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DEFINITION OF CHEMICAL AND ELECTROCHEMICAL PROPERTIES OF A FUEL--ETC(U)
JUL 78 T SARADA, J F MCINTYRE, R T FOLEY

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The present status of the project and the outstanding problems are reviewed.

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DEFINITION OF CHEMICAL AND ELECTROCHEMICAL
PROPERTIES OF A FUEL CELL ELECTROLYTE

Interim Technical Report

T. Sarada, John F. McIntyre and R. T. Foley

July 1978

to

U.S. Army Mobility Equipment Research and
Development Command
Fort Belvoir, Virginia

Prepared by

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SUMMARY

The present research is oriented toward the task of developing an improved electrolyte for the hydrocarbon-air fuel cell. The following compounds are being evaluated as potential fuel cell electrolytes: sulfoacetic acid, methane sulfonic acid, sulfosalicylic acid, 10-camphorsulfonic acid-dl, benzene sulfonic acid, ethylene disulfonic acid, 1,3,6-naphthalene trisulfonic acid, sulfosuccinic acid, sulfopropionic acid, ethane sulfonic acid, methane disulfonic acid, and propane sulfonic acid. These compounds are being evaluated in terms of their ionic conductivities, vapor pressures, surface properties, chemical stabilities, and electrochemical behaviors.

The present status of the project and the outstanding problems are reviewed.

FOREWORD

This research on the chemical and electrochemical properties of fuel cell electrolytes has been sponsored by the U.S. Army Mobility Equipment Research and Development Command at Fort Belvoir, Virginia, under Contract No. DAA70-77-C-0080 with The American Universtiy. The work was authorized under DA Project/Task Area/Work Unit No.

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DEFINITION OF CHEMICAL AND ELECTROCHEMICAL
PROPERTIES OF A FUEL CELL ELECTROLYTE

I Scope of the Present Research

The orientation of the present research to the entire fuel cell program was established in the last interim progress report (1). The overall objective is to contribute to the increase in fuel cell performance by the improvement of the electrolyte, or, more specifically, to identify new improved fuel cell electrolytes.

The evaluation of a new electrolyte is conducted in terms of a list of desired properties of a fuel cell electrolyte, namely,

- a) the electrolyte should be a good ionic conductor,
- b) the electrolyte should possess proper vapor pressure and viscosity characteristics,
- c) the electrolyte should be a good medium for the oxidation of the fuel,
- d) the electrolyte should be a good solvent for active materials and for material transport,
- e) the electrolyte should be chemically and electrochemically stable over the operating temperature range,
- f) the electrolyte should not be corrosive to fuel cell container materials,
- g) the electrolyte should possess desirable surface tension characteristics; preferably the solution should not wet Teflon or foam excessively when gases are bubbled through the solution.

With these requirements in mind a number of organic compounds are

being evaluated.

II Chemical and Physical Properties of Potential Electrolytes

Compounds Being Investigated

The compounds which are now receiving attention may be generally characterized as strong organic acids. These are tabulated in Table I, along with their melting points, boiling points and solubilities in water.

Specific Conductance

The specific conductances of a number of these compounds or of their aqueous solutions were measured at temperatures up to 80°C. These data are assembled in Table II. It appears characteristic of the aqueous solutions of these acids to exhibit a maximum in the conductivity-composition curve and this maximum usually falls about 50% (recall similar behavior in the phosphoric acid, sulfuric acid and trifluoromethanesulfonic acid monohydrate systems (2)). The conductivity-composition curves for sulfosalicylic acid and benzene-sulfonic acid monohydrate are shown in Figures 1 and 2 and are representative of these systems.

The Vapor Pressure Problem

Theory

The objective of this part of the project is to determine the vapor pressures of potential electrolytes and their aqueous solutions over fuel cell operating temperatures. Further, it is in order to examine those theoretical relationships which have been useful in

Table I Compounds Being Investigated As Potential Electrolytes

<u>Compound</u>	<u>Melting Point °C</u>	<u>Boiling Point °C</u>	<u>Solubility in Water</u>
Sulfoacetic acid HO ₃ S-CH ₂ -COOH	84-6°	245d	Very soluble ~ 510g/100ml
Methane sulfonic acid CH ₃ SO ₃ H (forms a mono or trihydrate)	19-20°	167°/10mm 121°/1mm decomp. over 220°	Miscible in all proportions
5-Sulfosalicylic Acid·2H ₂ O C ₆ H ₃ (COOH)(OH)(SO ₃ H)·2H ₂ O	120° 180d	---	Very soluble 145-150g/100ml at ~ 25°C
10-Camphorsulfonic Acid-d1 C ₁₀ H ₁₆ O ₄ S	202°d	---	250g/100ml (50°) 340g/100ml (60°)
Benzene sulfonic acid C ₆ H ₅ SO ₃ H·1.5H ₂ O	65-6 (anhyd.) 45-6	---	Very soluble
Ethylene disulfonic acid HO ₃ S-CH ₂ -CH ₂ -SO ₃ H·2H ₂ O	174 (anhyd.) 111-112°	---	Very soluble 7.4g/1ml (52°)
1,3,6-Naphthalene Trisulfonic acid	---	---	Very soluble
Sulfosuccinic acid (meso)	160°	---	Very soluble
Sulfopropionic acid (α,dl)	100.5	---	Very soluble
Ethane sulfonic acid	-17°	123°/1mm	Very soluble

Table I (Continued)

<u>Compound</u>	<u>Melting Point °C</u>	<u>Boiling Point °C</u>	<u>Solubility in Water</u>
Methane disulfonic	---	> 160 slight decomposition	Very soluble
Propane sulfonic acid	+7.5°	136/1mm	

Table II Specific Conductances of Organic Acids
and Their Aqueous Solutions

Compound	Concentration (Weight Percent)	Temperature (°C)	Specific Conductance (ohms ⁻¹ cm ⁻¹)
Sulfoacetic acid	18	40	0.309
	58	40	0.464
	60	80	0.398
	80	80	0.145
Methane sulfonic acid	98	40	0.019
Sulfosalicylic acid	5	40	0.0767
	30	80	0.452
	40	80	0.498
	50	80	0.487
	60	80	0.386
	70	80	0.296
10-Camphorsulfonic acid(d 1)	80	80	0.168
	20	40	0.214
	50	40	0.292
	60	80	0.266
Benzene sulfonic acid monohydrate	80	80	0.0639
	5	40	0.1217
	20	80	0.471
	30	80	0.593
	40	80	0.628
	50	80	0.582
	60	80	0.457
80	80	0.173	
Ethylene disulfonic acid dihydrate	80	80	0.257
1,3,6-Naththalene trisulfonic acid	20	80	0.150
	30	80	0.180
	40	80	0.197
	50	80	0.185
	60	80	0.198
Sulfosuccinic acid	21	80	0.112
β-Sulfopropionic acid	5	80	0.114

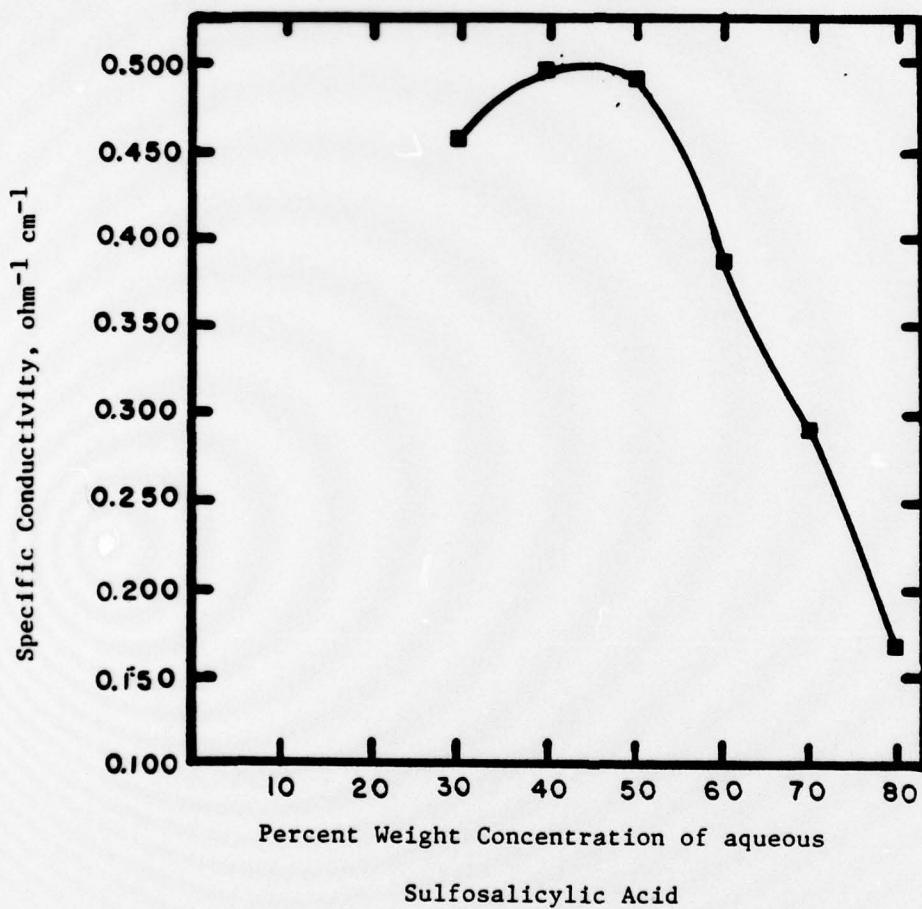


Figure 1. Conductance - Composition plot for aqueous solutions of sulfosalicylic acid, 80°C.

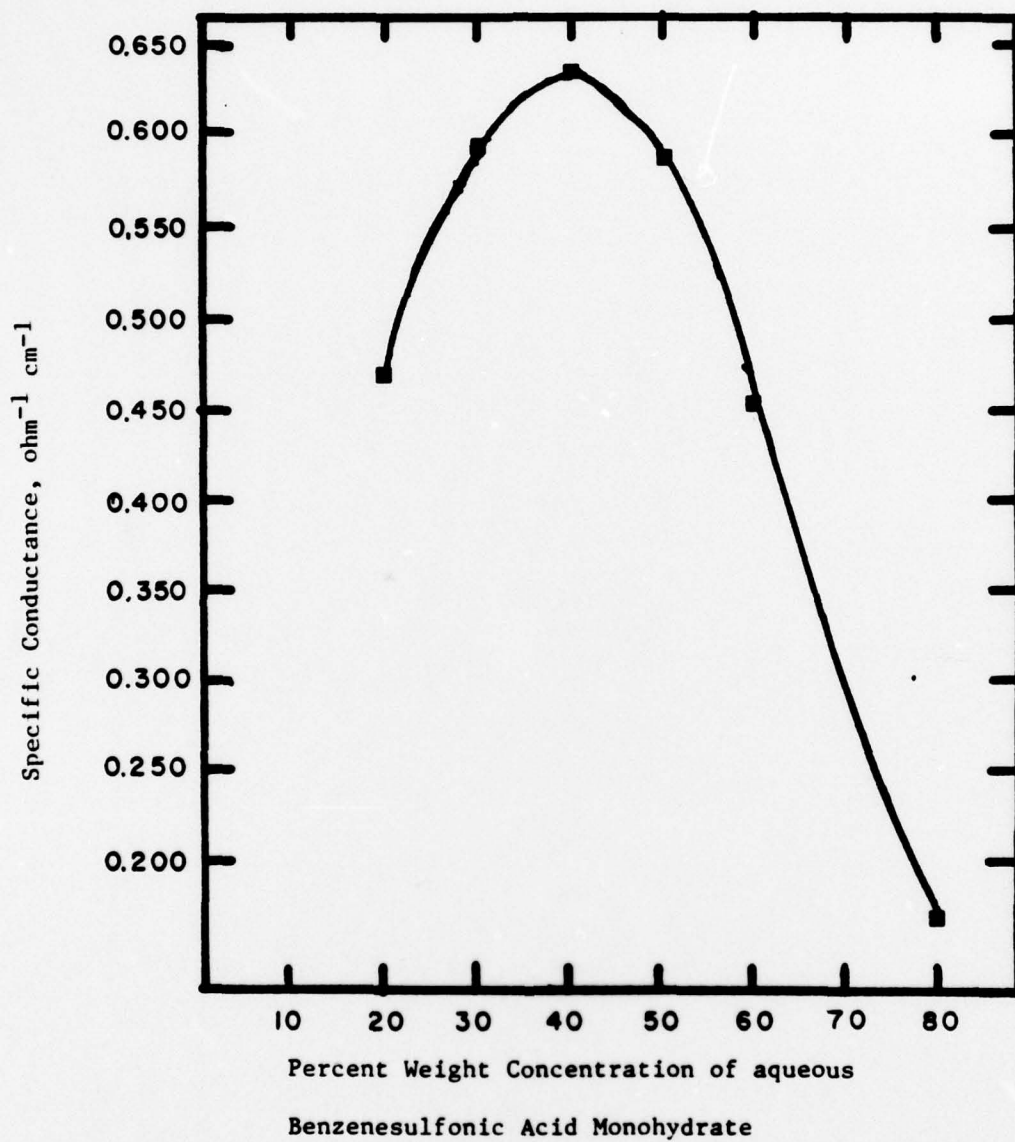


Figure 2. Conductance - composition plot for aqueous solutions of benzenesulfonic acid monohydrate, 80°C

interpreting experimental vapor pressure data so that actual data collection may be minimized.

The vapor pressure-temperature plot for a compound may be represented by the integrated form of the Clausius-Clapeyron equation

$$\log \frac{p_2}{p_1} = \frac{\Delta H_v (T_2 - T_1)}{2.303 R T_1 T_2}$$

wherein p_1 is the vapor pressure at temperature T_1 , p_2 is the vapor pressure at T_2 , R is the gas constant, and ΔH_v is the heat of vaporization. This assumes that the heat of vaporization is constant over the temperature range of interest and, in fact, the $\log p$ versus $1/T$ plot for many liquids is linear up to the normal boiling point. This means that if the ΔH_v for a liquid is known, and a vapor pressure measurement is available at one temperature, then the vapor pressure-temperature diagram for the compound may be constructed. It then follows that it would be desirable to consider relationships which allow the estimation of heats of vaporization of compounds.

Trouton's Rule relates the heat of vaporization to the normal boiling point (T_b),

$$\frac{\Delta H_v}{T_b} = 21 \text{ e.u.}$$

which says that the entropy change on vaporization is the same for all liquids.

This basic rule has been modified by Bingham to give,

$$\frac{\Delta H_v}{T_b} = 17 + 0.011 T_b ,$$

and by Nernst to give,

$$\frac{\Delta H_v}{T_b} = 9.5 \log T_b - 0.007 T_b .$$

These are improvements over Trouton's Rule but Bingham's equation usually gives high values and Nernst's gives values that pass through a maximum.

Kistiakowsky's equation applies only to nonpolar liquids and reads

$$\frac{\Delta H_v}{T_b} = 8.75 + 4.571 \log T_b$$

The relationship given by Watson (3) for deriving ΔH_v is

$$\Delta H_v = 0.95RB \left(\frac{T_b}{T_b - 43} \right)^2$$

wherein R is the gas constant, B is a constant and T_b is the normal boiling point.

B is obtained if the vapor pressures are known at two different temperatures and is given by

$$B = \ln \frac{P_2}{P_1} / \left(\frac{1}{T_1 - 43} \right) - \left(\frac{1}{T_2 - 43} \right)$$

When such vapor pressure data are not available, ΔH_v can be estimated within 5% for a wide variety of liquids, polar and nonpolar, using the method outlined by Janz (4). This makes use of the Watson equation and involves B. This is done by estimating the critical constants and modifying the equation to read

$$B = \frac{\ln \frac{P_c}{P_b}}{\left(\frac{1}{T_b - 43} \right) - \left(\frac{1}{T_c - 43} \right)} .$$

wherein

p_c is the critical pressure,

p_b is pressure at normal boiling point,

T_b is the boiling point on the Kelvin Scale, and

T_c is the critical temperature on the Kelvin scale.

The critical constants for this equation can be calculated by the method of Meissner and Redding (5). For polar liquids or for liquids wherein the density is not known, the following equations are used for estimating the critical temperatures.

a) Compounds with $T_b < 235^\circ\text{K}$ and all elements

$$T_c = 1.70 T_b - 2.0$$

b) Compounds with $T_b > 235^\circ\text{K}$

i) compounds with halogen or sulfur

$$T_c = 1.41 T_b + 66 - 11 F$$

(F = number of halogen atoms in molecule)

ii) aromatic or naphthalene compounds free of halogens or sulfur

$$T_c = 1.41 T_b + 66 - r(0.383 T_b - 93)$$

(r = ratio of noncyclic C atoms to the total number of C atoms in the compound)

iii) components other than those included in i) or ii).

$$T_c = 1.027 T_b + 159$$

These equations have not been applied for liquids with $T_b > 600^\circ\text{K}$.

With the exception of water, a polar molecule, the estimated values are within 5% of the experimental values.

If the critical temperature, T_c , and the critical volume, v_c ,

are known, the critical pressure may be estimated by

$$P_c = \frac{20.8 T_c}{(v_c - 8)} = \frac{20.8 T_c}{(M/d_c - 8)} \text{ atm.}$$

In this equation, M is the gram molecular weight and d_c is the critical density. The critical volume is given by

$$v_c = (0.377 \bar{P} + 11)^{1.25} \text{ cc mole}^{-1}$$

in which \bar{P} is the value of the parachor for the compound. Parachor value tables for elements and bonds are available and the parachor for a molecule can be calculated by addition. The equation allows the calculation of the critical pressure to 10% agreement with the experimental value.

Having calculated the critical temperatures and the critical pressures, substitution in the above equation allows the calculation of a relative ΔH_v within 5% of the experimental for a wide variety of polar and nonpolar liquids.

This method is applied to several compounds and aqueous solutions

1) 85% H₃PO₄

$$T_b = 428^\circ\text{K}$$

$$T_c = T_b(1.027) + 159 = 598.56^\circ\text{K}$$

$$\bar{P} = 192.2$$

$$v_c = (0.377 \bar{P} + 11)^{1.25} = 252.26 \text{ cc mole}^{-1}$$

$$P_c = \frac{T_c (20.8)}{v_c - 8} = 50.97 \text{ atm.}$$

$$\Delta H_v = R (2.303) \log \frac{P_c \left[\frac{T_c^* T_b^*}{T_c - T_b} \right]}{P_b}$$

*values are (T - 43)

$$\Delta H = 0.95RB \left(\frac{T_b}{T_b - 43} \right)^2$$

or through a calculation of B which is given by

$$B = \frac{\ln \left(\frac{P_2}{P_1} \right)}{\left(\frac{1}{T_1 - 43} \right) - \left(\frac{1}{T_2 - 43} \right)}$$

$\Delta H = 9.83$ kcal (Janz method)

Experimental (6), $\Delta H_v = 9.813$ kcal

Error, 0.07%

2) H₂SO₄ (95.94% Acid)

Janz method $\Delta H_v = 11.922$ kcal

Experimental (7) $\Delta H_v = 11.99$ kcal

Error, 5.6%

3) Trifluoromethanesulfonic acid monhydrate

Janz method $\Delta H_v = 9.326$ kcal

Experimental (8) $\Delta H_v = 9.725$ kcal

Error, 4.1%

4) Methane sulfonic acid (b.p. = 559.93°K)

Janz method $\Delta H_v = 12.915$ kcal

5) Sulfoacetic acid (b.p. = 518°K)

Janz method $\Delta H_v = 9.082$ kcal

A comparison of the method with experimental data is given in Figure 3.

The foregoing applies to the estimation of the ΔH_v , which would be substituted in the integrated form of the Clausius-Clapeyron equation to give the vapor pressure of a liquid at a fuel cell operating temperature. It should be pointed out that in a practical fuel cell it would be unlikely to use a pure organic acid because of the conductivity considerations pointed out above. For this reason the measurement of the vapor pressures of some of the concentrated solutions will be required.

Experimental

The isopiestic method used to measure vapor pressures was described in the previous interim technical progress report (1). The use of this technique to construct the vapor pressure-temperature curve for benzene sulfonic acid monohydrate is illustrated here. The equilibrium data are given in Table III for three temperatures. With these data a vapor pressure-composition curve is constructed (Figure 4). From this plot the vapor pressures of a given composition may be estimated at the three temperatures (Table IV). Finally, a vapor pressure-temperature plot may be constructed for the several compositions (Figure 5).

The vapor pressures of concentrated solutions of 10-camphor(d 1) sulfonic acid were measured at 100°C using a 6 day equilibration time.

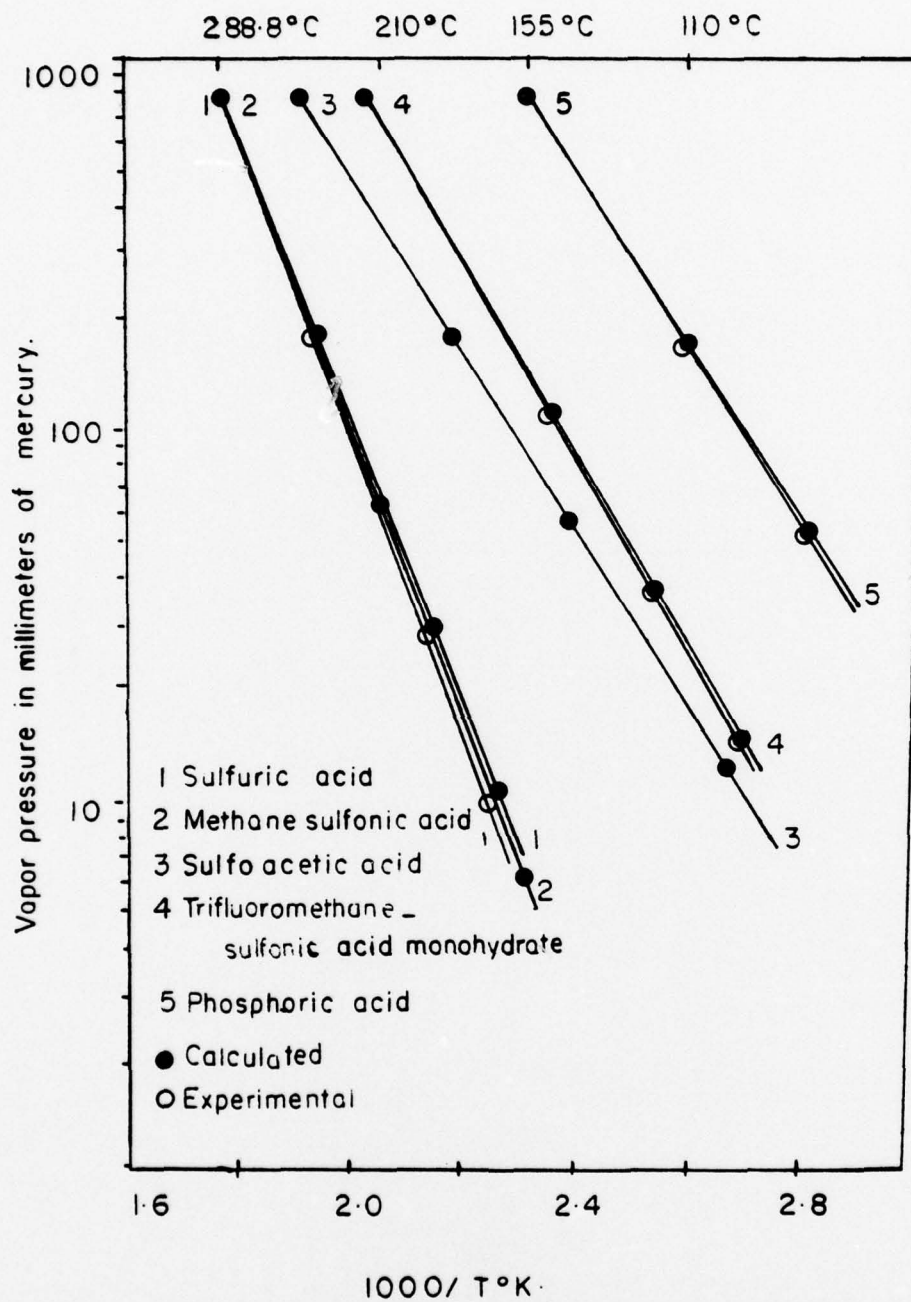


Figure 3. Vapor pressure-temperature plot for several electrolytes. Experimental and calculated compared.

Table III Isopiestic Method Data for the Vapor Pressure of Benzene Sulfonic Acid Monohydrate
(Phosphoric Acid Comparison Liquid)

Experiment Number	Final Composition, Weight Percent				Number of Days Equilibration	Temperature °C	Pressure (mm of Hg)
	Benzene Sulfonic Acid Monohydrate	Phosphoric Acid					
1	50.91	52.04			7	100	560
2	53.26	52.47			7	100	550
3	55.10	58.59			8	100	490
4	59.82	60.33			8	100	455
5	88.29	84.83			7	100	120
6	88.39	84.91			7	100	115
7	95.25	92.57			7	100	50
8	95.51	92.64			7	100	46
1	52.15	45.96			6	80	270
2	53.00	46.14			6	80	265
3	54.00	52.28			7	80	250
4	62.31	60.66			7	80	200
5	82.77	76.29			7	80	107
6	82.80	76.30			7	80	105
1	53.21	46.49			1	28.5	22.5
2	53.80	46.79			1	28.5	22.5
3	54.05	52.34			1	28.5	21.0
4	62.37	60.78			1	28.5	17.5
5	80.42	75.41			1	28.5	9.0
6	80.58	75.67			1	28.5	9.0

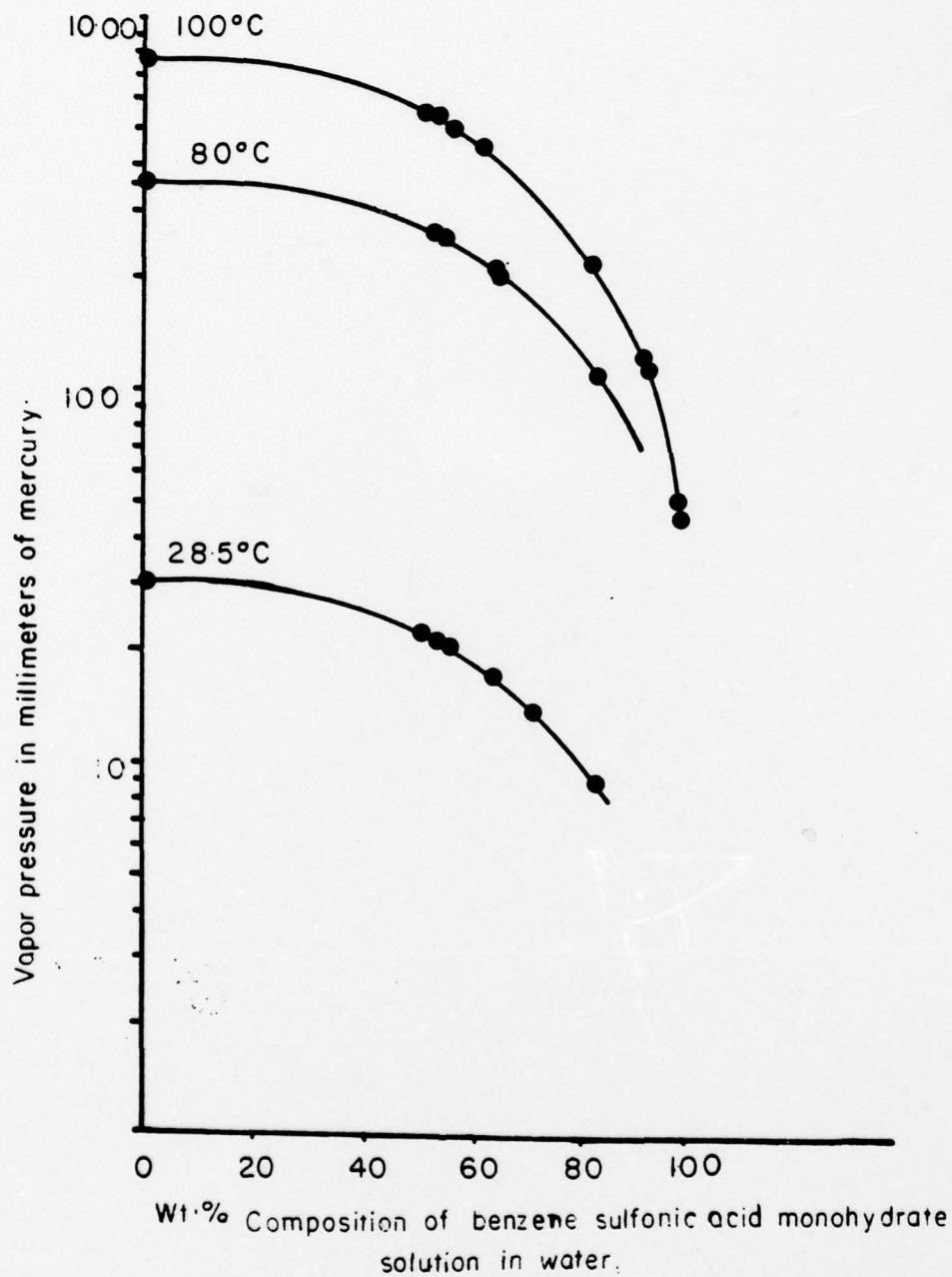


Figure 4. Vapor pressure-composition plot for benzene sulfonic acid monohydrate. Data from isopiestic method.

Table IV Vapor Pressure of Benzene Sulfonic Acid Monohydrate

Weight Percent	Temperature °C	Pressure (mm of Hg)
80	100	225
	80	110
	28.5	9
70	100	340
	80	165
	28.5	14
60	100	460
	80	210
	28.5	18.5
50	100	580
	80	275
	28.5	13

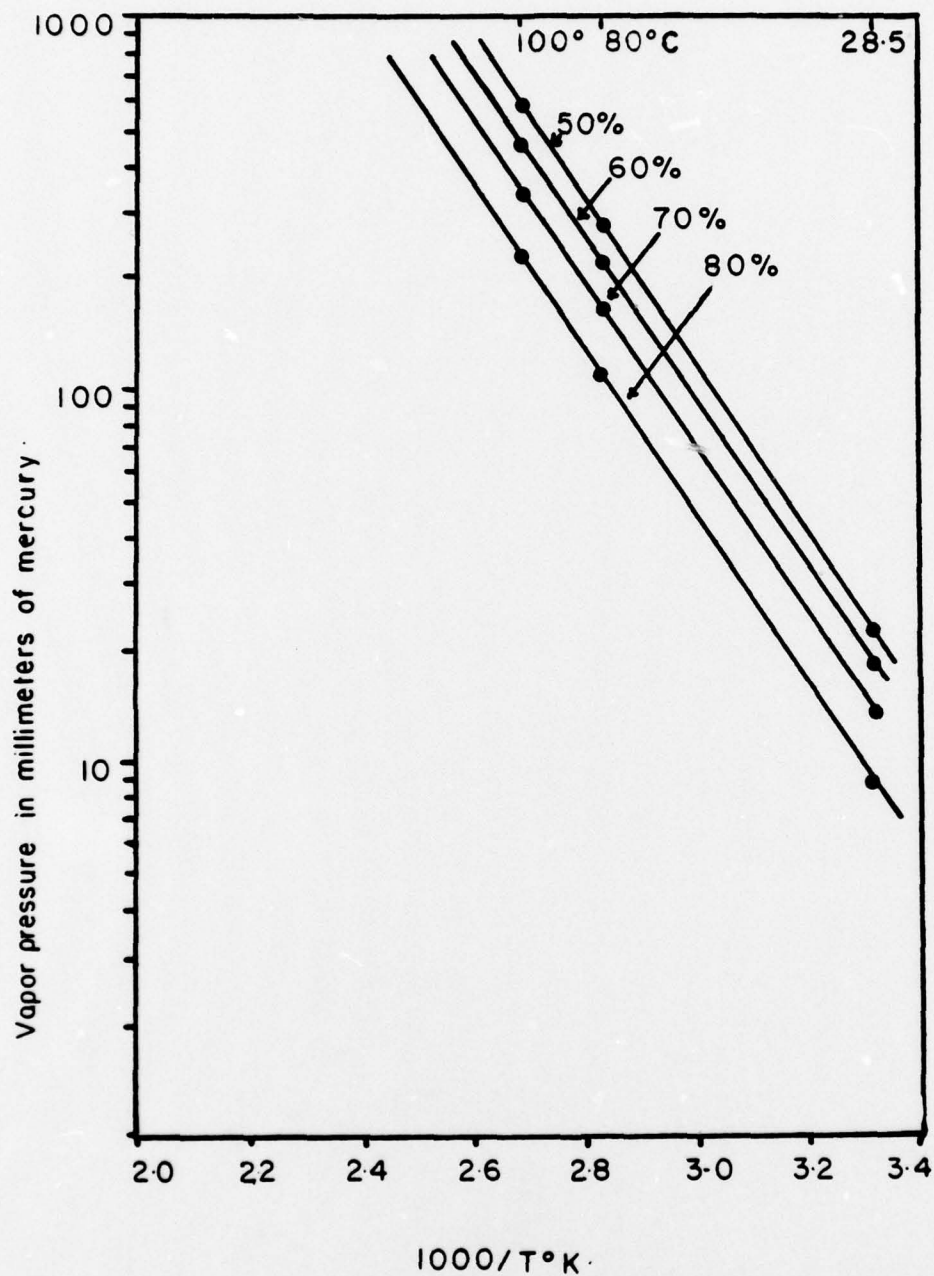


Figure 5. Vapor pressure-temperature plot for benzene sulfonic acid monohydrate.

	<u>Final Concentration</u> <u>(weight percent)</u>	
<u>10-CSA</u>	<u>H₃PO₄</u>	<u>Pressure</u> <u>(mm Hg)</u>
92.76	80.47	160
93.21	80.61	158

Similar measurements were made with concentrated solutions of 5-sulfosalicylic acid

	<u>Final Concentration</u> <u>(weight percent)</u>	
<u>5-SSA</u>	<u>H₃PO₄</u>	<u>Pressure</u> <u>(mm Hg)</u>
83.98	63.02	415
83.10	59.19	477

Surface Properties

There are three surface properties or reactions of importance in the characterization of a fuel cell electrolyte:

- a) the tendency of the electrolyte to wet Teflon and lower the efficiency of a Teflon-bonded catalytic electrode,
- b) the tendency of the electrolyte to foam when gases are bubbled through, and
- c) the tendency of the compound to adsorb on the electrode and compete with the oxidation or reduction of fuel cell reactants.

The third reaction will be considered below under electrochemical behavior. The second is also observed in the electrochemical experiment but in a qualitative fashion. The first reaction, the wetting of

Teflon by the compound, is amenable to direct measurement. The technique has been described in a previous report (1). In Table V are given some contact angle data for some of the electrolytes under consideration. It is noted that several of the sulfonic acids have fairly high contact angles, i.e., the compounds do not wet Teflon.

Chemical Stability

A detailed literature survey showed that aromatic sulfonic acids which are not halogen or hydroxy substituted are stable under the conditions commonly employed in fuel cells. The pertinent data are presented in Table VI.

The method followed to monitor the hydrolysis reaction is the reverse of the procedure adopted in monitoring the extent of sulfonation (14). This uses the increase in acidity in the reaction mixture since every mole of sulfonic acid hydrolyzed increases the acidity by one equivalent. The experimental method, therefore, consists in refluxing a known weight of an aqueous solution of the acid and measuring acidity before and after the refluxing. Any water loss is compensated for by weighing the solutions before and after a number of hours of refluxing. The boiling point of these solutions is about 105°C.

The method was evaluated by following the hydrolysis of monochloroacetic acid, one of the acids known to hydrolyze even in the absence of acid or base, i. e., in the presence of water alone. Fifteen hours of refluxing of an aqueous solution of this acid produced an acidity increase of 11%.

Table VII tabulates the stoichiometry associated with the

Table V Contact Angle Data for a Few Sulfonic Acids
at Room Temperature on Teflon

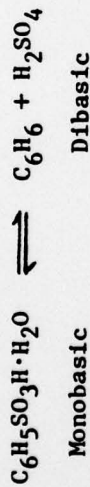
Electrolyte	Concentration (Weight Percent)	Contact Angle (Angle in Degrees & 2 Significant Decimal Places)	Temperature (°C)
Benzene sulfonic acid monohydrate	80	72.40	25.5
Benzene sulfonic acid monohydrate	40	90.75	25.5
5-Sulfosalicylic acid	62	93.88	25
Meta-Benzene disulfonic acid	74 g/100 ml	95.21	25.5
Methane sulfonic acid	98	83.05	26
1,2-Ethane disulfonic acid	70	99.64	25

Table VI Hydrolysis of Sulfonic Acids (Literature)

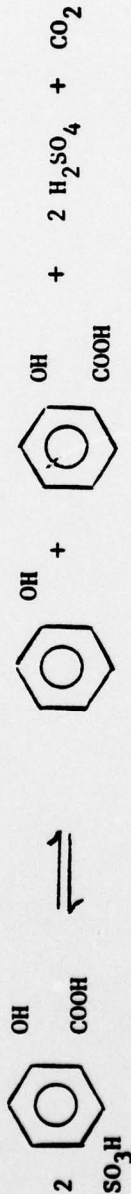
Acid	Conditions	Reference
Benzene sulfonic acid	in the presence of dilute acids between 135-200°C, all aromatic sulfonic acids hydrolyze to some extent	(9)
	H ₃ PO ₄ decomposes BSA·H ₂ O > 227°C	(10)
5-Sulfosalicylic acid	gives a mixture of phenol and salicylic acid with KOH at 230-240°C, with fused alkali at 200°C or below and apparently no sulfo group is removed	(11)
Metabenzene sulfonic acid	readily converted into resorcinol with alkali fusion	(11)
Aliphatic sulfonic acids (Ethane disulfonic acid, etc.)	boiling with dilute NaOH is without effect. Heating in 5% NaOH above 300° under pressure results in slow decomposition	(12)
Monochloroacetic acid	boiling water converts it into glycolic acid	(13)

Table VII Hydrolysis Reactions (Stoichiometric) with Only Water Present

1. Benzene sulfonic acid monohydrate solution

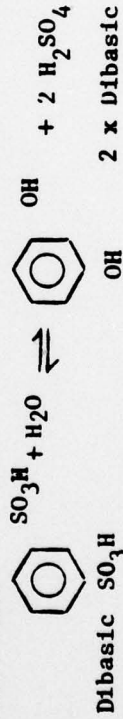


2. 5-Sulfosalicylic acid



Dibasic and hence 4 equivalents in all Monobasic Dibasic acid
 Total of 5 equivalents

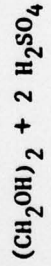
3. Metabenzene disulfonic acid



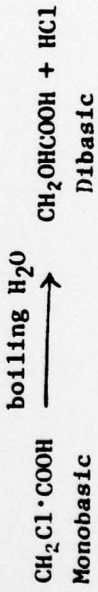
$k_a = 1.0 \times 10^{-3}$; 4×10^{-1}

4. $[\text{CH}_2(\text{SO}_3\text{H})]_2$

Not known to hydrolyze in water. In the presence of alkalis or fused alkali



5. Monochloroacetic acid



hydrolysis of five of the acids. It is apparent that the extent of reaction can be followed by a simple titration.

Table VIII gives the results of a number of hydrolysis experiments. According to these tests most of the sulfonic acids are stable to hydrolysis.

Benzene sulfonic acid and ethane 1,2-disulfonic acid were subjected to a further test involving the refluxing for 18 hours at about 105°C in the presence of platinum black. No evidence for hydrolysis was observed.

Electrochemical Behavior

The experimental set-up and the electrochemical cell were similar to that previously described (2). Voltage sweeps were run over the range from 0 mV (vs DHE) to about +1500 mV, first in the anodic direction and returning in the cathodic direction. Smooth platinum electrodes were used and the sweep rates were varied from 5 mV/sec to 50 mV/sec--relatively slow for this technique. Runs were made at 80°C and about 100°C. Usually, the voltammogram was compared with those obtained with platinum electrodes in perchloric, sulfuric, or phosphoric acid, wherein the distinguishing features are the oxidation and reduction of hydrogen and the oxidation and reduction of the platinum surface.

The voltage sweep with smooth platinum electrodes at a sweep rate of 25 mV/sec at 80°C in ethane disulfonic acid is shown in Figure 6. The clear cut oxidation of hydrogen near 0 V and the oxidation maximum near 0.8 V appear to be obscured although there is an inflection at about +0.8 V (oxidation). The cathodic curve

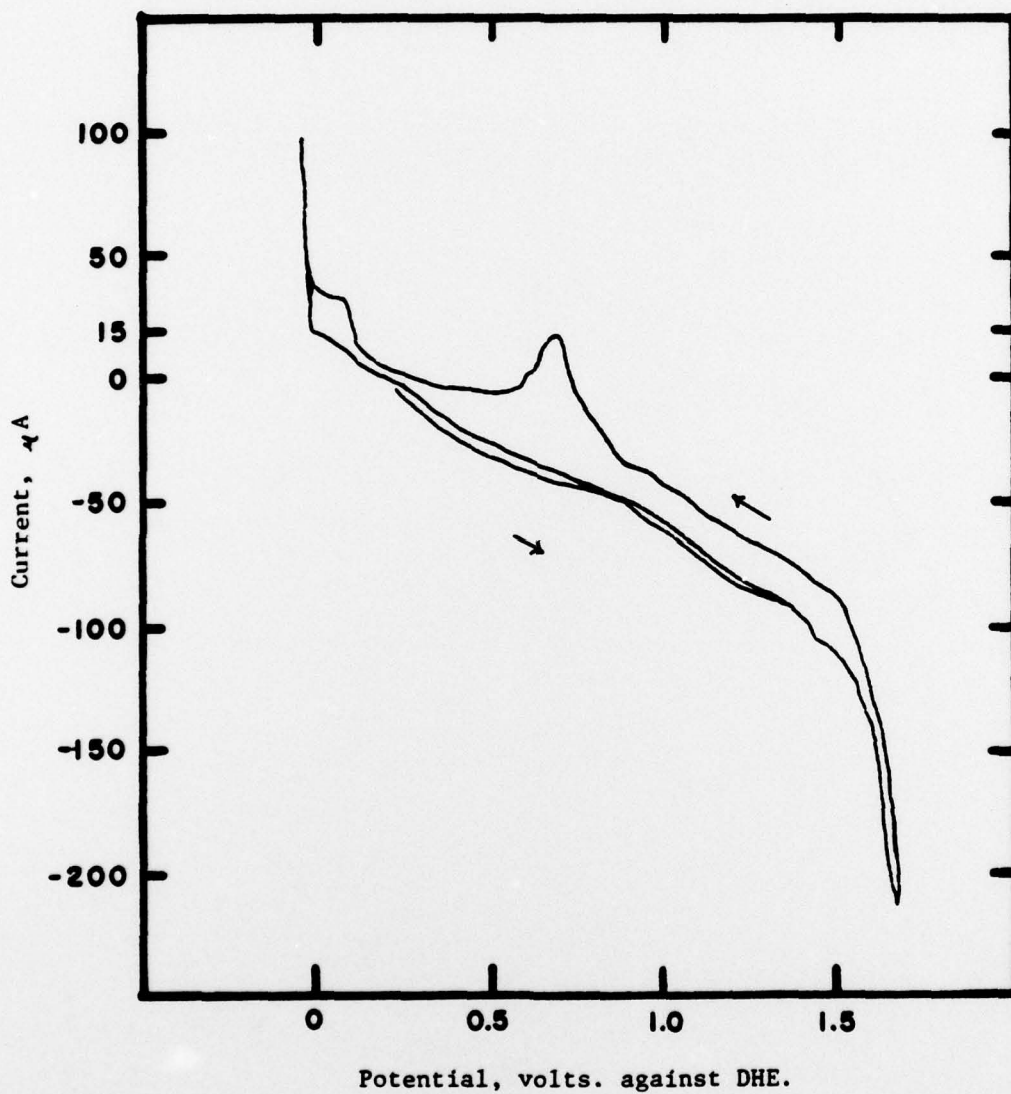


Figure 6. Cyclic Voltammogram for Pt. electrode in ethane disulfonic acid. (42% solution). Sweep rate 25 mV/sec. 80°C.

resembles what would be expected from a stable electrolyte. Figure 7 shows a sweep in the same acid at 98°C with somewhat similar character. The oxidation wave appears to be displaced in the positive direction. These curves are quite reproducible with continual cycling.

The sweep in benzene sulfonic acid monohydrate, one of the aromatic acids of interest, is shown in Figure 8. The oxidation current in this acid is high and the increase in current in the double layer charging potential range suggests adsorption of the aromatic acid. Continual cycling over the voltage range yields reproducible plots.

In the next step the rate of oxidation of hydrogen and propane will be measured in these electrolytes.

III Conclusions and Direction of Future Work

A number of strong organic acids have been identified as potential fuel cell electrolytes. These include sulfonic acids as well as carboxylic acids. One point of uncertainty is the high temperature ($\sim 150^\circ\text{C}$) stability of carboxylic acids and this must be resolved in future work. These strong organic acids are being evaluated in terms of specific properties.

The ionic conductances of aqueous solutions of these compounds appear to be adequate for fuel cell operation. Most of the aqueous solutions of the compounds give conductance-composition curves with maxima at about 50-60 weight percent of the acid following the pattern of sulfuric and phosphoric acid. These solutions give high conductivities but pose a problem with their high vapor pressures.

The vapor pressures of many of these pure compounds are low

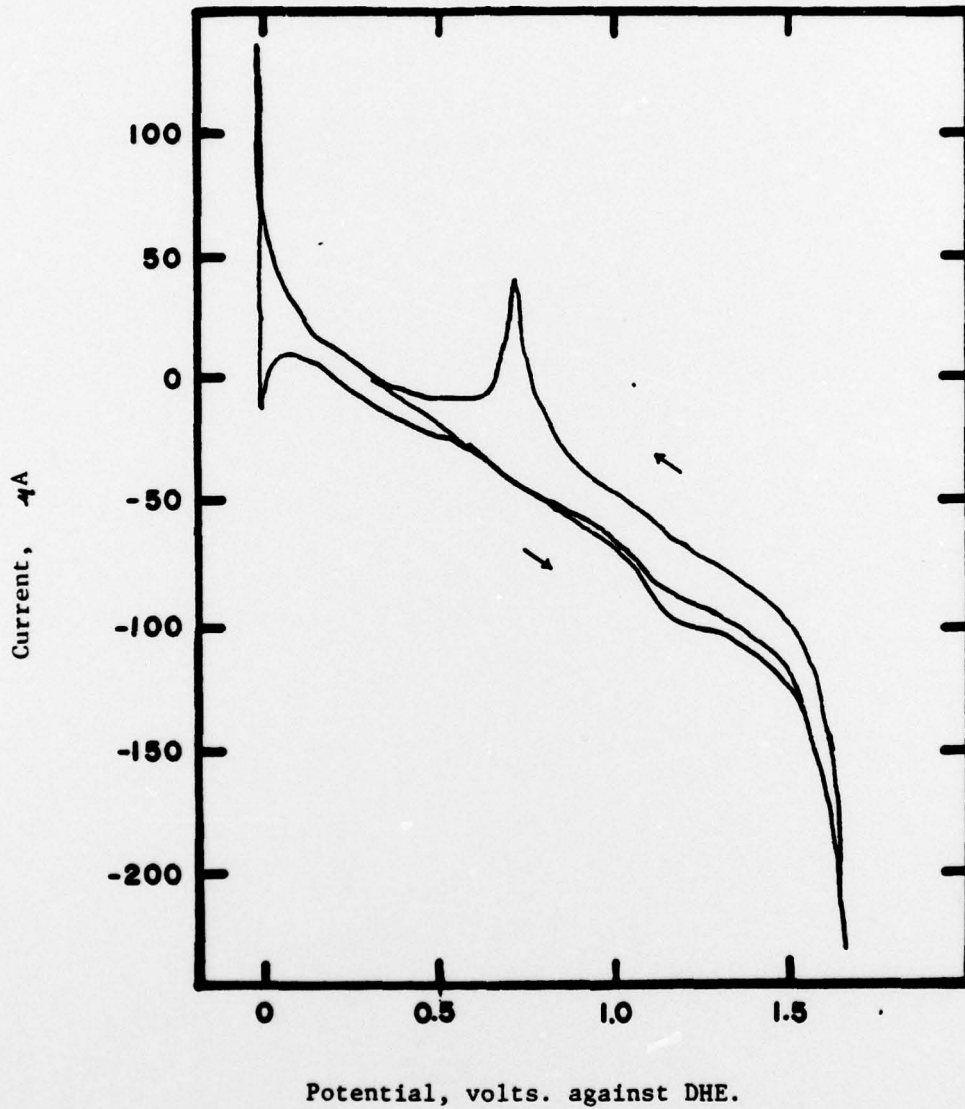


Figure 7. Cyclic Voltammogram for Pt. electrode in ethane disulfonic acid. (42% solution). Sweep rate, 25 mV/sec. 98°C.

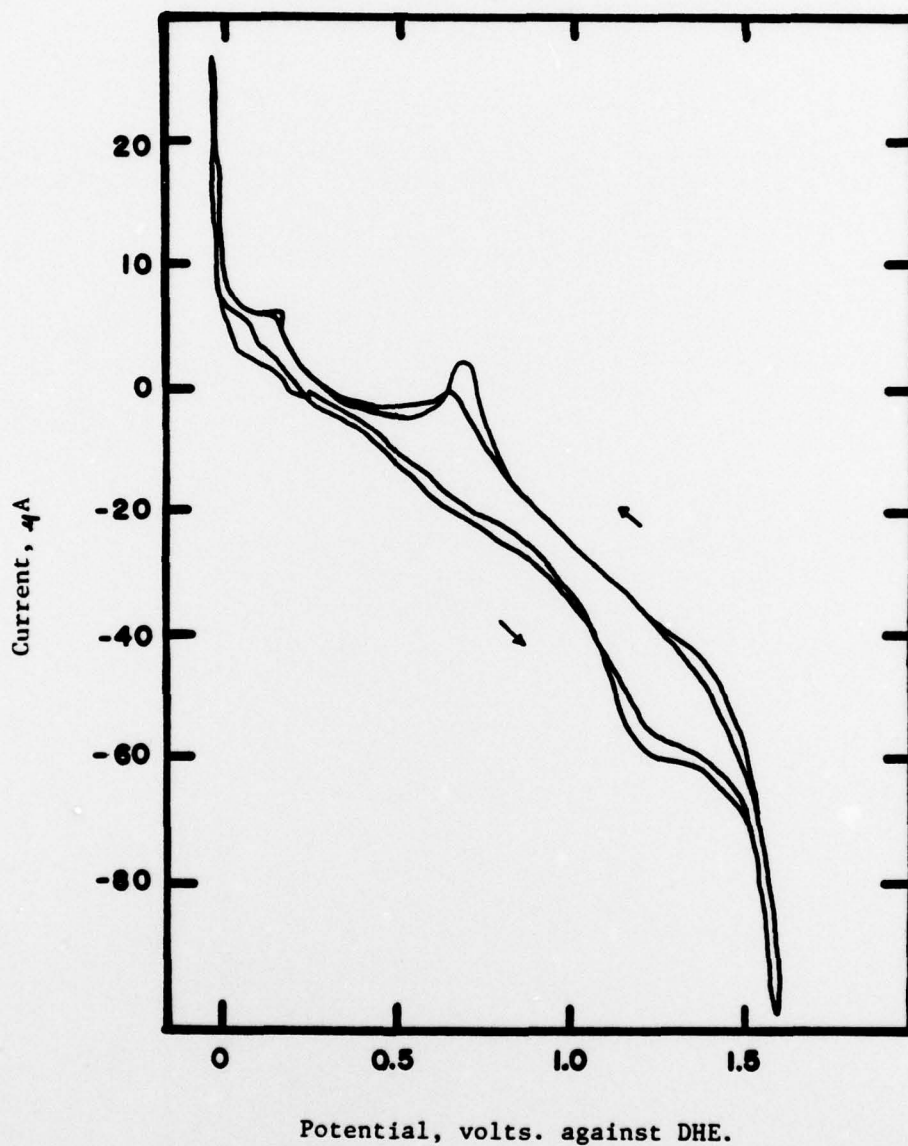


Figure 8. Cyclic Voltammogram for Pt. electrode in benzenesulfonic acid monohydrate. (80% solution) Sweep rate, 25 mV/sec. 80°C.

enough to be useful fuel cell electrolytes. However, if it is necessary to work with aqueous solutions then the vapor pressure will be higher. At any rate, the vapor pressures can be measured by the isopiestic method. Further, from theoretical relationships, the heat of vaporization can be estimated and, from a single vapor pressure measurement at a specific temperature, the vapor pressure-temperature curve can be constructed.

With respect to chemical stability, experiments show that sulfonic acids do not hydrolyze appreciably in the test used. This applies to aromatic sulfonic acids which, the literature indicated, would be unstable at the boiling point.

The sweep voltammetry experiments demonstrate that some acids such as ethane disulfonic are stable over potentials in the fuel cell operating range. With other compounds such as benzene sulfonic acid there appears to be excessive adsorption in the double layer region.

These latter results furnish the basis for the experimental work to be done in the near future. This will involve the electrooxidation of hydrogen and propane in these strong organic acids and the evaluation of certain type compounds as fuel cell electrolytes.

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