of the solvent but decreases gradually with decreasing permittivity, *viz.* from $a = 5.8$ Å for methanol to $a = 3.0$ Å for 1-butanol, *cf.* Table 7. Hence, the solvent separation of the paired ions decreases with decreasing permittivity of the solvent, *i.e.* the character of the ion pairs changes from loose to tight when going from methanol to 1-butanol. In this connection we may recall the discrimination between contact ion pairs and solvent-separated ion pairs of Winstein *et al.*[21]

The crystallographic radii[19] of the rubidium and iodide ions amount to 1.48 and 2.16 Å, respectively. Hence, for these ions in contact the distance between their charges is 3.6 Å. This value exceeds slightly the minimum ion-ion distance in the ion pair, $a = 3.0$ Å, derived from the experimental data for 1-butanol as solvent. This finding might be taken as evidence that rubidium iodide forms contact ion pairs in this solvent.

For ethanol, propanol, and 1-butanol as solvent media the minimum center-to-center distance between the ions in the ion pair is significantly less (by 4–6 Å) than the radii sum of the solvated rubidium and iodide ions, see data in Tables 6–7. Hence, we might conclude that the ions undergo partial desolvation in forming ion pairs in these solvents.

For methanol as solvent, on the other hand, the minimum distance of $a = 5.8$ Å is only slightly less than the radii sum of the solvated free ions (7.7 Å). It seems therefore that the rubidium iodide ion pair in methanol consists of almost fully solvated ions.

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