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Ionic Equilibrium and Ionic Conductance in the System Tetra-*Iso*-Pentyl Ammonium Nitrate—*p*-Azoxyanisole†

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Abstract—The variation of the current with concentration of solute in the system tetra-*iso*-pentyl ammonium nitrate (TIPAN)—*p*-azoxyanisole is shown to depend on ionic equilibrium. Variation of the current with temperature depends almost entirely on the fluidity of the solvent; in the nematic range, the fluidity depends on the orientation of the solvent with respect to the current direction. The extent of this orientation depends on solute concentration—an increase in solute concentration causes an increase in fluidity.

Introduction

The pioneering work of Fuoss and Kraus$^{(1-5)}$ on the influence of the solvent dielectric constant on the conductance of ionophoric solutions is well-known. For solvents with dielectric constants under 10, the equivalent conductance, Λ, depends on the concentration of the solution (c) in the following way:

$$\Lambda = \Lambda_0 \sqrt{\frac{K}{c}} + \lambda_0 k \sqrt{cK} \tag{1}$$

where Λ_0 is the limiting conductance for the electrolyte A^+B^-,

K is the equilibrium constant for the association reaction $A^+B^- \rightleftarrows AB$,

λ_0 is the limiting conductance for the species A_2B^+ and AB_2^- formed by the reactions $AB + A^+ \rightleftarrows A_2B^+$ and $AB + B^- \rightleftarrows AB_2^-$ whose equilibrium constant is k.

The value of K depends on two parameters, the dielectric constant

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ϵ of the solvent and the " ion size " a.

$$K^{-1} = \frac{4\pi N^0 a^3}{1000b}\left(1 + \frac{4}{b} + \cdots\right)e^b \qquad (2)$$

where N^0 is Avogadro's number and $b = e^2/a\epsilon kT$. The coefficient b represents the ratio of electrostatic to thermal energy. Applying this result to experimental data for the system tetra-*iso*-pentyl ammonium nitrate (TIPAN) in dioxane water mixtures, in which the dielectric constant varied from 2 to 80, the measured values of the equilibrium constant (which varied over 15 powers of 10) were fitted to the data with a single value of the parameter a, 6.40 Å.

In the range of concentrations in which Λ is proportional to $c^{-\frac{1}{2}}$, that is below the minimum, the current may be written

$$J = \frac{c}{1000}\Lambda_0\sqrt{\frac{K}{c}}\,\frac{VA}{\mathrm{d}} \qquad (3)$$

where c is in moles/liter,
V is the voltage, A the cell area and
d the electrode spacing.

At constant c, the current is thus proportional to $\Lambda_0\sqrt{K}$, Λ_0 being the fluidity contribution, and $\sqrt{K}$ representing the variation of the degree of association. The value of Λ_0 may be obtained from the Walden's rule(6,7) constant W (almost independent of temperature) and the solvent viscosity η through the relation $\Lambda_0 = W\eta^{-1}$.

Experimental Procedure

Conductivity cells were made using carefully cleaned tin oxide on quartz, of area 2.25 cm^2 and a spacing of 2.5×10^{-3} cm. The currents were measured with a Ballantine AC voltmeter using a proper load resistor which gave a 0.1 V drop, at voltages of 1 Vrms 60 Hz. This frequency was high enough to avoid polarization effects, but below the frequency at which the capacitative effects would contribute to the current. No significant difference was noticed in Λ measured at 1 V and at 10 V; 1 volt was chosen because it is significantly below the threshold voltage for appearance of orientation phenomenon.(8)

The cells were prepared by filling above the isotropic temperature in a nitrogen atmosphere. The *p*-azoxyanisole was a zone refined sample; the tetra-*iso*-pentyl ammonium nitrate was obtained from

Eastman and purified once by recrystallization from a mixture of anhydrous ethyl acetate and petroleum ether.

Measurements of the temperature variation of current were made with a calibrated hot stage microscope, the isotropic temperature and the melting point furnishing additional calibration points. Measurements were taken both with rising and falling T. Conductance of the undoped *p*-azoxyanisole was less than 5% of the lowest value, that of the 3.7×10^{-5} m/l sample.

Results

Figure 1 shows the equivalent conductance for tetra-*iso*-pentyl ammonium nitrate in *p*-azoxyanisole at 152 °C (isotropic range) plotted on a double log graph against the concentration in moles per liter. Note the $c^{-\frac{1}{2}}$ dependence, but the absence of any minimum in Λ. This may be due to neglecting variation in current due to changes in orientation with solute concentration and some ruggedness in the in the data. On the same graph are placed data(1) for the equivalent conductance of the same solute with the solvent a mixture of dioxane and water of dielectric constant 5.84 (upper curve) and 4.4 (lower

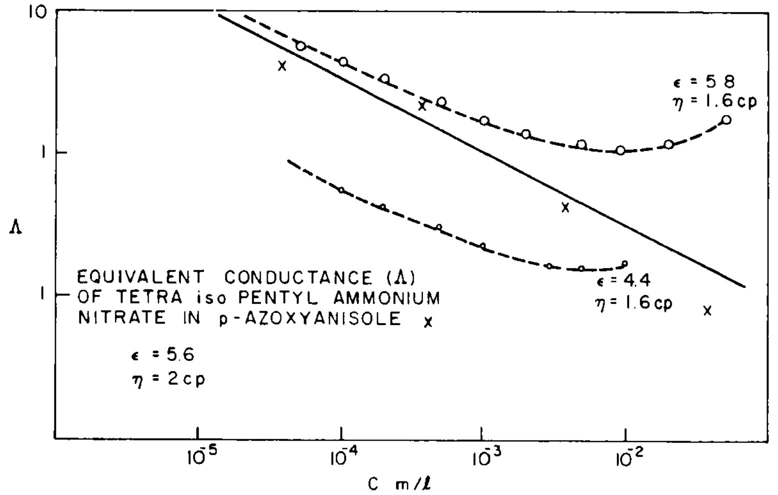

Figure 1. Equivalent conductance Λ of tetra-*iso*-pentyl ammonium nitrate in *p*-azoxyanisole as a function of concentration. $\Lambda = \alpha\mu N^{\circ}e$ where α is the fraction of dissolved material in ionic form, μ is the mobility (in cm²/Vsec), N° is Avogadro's number and e the electronic charge.

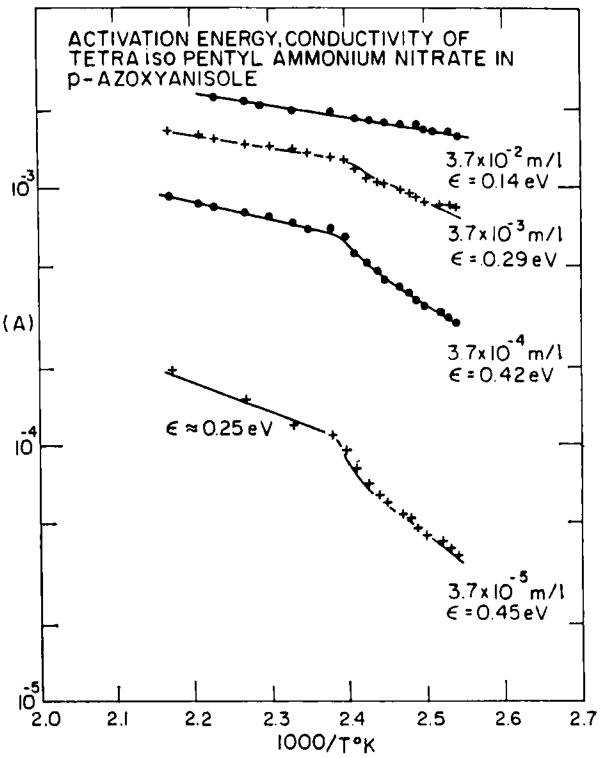

Figure 2. Current vs. $1/T$, activation energy for conductance as a function of concentration of TIPAN.

curve), and solvent viscosity 1.6 c poise. The data for the TIPAN in p-azoxyanisole, with viscosity of 2 c poise(9) and dielectric constant 5.6,(10) fits between the two curves. The $c^{-\frac{1}{2}}$ variation of Λ with c is certainly indicative of ionic equilibrium. (The appearance of a minimum in the curve would certainly be an additional proof.) The value of the equilibrium constant was calculated from the current (Fig. 2) in the isotropic region using known values of the solvent viscosity(9) and a Walden's constant of 0.5. Table 1 shows these results. The constant at each temperature was obtained by averaging the result at four concentrations. Values at $T = 161$ °C for concentrations at 3.7×10^{-2}, 10^{-3}, 10^{-4} and 10^{-5} m/l were respectively 5.4×10^{-7}, 8×10^{-7}, 2.4×10^{-6}, and 1.55×10^{-6}.

Note the relative constancy of K, which would indicate a constant value of b with variation in T. Assuming an ion size of 6.4 angstroms,

TABLE 1 Equilibrium Constants for Ion Association, Isotropic Region

T °C	K_{exp}(average)	b calculated	K calculated
152	1.5×10^{-6}	11.85	3.0×10^{-6}
161	1.32×10^{-6}	11.8	3.12×10^{-6}
170	1.25×10^{-6}	11.7	3.45×10^{-6}
181	1.2×10^{-6}	11.6	3.6×10^{-6}

the value of b at these four temperatures was calculated using values of the dielectric constant(10) extrapolated to slightly higher temperatures, and used to calculate K by (Eq. 2). These values appear in the third and fourth columns of Table 1. The agreement is within a factor of three which is reasonably good.

Variation of the Current with Temperature

Figure 2 shows the current in the sandwich cells as a function of concentration of TIPAN and of temperature as an activation energy plot. A good deal of structure is noticeable particularly in the region of the nematic-isotropic transition. Note also that the activation energy for the conductance in the nematic region shows a decrease with increasing TIPAN concentration. A calculation of the equilibrium constant was made using reported values of the two dielectric constants of the nematic liquid, and averaging them using the relation $\epsilon_a = (2\epsilon_2 + \epsilon_1)/3$. The a value was 6.4 angstroms. These results appear in Table 2.

TABLE 2 Equilibrium Constants, Nematic Range

T °C	K calculated	b	K experimental
119	6×10^{-6}	11.10	1.59×10^{-6}
127	5.2×10^{-6}	11.27	1.55×10^{-6}
134	5×10^{-6}	11.32	1.51×10^{-6}

Because of the almost constant value of K, the variation in the current must lie almost wholly in the variation of the solvent fluidity. A comparison with the variation of the solvent fluidity, Fig. 3, is illuminating. The fluidity of the solvent (the reciprocal of the

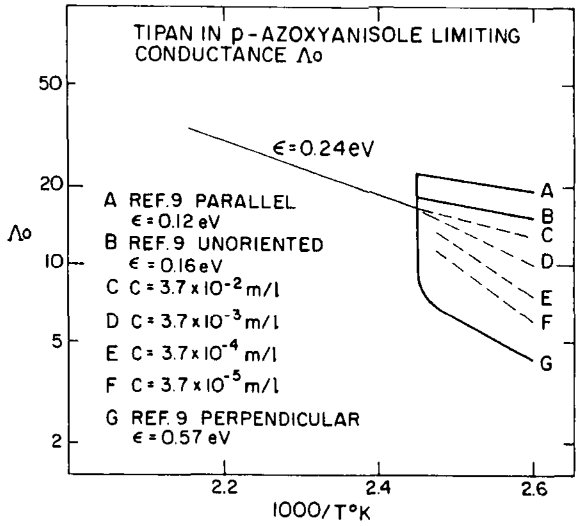

Figure 3. Fluidity of *p*-azoxyanisole. Curves A, B and G adopted from Reference 9. Curves C, D, E and F (shown dotted) represent super position of Fig. 2 upon Fig. 3 with the isotropic range made to coincide.

viscosity)(9) is shown as an activation energy plot. In the nematic range there are two extremes, the flow parallel to the orientation (" flow oriented ") which apparently is the high fluidity direction, activation energy 0.12 eV, curve A, and the " gradient oriented " in which the flow is perpendicular to the orientation. The latter has a lower fluidity and a higher activation energy of 0.57 eV, curve G. (The activation energy for the isotropic liquid is 0.24 eV.)

Thus, in order to calculate an equilibrium constant, a value of Λ_0 must be chosen which reflects the orientation (or degree of disorder) of the fluid. Since the curves agree in activation energy in the isotropic region, the current activation energy plots were superposed on the fluidity, the isotropic regions made to coincide. These are shown dotted in Fig. 3. Values of Λ_0 could then be obtained directly from the plot which depended on temperature as well as concentration and values of K were calculated. These appear in Table 2. Typical values of K at $T = 127°$ at $c = 3.7 \times 10^{-2}$, 10^{-3}, 10^{-4}, and 10^{-5} were respectively 7.4×10^{-7}, 1.32×10^{-6}, 3.1×10^{-6}, and 1.04×10^{-6}. Again, the agreement is satisfactory. Apparently then, in the nematic range, the variation in conductance with temperature is also a function of the concentration of the solute, acting through the fluidity variation in the liquid. The mechanism of the effect is still unclear, but may reside in the ionic nature of the solute; in other work, the addition of a non-electrolyte had no effect on the bulk fluidity.(11) Visual examination of the samples indicate that all are homeotropic but between crossed polarizers show birefringence; application of 1V shows no visual change. This indicates that the variation in fluidity can reside in either a variation in the bulk order, viz, a decrease in the S parameter with increasing solute concentration, or a reorientation of the optical axis which may be caused by wall forces. The change in S has been shown to be proportional to the mole fraction of the second (nematic) component,(12) but no ionic effects have been reported.

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