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NON-AQUEOUS SOLVENT ELECTROCHEMICAL SYSTEMS

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INTRODUCTION

A considerable amount of work on non-aqueous electrolyte systems has been reported in the past year. Most of that which might be of interest to us here is of a fundamental nature and deals with the conductivities of various systems under a variety of conditions. We have attempted to include only those systems which appear to show something fundamentally new or which have practical significance. Where possible we have correlated the results of our experiments at the University of Missouri with those reported in the literature. All data pertaining to cell systems were taken in our laboratories.

WALDEN RULE VARIATIONS

The Walden rule is usually interpreted to mean that the product, $\Lambda \cdot \eta$, is constant for a given solute and is independent of temperature and solvent, provided no ion solvation occurs. Walden found that the value of this product is 0.563 for tetra-methyl ammonium sulfate in a number of solvents and suggested that smaller products would indicate solvation.

The product, $\Lambda \cdot \eta$, in pyridine and in aniline is greater than 0.563. Elliott and Fuoss¹ have suggested that a large product would appear when the solvent molecules are large enough to permit the solute ions to slip between them without overcoming the macroscopic viscosity of the solvent. Yet, pyridine and aniline cannot fall into this classification, because these molecules are no larger than the solute ions.

French and Singer² in their work on picrates in solvents consisting of phthalates of various sizes, found that the value of $\Lambda \cdot \eta$ decreased as the solvent molecule became larger. Since dimethylphthalate, the smallest solvent molecule used, has a high dipole moment, but low dielectric constant, French and Singer believe that the solvent molecules associate into a structure which tends to shield the solvent dipoles. As the solvent molecules increase in size, this type of association becomes less likely and there is greater possibility of solvent-solute association instead of solvent-solvent association. It would appear, then, that Walden observed constant solvation rather than no solvation.

Amis³ suggests that dissolved ions are selectively solvated in mixed solvent systems. He presents the equation for the limiting equivalent conductance for a

$$1-1 \text{ salt as } \Lambda_0 = \frac{\epsilon F}{1800\pi\eta} \left(\frac{r_+^0 + r_-^0}{r_+^0 r_-^0} \right) \quad (1)$$

where $\left(\frac{r_+^0 r_-^0}{r_+^0 + r_-^0} \right)$ is defined as the *r-function*.

ξ , F and η are the electronic charge, the Faraday, and the viscosity, respectively. Walden's rule would be valid if the *r-function* were a constant. Figure 1 shows that the *r-function* is not constant but increases very rapidly as the relative amount of water in the solvent

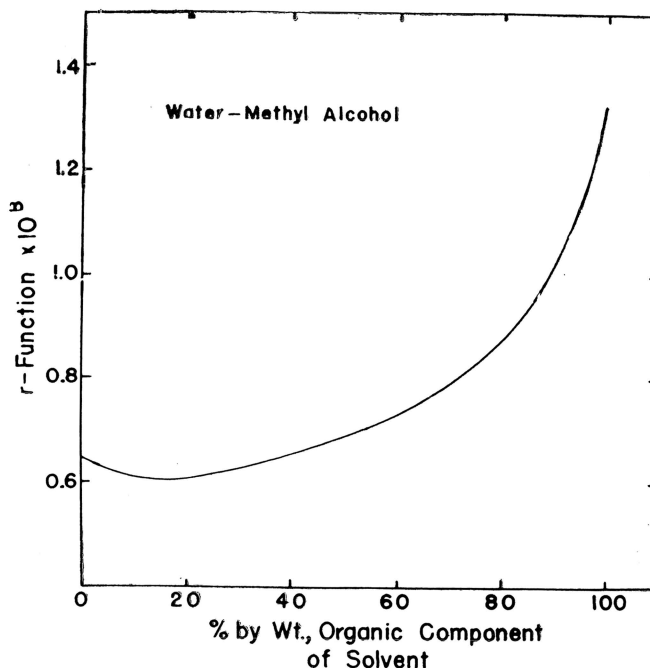


Figure 1. Effect of Water on Solvation in Methanol

decreases. Amis infers that water will preferentially interact with the solute. He derives an expression for a 1-1 electrolyte:

$$r_s = \left(\frac{1800\pi\eta K \mu \Lambda_0}{DF} \right)^{1/3} \quad (2)$$

where

$$F = \frac{2z_1 \epsilon \mu \cos \theta}{D r_s^3} \quad (3)$$

K is a constant and r_s is the distance between the ion and the dipole at which the force is F . If variation in D and μ are comparable, r_s might remain fairly constant.

Then

$$\frac{\Lambda_0 \eta \mu}{D} = \text{constant} \quad (4)$$

Amis' data agree better with equation (4) than with Walden's rule. However, the development of equation (4) depends on the constancy of μ/D ; yet, if this is true, the equation reduces to an expression of Walden's rule. Probably the fact that r_s depends on $(\mu/D)^{1/2}$ permits the approximation to be reasonably good.

CONDUCTIVITY IN NON-AQUEOUS SYSTEMS

Numerous papers have been published in the past year on conductivities in non-aqueous systems. Only a few of these report new fundamental ideas.

Sears and co-workers^{4,5,6} found several systems in which the plot of $\log \Lambda$ versus $1/T$ was linear at constant concentration, provided the concentration did not exceed $2 \times 10^{-2} M$. For a given salt and solvent, the slope of this plot was constant for each concentration.

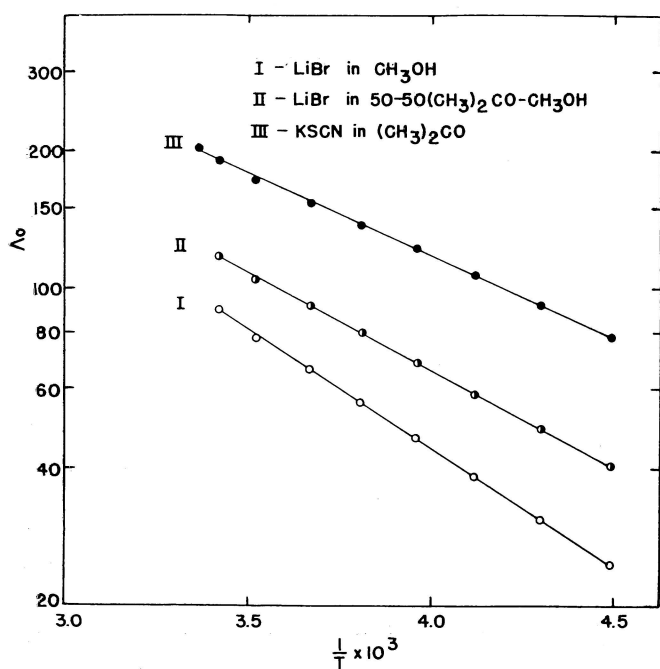


Figure 2. Relationship Between Temperature and Limiting Equivalent Conductance in Alcohol and Acetone Systems

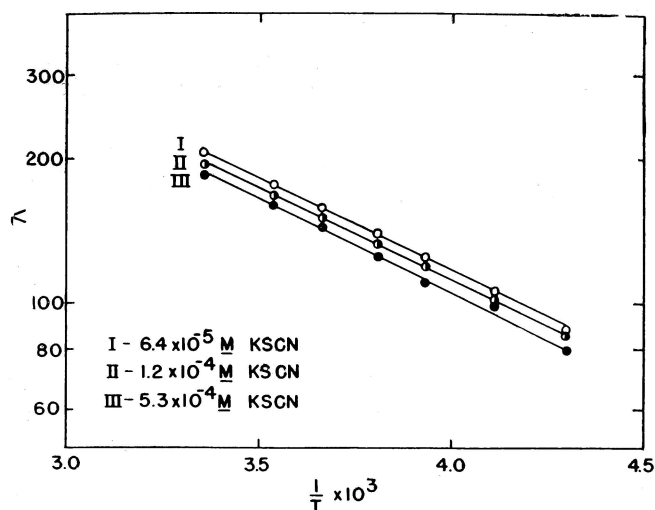


Figure 3. Relationship Between Temperature and Equivalent Conductance in Acetonitrile

Thus, if one slope and Λ_0 at one temperature were determined, Λ_0 at any other temperature could be calculated. Several of the plots made by Sears and co-workers are shown in Figure 2.

Figure 3 shows some of our data treated by this method. The linear relationship appears to exist at the low concentrations, although there is some doubt at the low temperatures. There is a definite curvature in the plot when the concentration is $5.3 \times 10^{-4} M$, a concentration roughly equal to the lowest concentration reported by Sears' group.

Dawson and co-workers⁵ state that the plot of $\log (\Lambda\eta)$ versus $1/T$ is linear up to concentrations of $4.14 M$. Figure 4 shows the results of such a treatment of our data. There appears to be some curvature even at the very low concentrations which are shown. Again, the curvature is more pronounced at low temperatures.

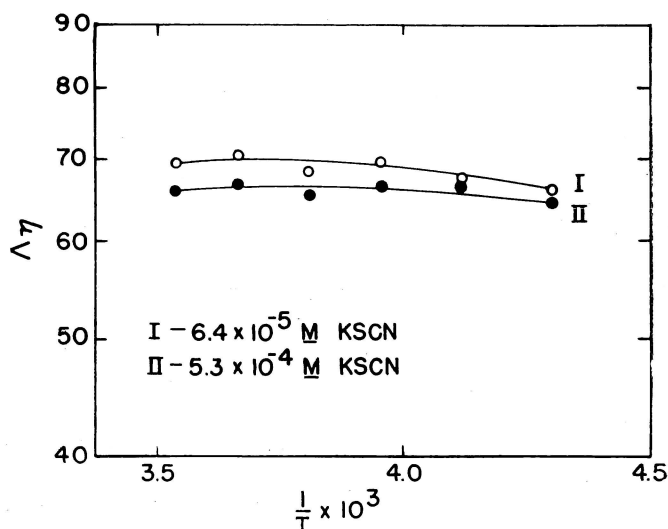


Figure 4. Relationship Between Temperature and η in Acetonitrile

No explanation has been offered for these observations. The solutes reported by the Sears group all acted as weak electrolytes as does potassium thiocyanate in acetonitrile at temperatures above -20° . Although we have not calculated dissociation constants for this system, Kohlrausch plots are linear below -20° , indicating that the salt is strongly ionized. Thus, the treatment suggested by Sears may be valid only when the salt is weakly ionized throughout the temperature range. There does not seem to be any theoretical basis for this effect. We have attempted to arrive at an explanation by means of the van't Hoff relationship, but the experimental data are not sufficient to justify such an explanation at this time.

Potassium thiocyanate in acetonitrile shows promise as an electrolyte for a practical battery. The specific conductance of a $0.541 M$ solution varies from $2.18 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25° to $9.6 \times 10^{-3} \text{ ohm}^{-1}$ at -40° . This system essentially meets the condition that the minimum specific conductance for a practical system

be 10^{-2} ohm $^{-1}$ cm $^{-1}$. Both sodium and ammonium thiocyanate systems of comparable concentration yield lower specific conductances. Lithium bromide is more soluble but its solutions do not conduct as well as the others and are more affected by temperature.

Sears and co-workers⁷ found that some perchlorates are highly soluble in 50-50 methanol-acetone mixtures and that these solutions have maximum specific conductances of about 4×10^{-2} ohm $^{-1}$ cm $^{-1}$ at 20°. However, the specific conductances are only about 1×10^{-2} ohm $^{-1}$ cm $^{-1}$ at -50°. The specific conductance of magnesium perchlorate in this solvent was increased about 10% at 20° on addition of 20% water, but was decreased by about 50% at -50°. No attempt was made to increase the concentration of the material.

We have found that the solubility of potassium thiocyanate in the acetonitrile system is approximately doubled on addition of 10% water. This permits a doubling of the specific conductance of the electrolyte throughout the temperature range and also results in a lower melting point for the system.

An interesting temperature effect has been observed in some electrolyte solutions which would be useful if it could be applied to practical systems. The specific conductance of zinc iodide in acetonitrile increases with decreasing temperature, while those of both zinc chloride and cadmium iodide in propionitrile show maxima. Unfortunately, the materials are not sufficiently soluble in these solvents to permit practical values of specific conductance.

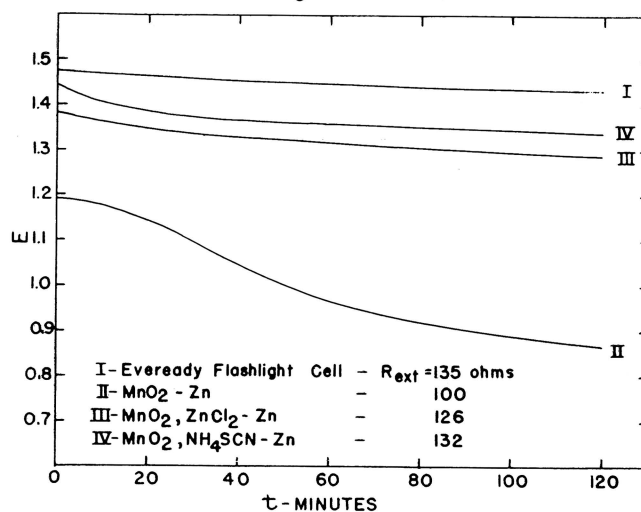
The explanation of this phenomenon is not known. It is interesting that the salts which lead to this behavior all tend to form complex ions with their anions in aqueous solutions. This, along with the observation that the effect is more pronounced at higher concentrations, may suggest a triple-ion formation. However, the data are insufficient.

CELL SYSTEMS

In our laboratories, we have measured a number of half-cell potentials in the potassium thiocyanate-acetonitrile electrolyte. By using this information, we have been able to fabricate several crude cells of the Leclanché type having dimensions similar to those of a standard flashlight cell. A zinc anode and manganese dioxide (Shawinigan Black mix) cathode were used in the systems reported here.

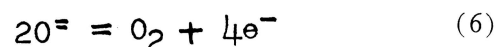
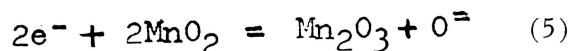
Open circuit voltages are about 1.5 volts at room temperature with some variation depending on the material added to the cathode mix. Figure 5 shows the results of several load tests. The current was held at approximately 10 ma and the cells were under continuous load over a two-hour period. Curve I shows the variation in voltage with time of a fresh Eveready flashlight cell. This is shown for comparison purposes.

Figure 5. Load Test on Cells Employing KSCN-CH₃CN Electrolyte

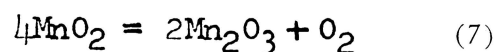


The other curves show this relationship for different cells constructed here. Curve II shows the performance of a cell employing only the Shawinigan Black mix as cathode. Curve III shows the performance of a cell in which zinc chloride has been added to the cathode mix, while curve IV shows that of a cell in which ammonium thiocyanate has been added to the mix. These last two show considerable improvement over the cell with the ordinary cathode mix, although they are not as good as the Eveready reference. These cells might be improved with better fabrication.

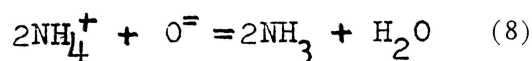
Although we do not understand the effect of the additives in the cathode mix, we might suggest a possible mechanism. Suppose we propose the following cathode half-reactions:



An overall reaction might be



We have no evidence of oxygen evolution so that nothing like equation (7) may actually occur. If it does, the oxide ions first formed may catalyze the decomposition of the manganese dioxide. Ammonium ion may then act as an acid according to the equation.



thus stabilizing the cathode material. The odor of ammonia has been detected during the operation of this cell, lending some support to a mechanism of this type. We do not maintain that it is correct, but submit it as one of several possibilities.

CONCLUSION

Some of the investigations of non-aqueous electrolyte systems during the past year have both fundamental and practical significance. Work at the University of Missouri indicates that a practical cell can be developed using non-aqueous electrolytes and having favorable low temperature characteristics.

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