NASA CR-

STUDY TO INVESTIGATE AND IMPROVE THE ZINC ELECTRODE FOR SPACECRAFT ELECTROCHEMICAL CELLS

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FINAL REPORT

30 MAY 1966 TO 30 JUNE 1967

Prepared under Contract #NAS 5-10231 by
YARDNEY ELECTRIC CORPORATION
New York, New York

for

Goddard Space Flight Center
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

OCTOBER 1967

ABSTRACT

The diffusivity of zincate in free alkaline electrolyte has been investigated as a function of KOH concentration and temperature. A qualitative explanation is given for deviations from the Einstein-Stokes equations.

Mossy zinc whiskers are deposited under activation controlled conditions and acicular dendrites are deposited under diffusion controlled conditions. No intermediate form of deposit has been found.

Plastic separator membranes in zincate electrolyte show varying degrees of selectivity for zincate ions. The distribution coefficient for zincate in the membranes in equilibrium with zincate electrolyte is less than one and varies by a factor of seven for the membranes tested.

The zincate diffusivity in plastic membranes is directly proportional to the conductivity of the membranes in the alkaline electrolyte. Both parameters are related to the pore sizes of the membranes.

When a membrane is in close abuttal to a zinc electrode in alkaline electrolyte, the overvoltage required to initiate zinc growth in the membrane has to be greater than that required to produce dendrites on the electrode. Once the overvoltage is sufficient to produce dendrites zinc growth occurs in cellulosic membranes. Membranes such as C-3 (Borden Chemical Co.) (1) can tolerate overvoltages up to 100 mV in excess of that required to produce dendrites without any zinc growth occurring in the membranes.

Silver zinc cells have been cycled using a zinc overvoltage cutoff (75 mV). No penetration of the membranes occurred under these conditions. High resistivity membranes accelerate shape change. The best shape retention was found with low resistivity cellulosic membranes.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

1. INTRODUCTION

This report summarizes the research carried out under Contract NAS 5-10231. The work was directed toward a study of zinc dendrite growth in alkaline solutions and a determination of the mechanism whereby zinc dendrites can penetrate membrane materials that are used in electrochemical cells which incorporate zinc negative electrodes.

In this program the zincate diffusivity in alkaline solutions was determined as a function of KOH concentration and temperature. The morphology of the zinc deposits was correlated with the deposition potential. Analytical work was carried out to determine zincate absorption in various membranes. Zincate diffusivities in the membranes were also determined. The membranes examined were PUDO-300 (DuPont), Ag treated PUDO-300 (YEC C-19) polyvinylalcohol, C-3 and 9107/5 (Borden Chemical Co.) and 2.2XH series 2 (Radiation Applications Inc.). The absorption and transport parameters for zincate in the various membranes were correlated with the overvoltage necessary to penetrate the membranes during zinc deposition.

2. TECHNICAL DISCUSSION

2.1 Zincate Diffusion in KOH Solutions

Since the rate of diffusion of zincate to the growing metal substrate determines the morphology of the zinc deposit, it is important to know the diffusion coefficient for zincate in KOH electrolyte. The dependence of the diffusion coefficient on KOH concentration and temperature must be known if the results are to be generally applicable to the analysis of zinc deposition. The diffusion coefficient of zincate was determined as a function of KOH concentration and temperature. The KOH concentrations used were 5%, 25%, 30%, 35%, 40%, and 44%. The temperatures studied were 0°C, 25°C, 35°C, and 50°C.

A polarographic technique was used to determine the diffusion efficients. For this purpose, solutions of 5×10^{-3} M zincate were prepared in the various concentrations of KOH. The solutions were saturated with Igepal to suppress any extraneous polarographic maxima. Portions of these solutions were transferred to a polarographic cell. The polarographic cell was then transferred to a water bath, thermostatted at the required temperature. The mercury column was also thermostatted by means of a water jacket. After 30 minutes the polarographic cell was flushed with nitrogen gas for a further 30 minutes. This procedure eliminated oxygen from the solution and brought the electrolyte to the required temperature. The polarogram was then recorded on a Sargent Model XXI Polarograph. In addition, polarograms of the Igepal-saturated blank solutions (KOH solutions without zincate) were recorded at the various temperatures. The drop time and drop weight for the mercury drops was also determined in the various KOH concentrations as a function of temperature. These two parameters were determined at the half wave potential for zinc. This procedure gave the values of the drop time and drop weight pertinent to the zincate polarograms.

The diffusion coefficient (D) was calculated from the modified Ilkovic equation.

$$i_d = B\, n\, D^{1/2}\, C\, m^{2/3}\, t^{1/6} \left(1 + \frac{A\, D^{1/2}\, t^{1/6}}{m^{1/3}}\right) \qquad 2.1$$

where i_d = the diffusion limited current in microamperes

$$B = \frac{F \cdot 6/7 \cdot \sqrt{7/3}\ \sqrt[3]{36}}{\pi^{1/6}\ (\rho_{Hg})^{2/3}} \cdot 10^{-2}$$

F = the Faraday

ρ_{Hg} = the mercury density

n = the number of electrons involved in the reaction

= 2.

C = the concentration of zincate in millimoles per liter.

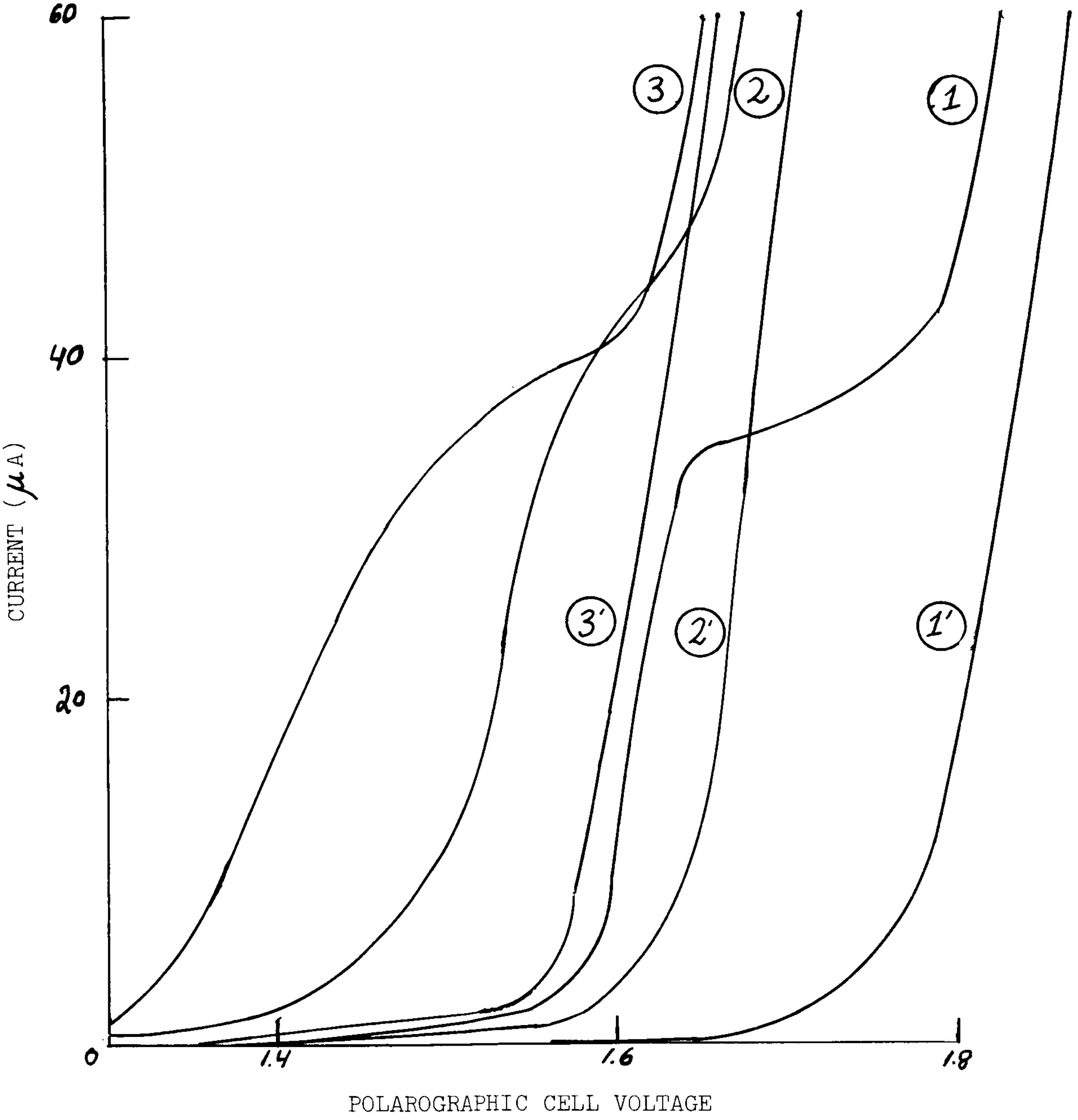
m = the capillary efficiency in mg/sec.

t = the drop time of mercury in sec.

A = a constant = 34.

The height of the polarographic wave was determined, using the blank curves to correct for the current of the supporting electrolyte. This gave us the value for i_d. This value, together with the drop time, drop weight and the appropriate value of the mercury density (depending on temperature) was inserted in Equation (2.1) to yield the diffusion coefficient.

Figure 1 shows a typical set of polarographic waves together with the blanks for various KOH concentrations. It can be seen that a single



1	5% KOH	1'	Blank 5% KOH
2	25% KOH	2'	Blank 25% KOH
3	30% KOH	3'	Blank 30% KOH

FIGURE 1 ZINCATE POLAROGRAPHS

5×10^{-3} M ZnO in KOH, 25°C for solutions 1,2 and 3.

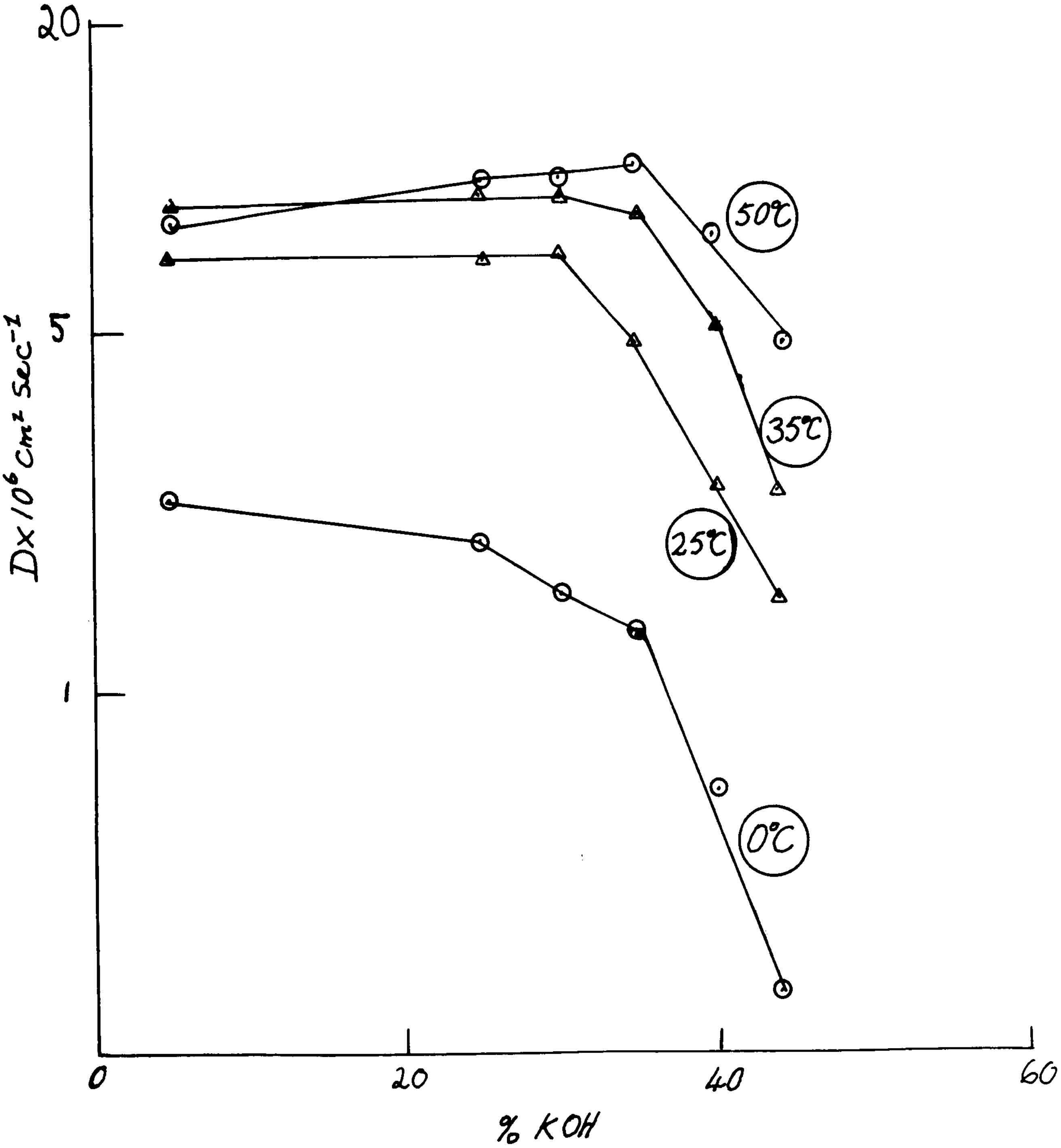


FIGURE 2 DIFFUSION COEFFICIENT FOR ZINCATE VS. KOH CONCENTRATION FOR VARIOUS TEMPERATURES

wave is obtained for the zincate ion discharge. The masking of the zincate wave by the potassium wave was more apparent at the higher concentrations of KOH and the higher temperatures. Subtraction of the blank wave from the zincate wave gives the corrected zinc wave for obtaining the values of i_d. The values of i_d and D for various temperatures and KOH concentrations are given in Table I. Figure 2 gives plots of the diffusion coefficient against percentage KOH for the various temperatures. It may be seen that the diffusion coefficient for zincate in the 5% KOH to 25% KOH concentration range is relatively constant. In concentrations in excess of 30% KOH the diffusion coefficient drops steadily with increase in KOH concentration.

Table I Values of i_d and D for Various KOH Concentrations and Temperatures

Temperature	0°C		25°C		35°C		50°C	
% KOH	$i_d \mu A$	$D \times 10^6$	$i_d \mu A$	$D \times 10^6$	$i_d \mu A$	$D \times 10^6$	$i_d \mu A$	$D \times 10^6$
5%	19.8	2.38	29.0	6.86	39.3	8.67	38.0	8.11
25%	18.6	1.95	37.8	6.99	40.2	9.21	42.3	9.73
30%	17.1	1.55	34.8	7.23	39.3	9.06	42.0	9.55
35%	14.7	1.34	29.1	4.82	38.7	8.50	44.0	10.5
50%	10.5	0.648	22.6	2.53	29.8	5.23	37.5	7.61
44%	6.75	0.269	15.4	1.52	19.7	2.36	29.3	4.93

Figure 3 gives a plot of the diffusion coefficient against the reciprocal of the viscosity. It is interesting to note that the curve does not follow the straight line behavior predicted by the Einstein-Stokes equation.

$$D = \frac{kT}{6\pi r \eta}$$

where

k = the Boltzman constant.

T = the absolute temperature.

r = the particle radius

η = the viscosity

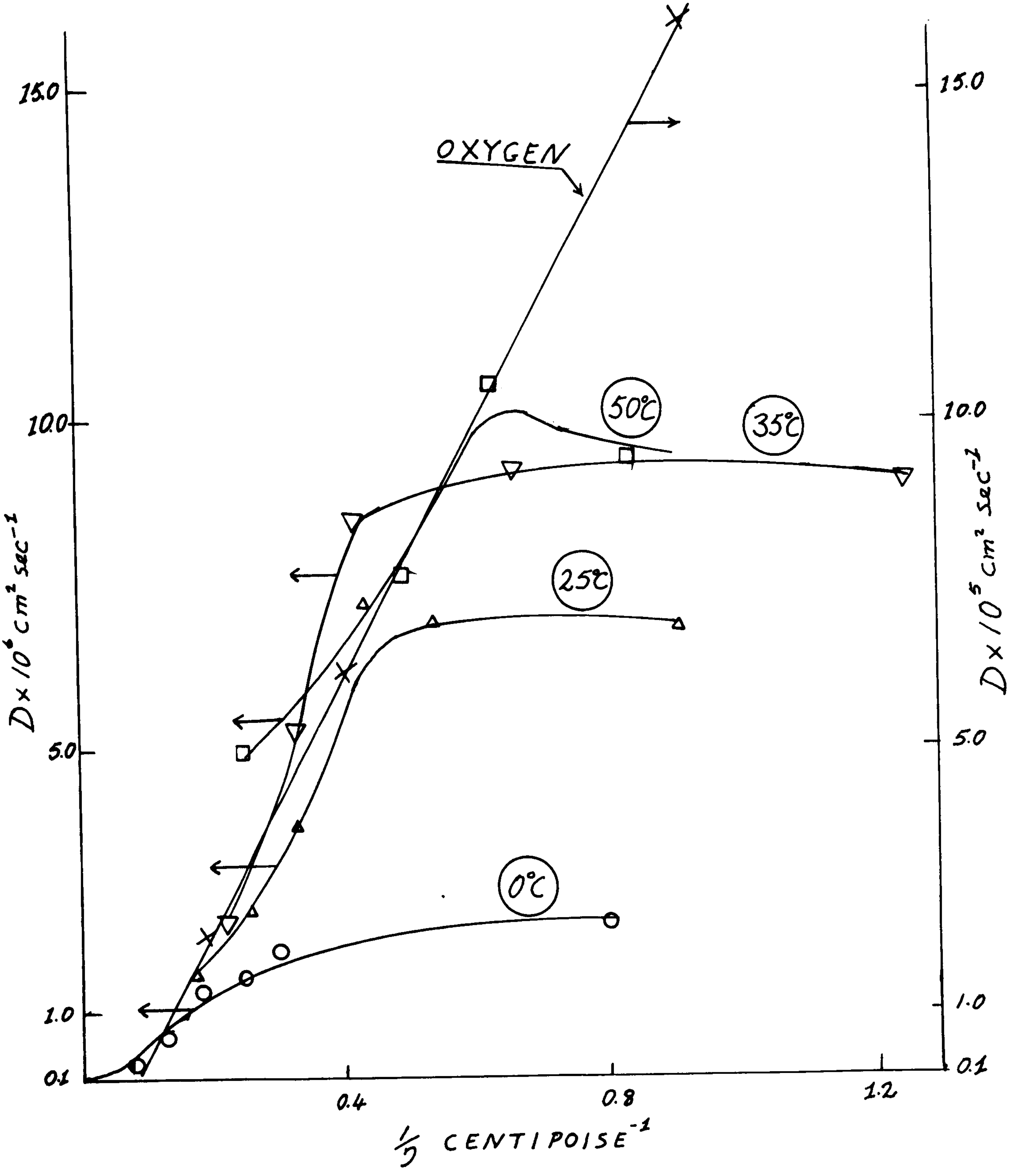


FIGURE 3 DIFFUSION COEFFICIENT FOR ZINCATE VS. RECIPROCAL VISCOSITY

Figure 3 also gives a plot of the diffusivity of oxygen against the reciprocal viscosity at room temperature in the same concentration range of KOH. (The values of the oxygen diffusivity are those of Gubbins and Walker.)[2] It may be seen that the plot is linear.

If one extrapolates the diffusivity data for zincate at high concentrations of KOH to low concentrations of KOH, the predicted diffusion coefficient is much larger than that found experimentally. A possible explanation for this result is that the radius of the diffusing zinc species is smaller at higher concentrations of KOH. At the higher concentration of KOH practically all the water is tied up as water of hydration for KOH, whereas at the lower KOH concentrations we have considerable amounts of free water molecules in the solution. Thus, it is possible that the diffusing zincate ion in low concentrations of KOH may be a large hydrated ion, whereas it is a small anhydrous ion in the higher concentrations of KOH. A hydrated zincate ion in 5% KOH with 2.5 times the radius of the zincate ion in 44% KOH would account for the discrepancy in the Einstein-Stokes relationship. In the case of oxygen we have an uncharged (hence, unhydrated) diffusing species whose radius will not change with the concentration of KOH; hence, the linear relationship between diffusivity and reciprocal viscosity.

Figure 4 gives Arrhenius plots for the diffusion coefficient in 35% KOH, 40% KOH and 44% KOH. It may be seen that the diffusivity can be expressed as:

$$D = D^{\circ} \quad \exp\left(-\frac{\Delta H}{RT}\right)$$

where D = the diffusion coefficient.

D° = a constant

ΔH = the energy of activation for diffusion.

T = the absolute temperature.

R = the gas constant.

Values of D° and H are given in Table II. It can be seen that the energy of activation for diffusion of zincate is quite large in the KOH concentration ranges that are practical for use in the silver-zinc system cells.

Table II Diffusion Parameters for Zincate in KOH Solutions

Percent KOH	D° cm^2 sec^{-1}	ΔH K cal
35%	0.29	6.52
40%	8.0	8.97
44%	54.5	10.40

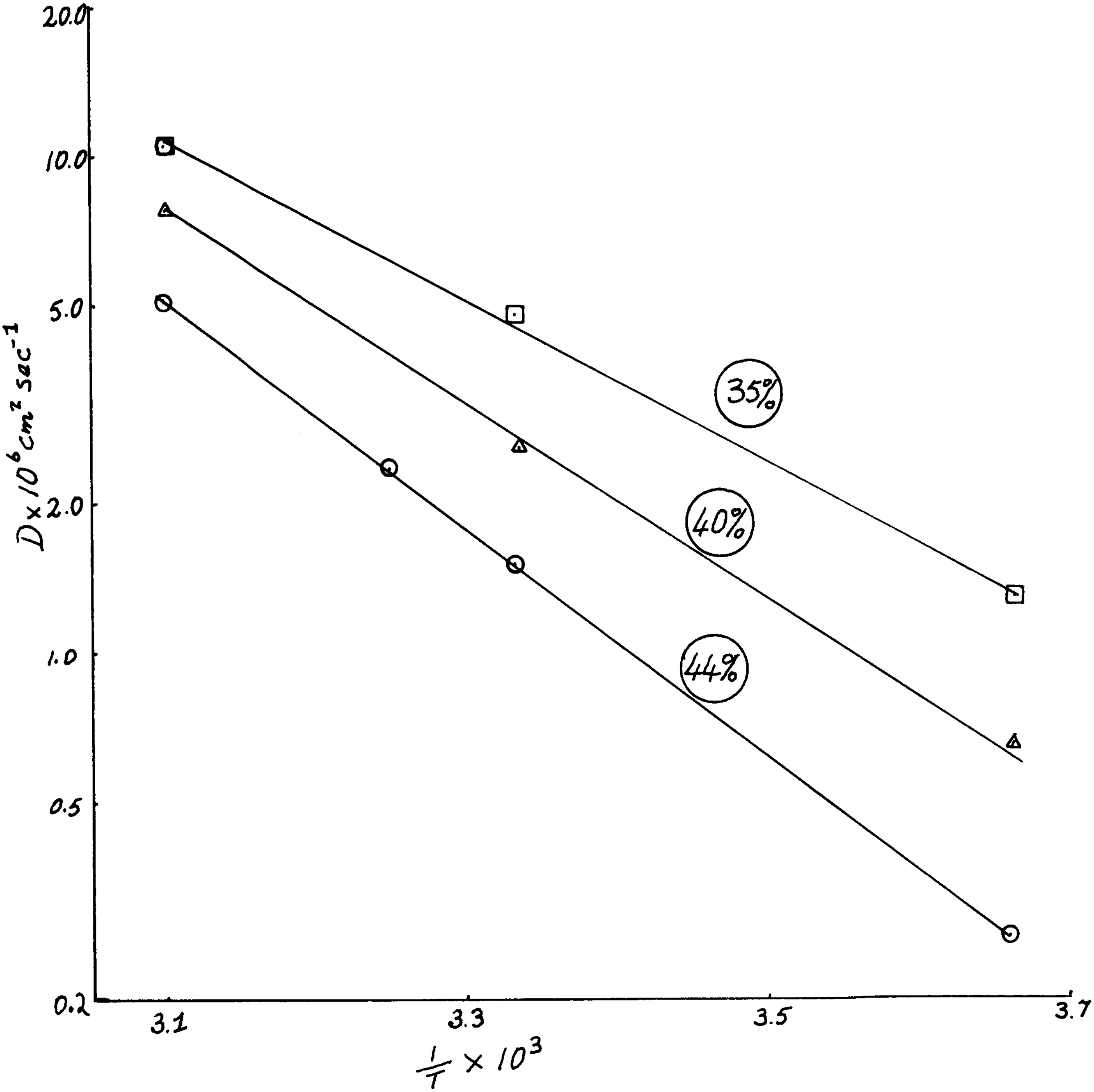


FIGURE 4 ARRHENIUS PLOTS FOR ZINCATE DIFFUSIVITY

2.2 Zinc Deposition on Rotating Disc Electrodes

To correlate the morphology of zinc deposits as a function of zinc overpotential a series of experiments was carried out in which zinc was deposited from a zincated saturated solution of 35% KOH on a rotating disc at various overpotentials while measuring the plating current.

For this investigation a rotating disc cathode (1 cm in diameter) was mounted in a pyrex cell (see Figure 5). The cell had a counter electrode in a separate compartment, and a zinc reference electrode with a Luggin capillary which was in close abuttal to the rotating disc. A Wenking potentiostat was used to maintain the zinc cathode at constant potential with respect to the reference electrode. During deposition the disc cathode was rotated at 8.8 r.p.s. Approximately 190 coulombs of zinc were deposited at various overpotentials. The deposition current was measured towards the end of plating. Separate runs were carried out for each overpotential that was investigated. Upon termination of a run the zinc deposit was scraped off the disc and the mean thickness of ten whiskers was determined microscopically.

Figure 6 Curve 1 shows the dependence of current on overpotential, and Curve 2 gives the diameter of the whiskers as a function of overpotential. The current-overpotential curve is similar to a polarographic wave in that the current rises with potential and tends towards a limiting value at about an overpotential of 200 mV. The limiting current density can not be determined accurately since at these high overpotentials considerable hydrogen evolution occurs along with the zinc deposition. However it can be seen that at overpotentials less than 125 mV zinc deposition it is not controlled by diffusion of zincate to the substrate whereas at overpotentials in excess of 175 mV zinc deposition occurs under diffusion controlled conditions. It is in this interval of overpotential (at approximately 150 mV) that the transition from mossy to dendritic zinc occurs. Thus it is evident that mossy zinc is deposited under activation controlled conditions and dendritic zinc under diffusion controlled conditions. Morphologically the main criterion which distinguishes the moss whiskers from dendrites is their diameters (3.6 μ for whiskers and 170 μ for dendrites). Mossy zinc has a very open structure and has a density of 0.1 g/cm^3 whereas dendritic zinc has a density of 0.25 g/cm^3.

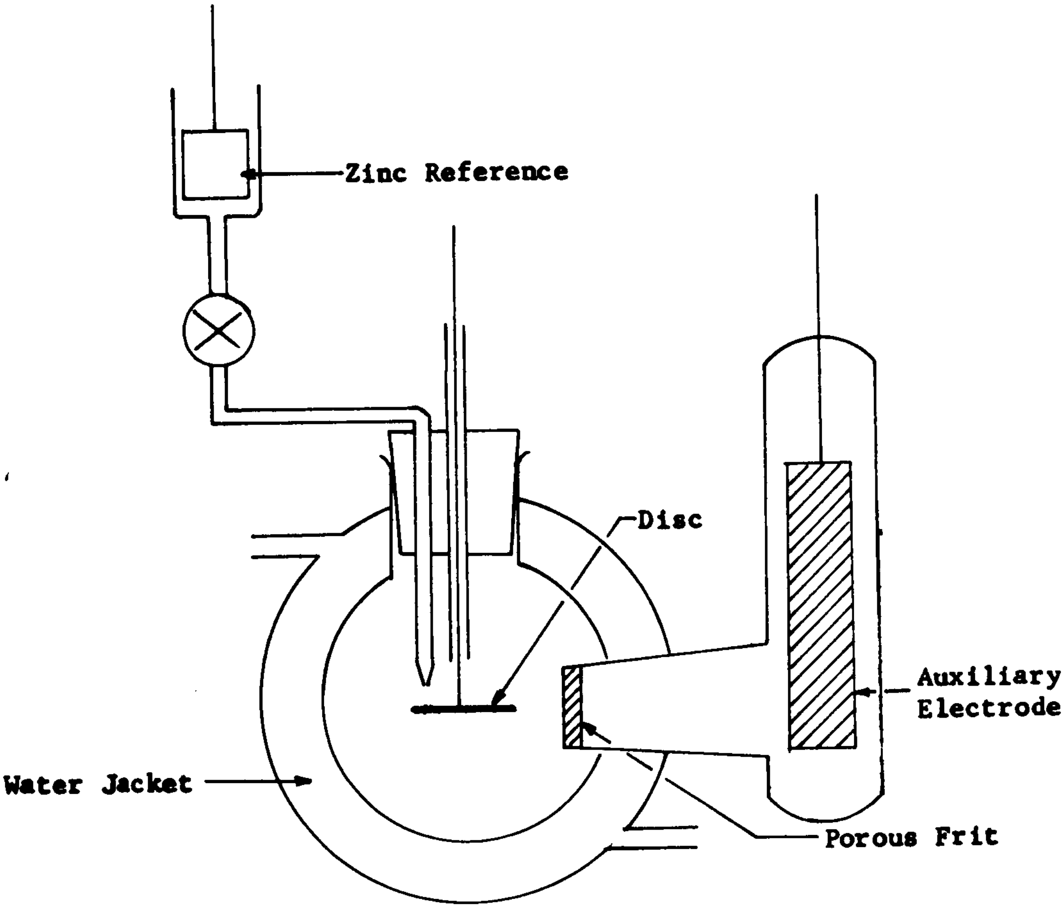


Figure 5 Rotating Disc Apparatus

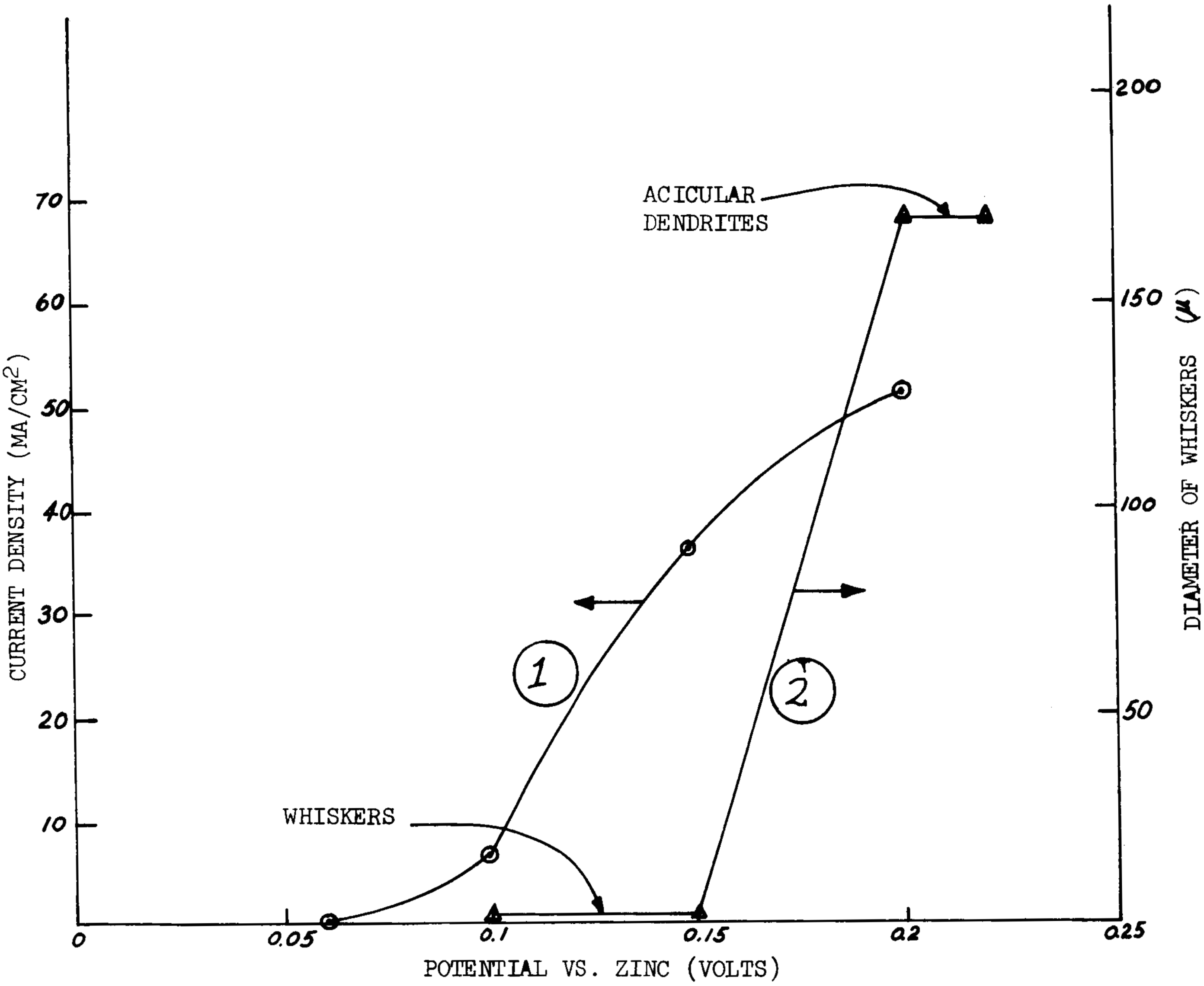


FIGURE 6 CURRENT AND DIAMETERS OF WHISKERS AS A FUNCTION OF POTENTIAL

Since dendrites are deposited under diffusion controlled conditions the parameter which governs the critical current at which dendrites form will be the product of the zincate diffusivity in the electrolyte. A plot of this parameter versus KOH concentration is given in Figure 7. It can be seen that the product of the zincate diffusivity and the solubility goes through a maximum at about 31% KOH. At this concentration the possibility of forming dendrites should be at a minimum.

2.3 Absorption of Zincate in Separators

For penetration of zinc through separators to occur zinc must be deposited in the body of the separator membrane. The concentration of zincate in the ambient whether it be free electrolyte or membrane is an important parameter for zinc deposition under both activation and diffusion controlled conditions. The concentration of zincate in various membranes was determined for various external concentrations of zincate in the ambient electrolyte.

In this study the membranes investigated were PUDO-300 (Du Pont cellophane), Ag-treated PUDO-300 (Yardney Electric Corp.), unplasticized polyvinylalcohol (Monosol-PVA supplied by Polyfilm Corp.), 2.2XH Series 2 grafted polyethylene (Radiation Applications Inc.), and C-3, 9107/5, 9107/21, 9107/22, 9107/27 (Borden Chemical Co.) (1)

The analytical method used was as follows. The separators were cut into pieces 3" x 3", weighed, and soaked in the desired alkaline zincate solution for three days. The membranes were taken from the electrolyte and towelled between two layers of absorbent papers and weighed as quickly as possible to minimize carbon dioxide pickup and evaporation losses. The dimensions of the membrane after the soak period were also determined. The membranes were then dissolved in 10 cc of 1:1 HNO_3 and the solution evaporated to dryness. The residue was dissolved in a solution containing 1N NH_4OH + 1N NH_4Cl (50 cc). This ammoniacal solution was analyzed polarographically for zinc using gelatin as a maximum suppressor. In this way the number of moles of zincate per sample was determined. The volume of electrolyte in the membrane was determined from the weight pickup of the electrolyte and the density of the specific electrolyte used. Thus the concentration of zincate in terms of volume of absorbed electrolyte could be determined. Furthermore the concentration of zincate per unit volume of soaked membrane could also be determined. The latter parameter is important from the point of view of zinc deposition in the membrane since

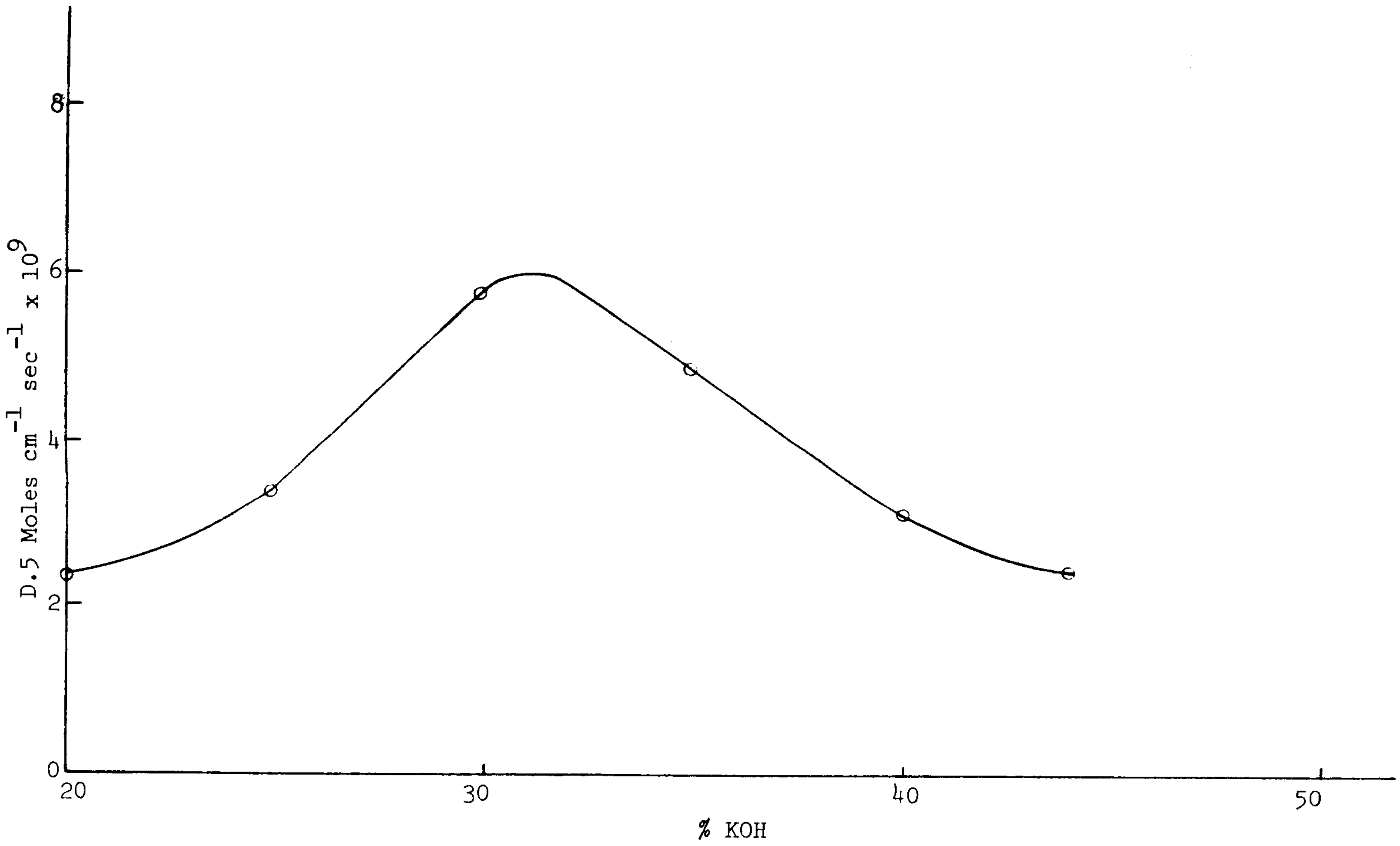


FIGURE 7 THE PRODUCT OF THE DIFFUSIVITY AND SOLUBILITY OF ZINCATE AS A FUNCTION OF KOH CONCENTRATION

together with the zincate diffusivity in the membrane it determines the zincate flux in the separator.

The absorption of zincate was determined for all membranes in 45% KOH at 25°C in the zincate concentration range of 0.1 M to 1.0 M. The absorption of zincate in C-19 and PUDO-30 was determined in 44% KOH saturated with Emulphogene BC-610 (General Aniline and Film Corp.), and in 31% KOH for PUDO 300, C-19 and 2.2XH. To determine if any changes in the film structure due to aging in KOH solutions affects zincate pickup the absorption of zincate in 44% KOH we determined for C-19, PUDO-300, PVA, C-3 9107/5 and RAI 2.2XH in 45% KOH at 60°C. In this case the membranes were soaked in the zincate solutions for three days at 60°C.

Curves for the absorption of zincate in the membranes under various conditions are given in Figures 8 - 14. In all cases except for 9107/27 the concentration of zincate in the separator was less than the ambient electrolyte. If one treats the membrane as a separate phase then

$$\frac{C_M}{C_E} = K$$

where C_M is the concentration of zincate in the membrane and C_E the concentration of zincate in the ambient electrolyte and K is the distribution coefficient for zincate. Table III gives values for K for the various membranes under various conditions.

Table III Zincate Distribution Coefficients, K and Conditions for Absorption Studies in Separator Membranes

Separator Type	Electrolyte and Stand Temperature			
	45% KOH at 25°C	31% KOH at 25°C	45% KOH at 60°C	45% KOH Saturated with BC-610 at 25°C
PUDO-300	0.84	0.94	0.86	0.84
C-19	0.81	0.84	0.79	0.83
PVA	0.592		0.610	
C-3	0.155		0.420	
2.2XH Series 2	0.63	0.60	0.55	
9107/5	0.455		0.75	
9107/22	0.84			
9107/21	0.91			
9107/27	1.06			

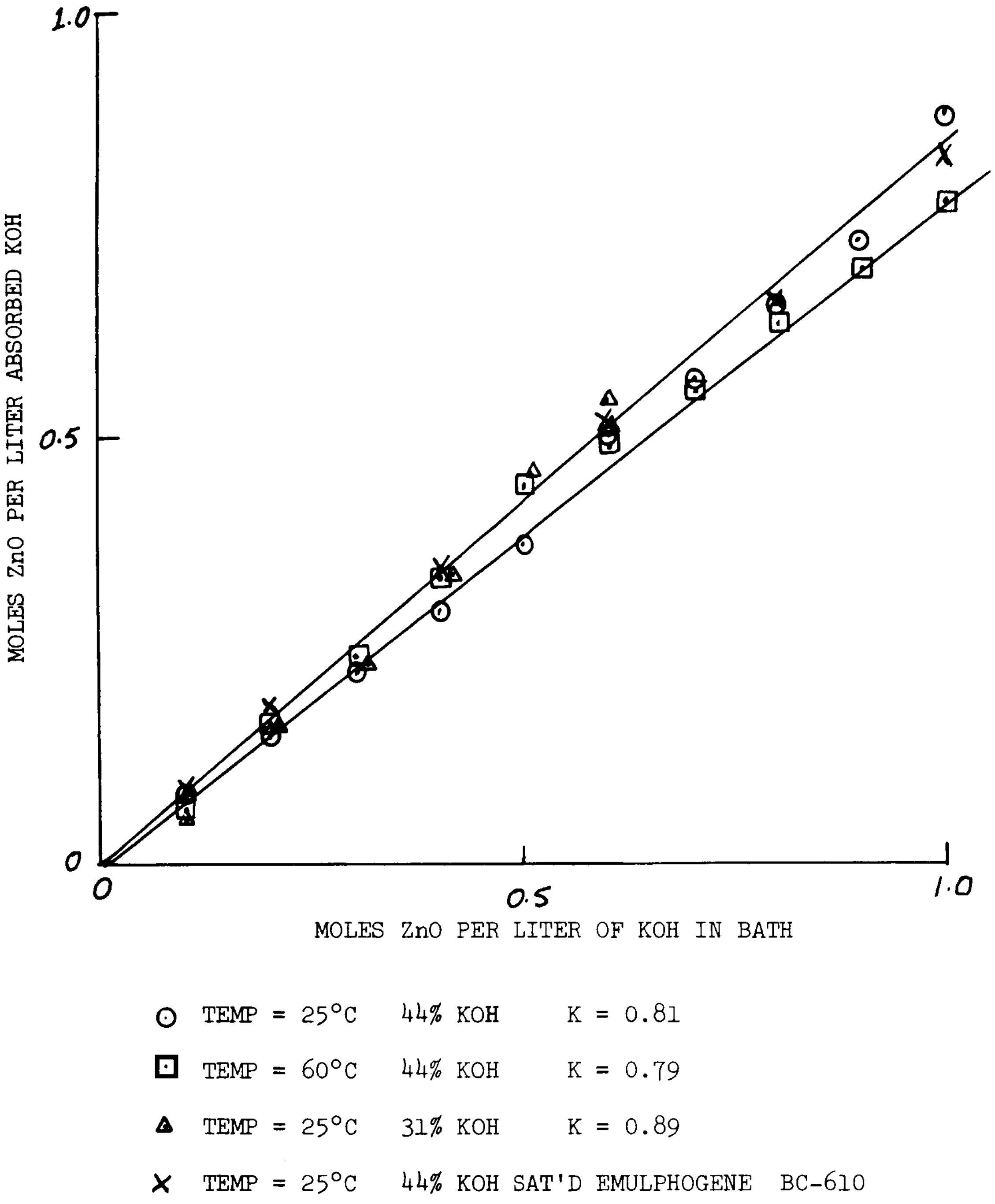


FIGURE 8 ABSORPTION ISOTHERMS FOR YARDNEY C-19

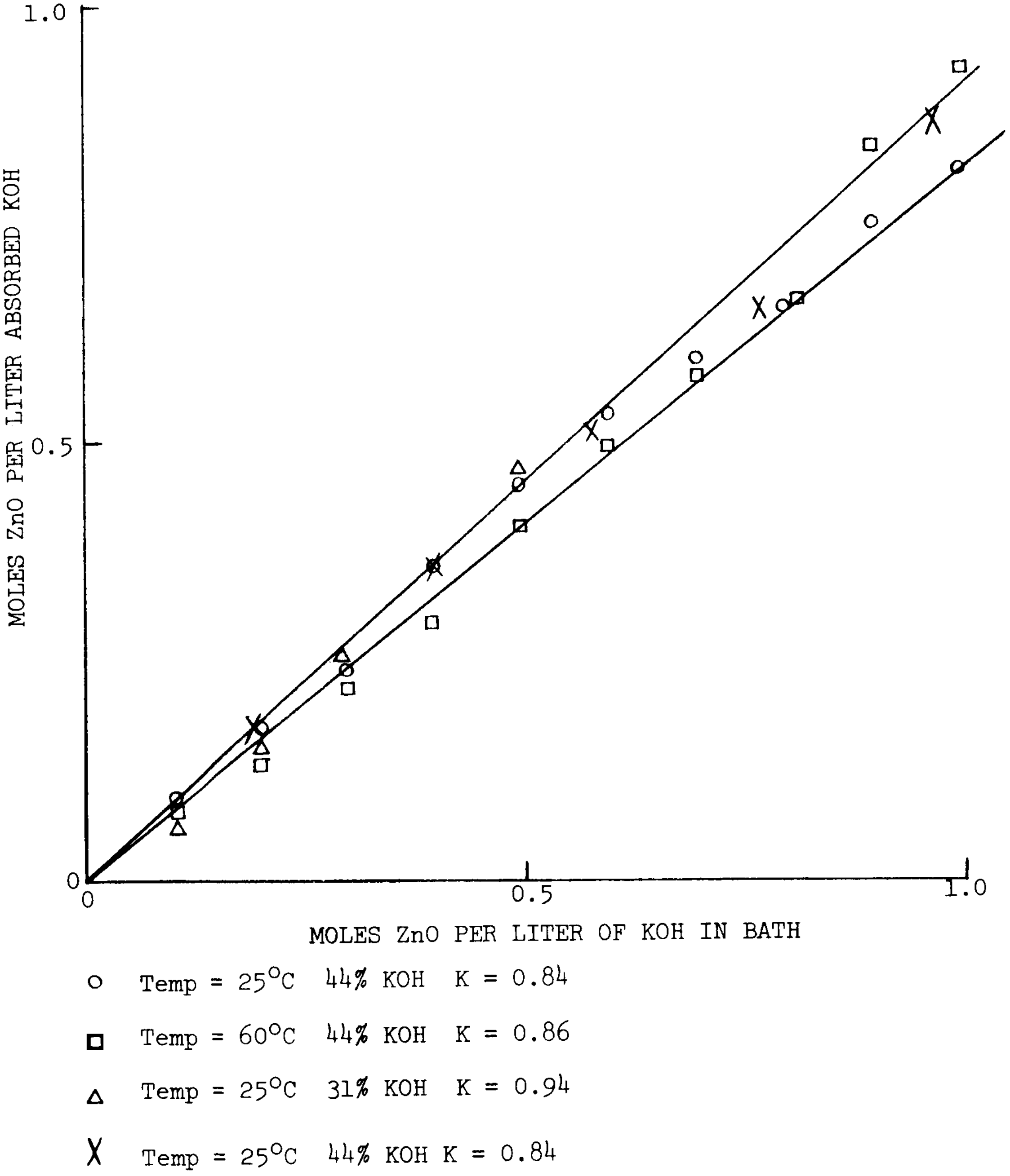


FIGURE 9 ABSORPTION ISOTHERMS FOR DU PONT PUDO 300

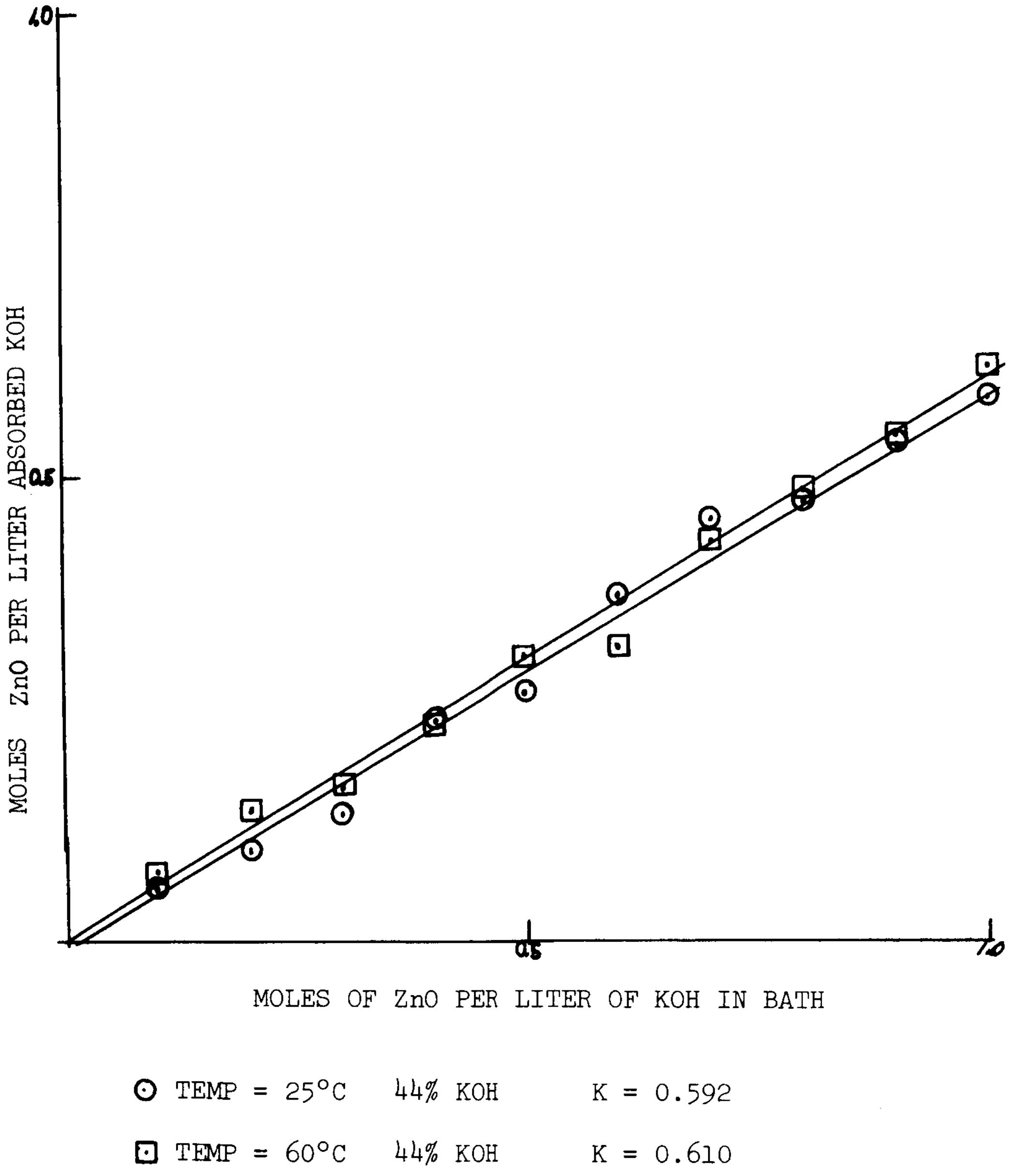


FIGURE 10 ABSORPTION ISOTHERMS FOR POLYFILM CORP. PVA

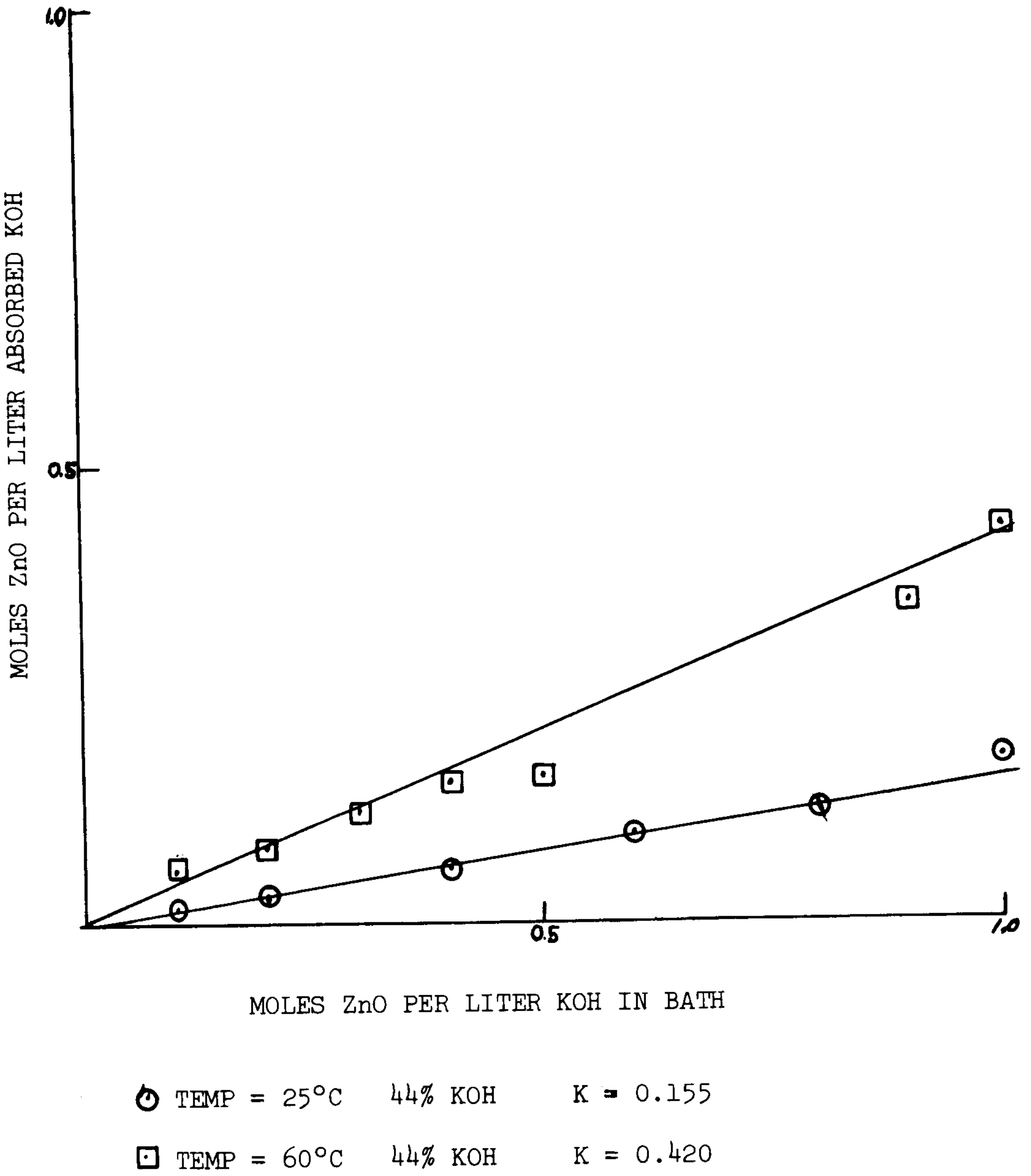


FIGURE 11 ABSORPTION ISOTHERMS FOR BORDEN C-3

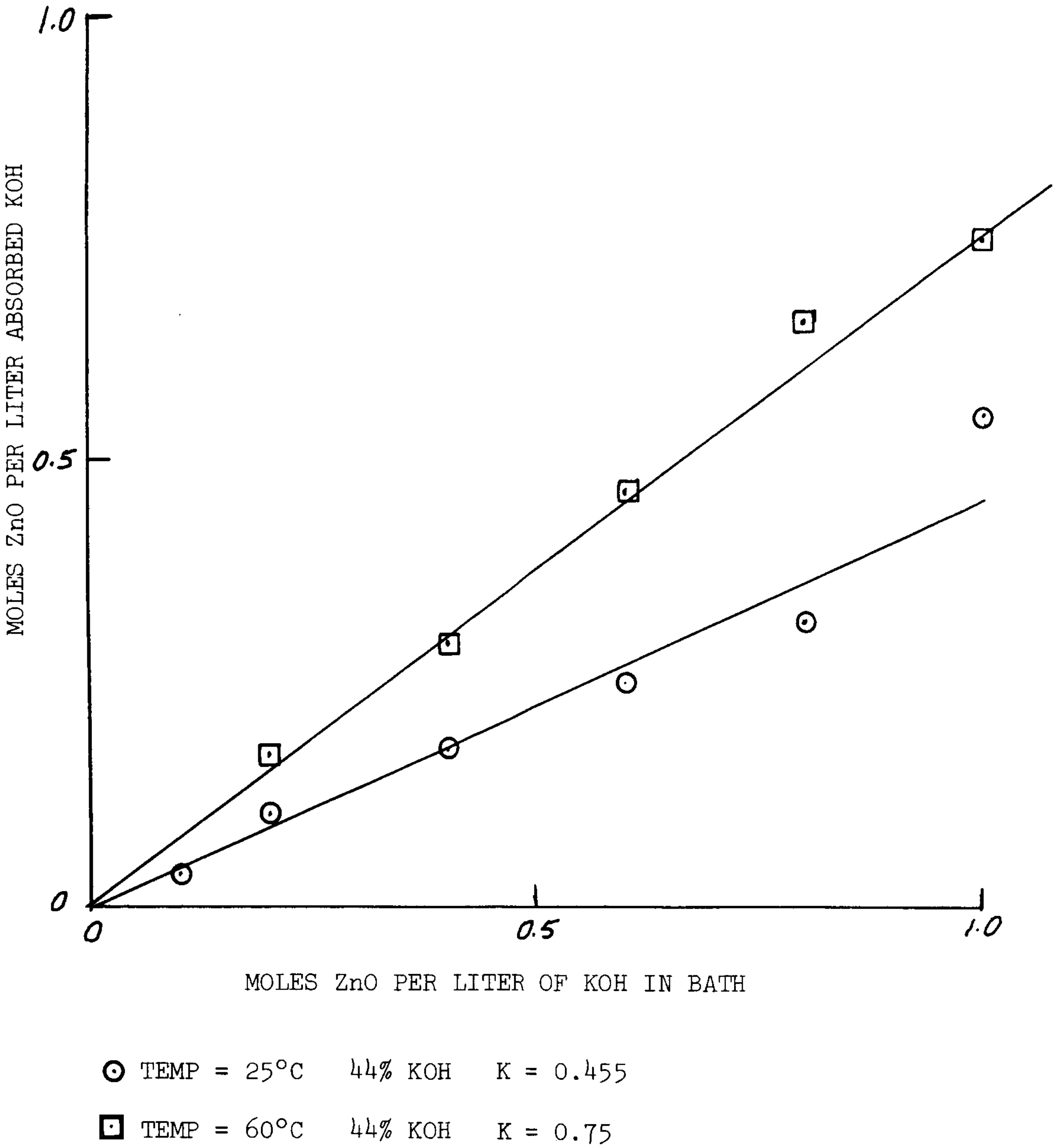


FIGURE 12 ABSORPTION ISOTHERMS FOR BORDEN 9107-5

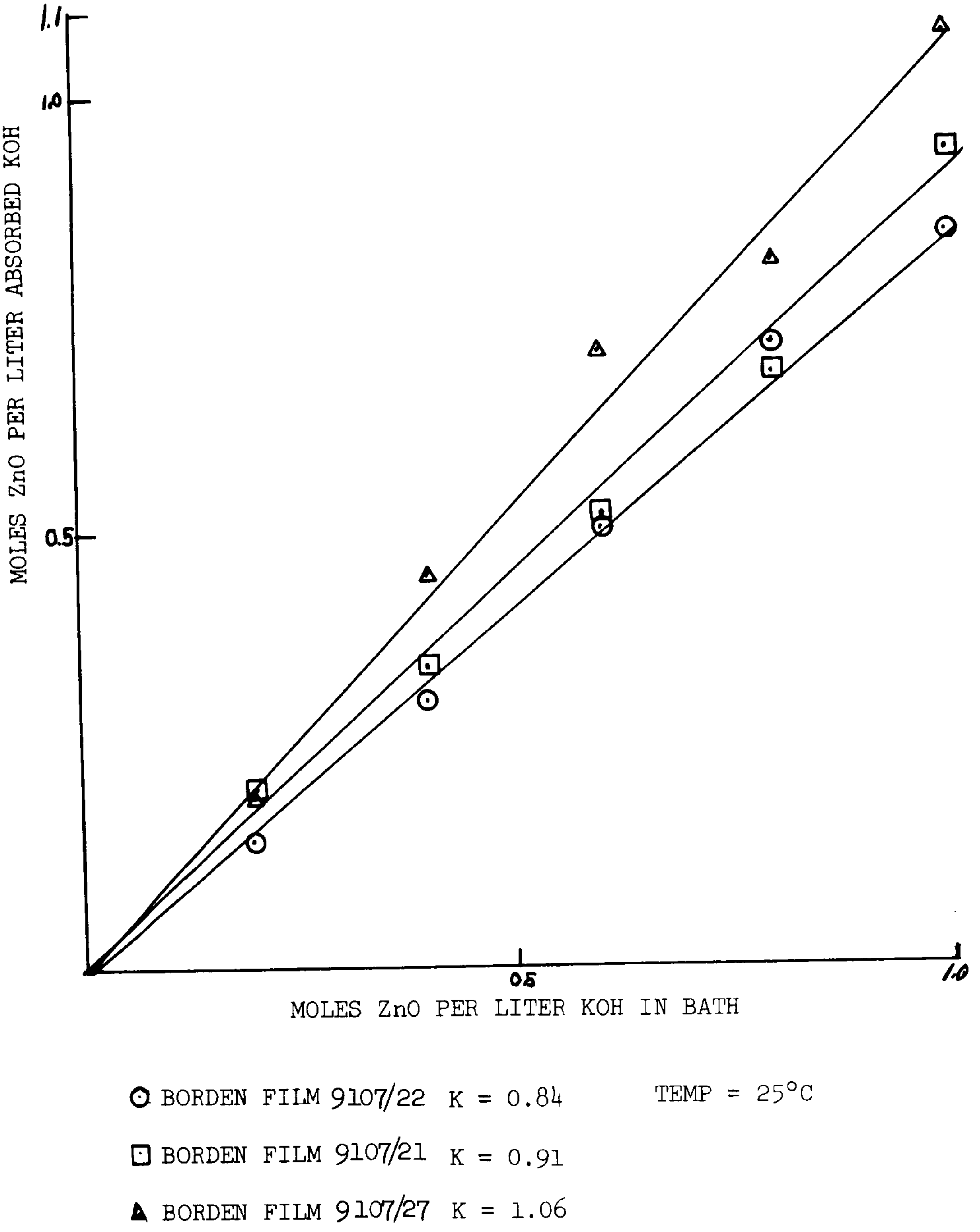


FIGURE 13 ABSORPTION ISOTHERMS FOR BORDEN FILM 9107/22, FILM 9107/21, and FILM 9107/27

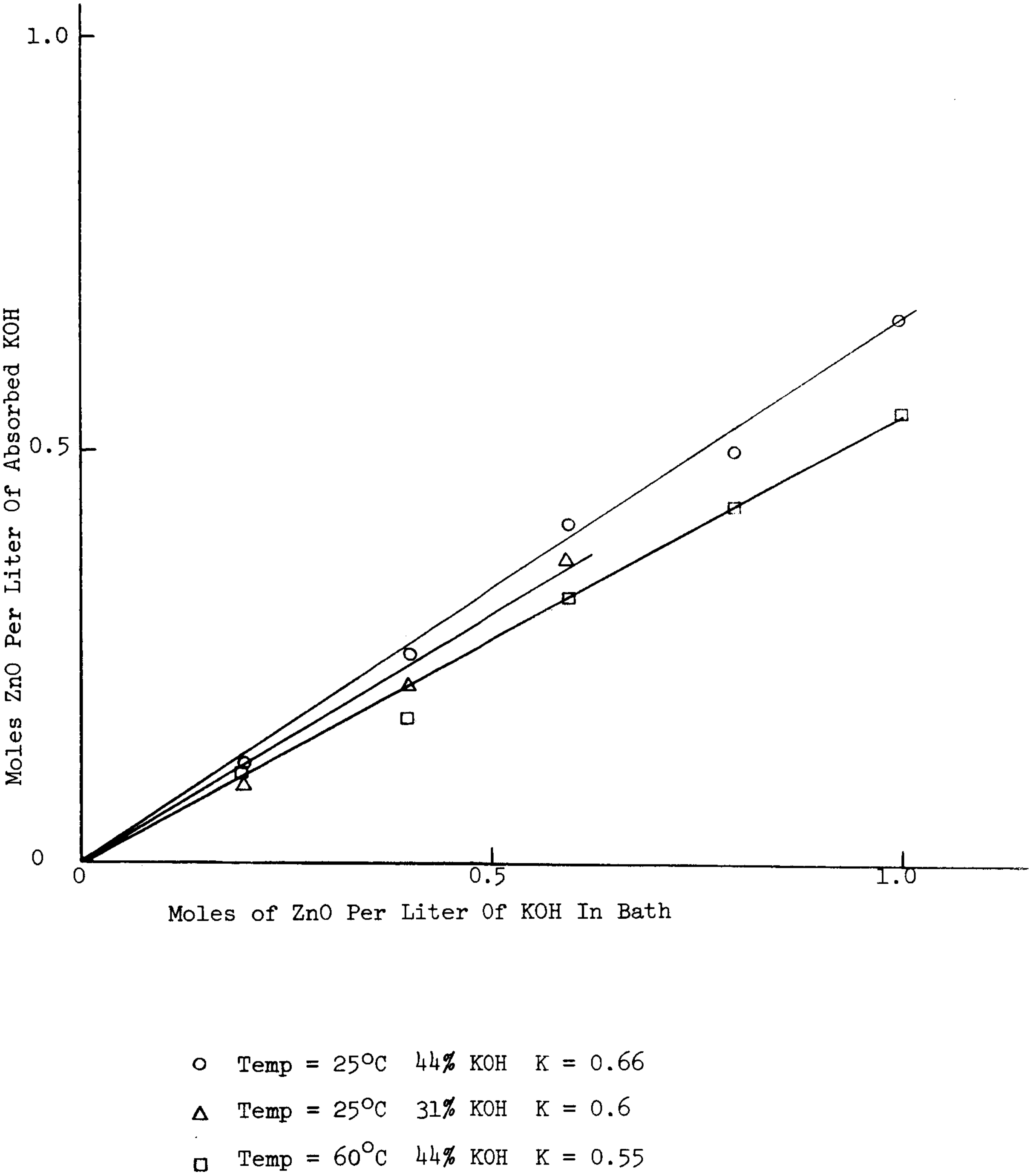


FIGURE 14 Absorption Isotherms for 2.2xH Series 2 (Radiation Applications Inc.)

It can be seen that the separation coefficient for the various membranes vary by a factor of seven. Except for 9107/27 all membranes exclude zincate to some degree.

Additions of Emulphogene BC-610 to the electrolyte do not change the separation coefficient for cellulosic materials, and the separation coefficient for cellulosic materials and grafted polyethylene is the same in 31% KOH and 45% KOH.

The separation coefficient for zincate in cellulosic films and polyvinyl alcohol does not change with increase in soak temperature. However, the separation coefficient for both C-3 and 9107/5 changes considerably with soak temperature. This must be due to degradation of the materials in the hot caustic solutions. The 9107/5 material changed from a transparent film to a dark amber color after three days stand at 60°C. This change in color must be due to chemical degradation of the film. No such visible changes occurred in the case of the C-3 material. The separation coefficient for 2.2XH was slightly reduced when the membranes were soaked at 60°C. This reduction in zincate absorption may be due to leaching out of loose grafted material.

2.4 Zincate Diffusion in Separators

Since the rate of diffusion of zincate to a growing dendrite in a separator will determine the rate of growth of zinc through the separator it is important to know the zincate diffusivity in the membrane. The diffusivity of zincate was determined for the following separators: Du Pont PUDO-300, YEC Ag-treated PUDO-300 (C-19), Borden Chemical Co. (1) C-3 and 9107/5, "Monosol" PVA (unplasticized polyvinyl alcohol Polyfilm Corp.) and Radiation Applications Inc. grafted polyethylene (2.2XH Series 2).

The above separators were cut into pieces 3" x 3" and soaked for three days in 44% KOH solution containing 1.0 M zincate. The separators were then dried by toweling and mounted in a two-compartment diffusion cell (see Figure 15). One compartment of the diffusion cell was filled with 17 cc of 44% KOH. Arrangements were made for stirring the solution on the zincate dilute side of the membrane by bubbling purified nitrogen through a capillary. Samples of the solution (0.2 cc) were removed from the zincate-dilute compartment periodically. The samples were dissolved in a solution containing 1N NH_4OH + 1N NH_4Cl (50 cc). The ammoniacal zinc solution was then analyzed polarographically. The amount of zincate that had penetrated the sample was determined. Corrections were made to take into account the volume of the samples removed.

Diffusivity measurements were also made for PUDO 300, C-19 and 2.2XH in 31% KOH. In this case, the membranes were soaked in 31% KOH + 0.6 M ZnO. In the diffusion cell the ambient on the zinc rich side of the membrane was 31% KOH + 0.6 M ZnO, while the electrolyte on the zinc dilute side of the membrane was 31% KOH.

Diffusivity measurements were also made for membranes that were soaked at 60°C for three days in 45% KOH + 1.0 M zincate. In this way we hoped to simulate changes in the membranes which might occur during prolonged stand in the caustic electrolyte at room temperature.

The reason for presoaking the membranes in zincate solutions instead of pure KOH was to eliminate any zincate absorption effects in the membranes during measurements. The possibility exists that such effects could interfere with the measurement of the zincate diffusivity in the membrane.

Figure 16 shows a schematic representation of the concentration profile for zincate that is encountered in these measurements. The permeation process consists of the following steps:

1. Transfer of zincate from the electrolyte at x=0 to the membrane at x=0.
2. Diffusion of zincate through the separator from x=0 to x-L.
3. Transfer of zincate from the membrane at x=L to the electrolyte at x=L.

Our absorption studies show that the concentration of zincate inside the membrane at x=0 (C_o^M) is not equal to the concentration of zincate in the ambient electrolyte at x-0 (C_o^E). The relationship between these two parameters is

$$C_o^M = kC_o^E \qquad \underline{\text{Equation 1}}$$

Other work in this laboratory shows that the rate of permeation of zincate through cellulosic membranes is inversely proportional to the thickness of the membranes. Thus, it can be concluded that the diffusion process is the rate determining step in the permeation process. If Q is the quantity of zincate that has penetrated a membrane, then the flux of zincate (J) is:

$$J = \frac{Q}{At} \qquad \underline{\text{Equation 2}}$$

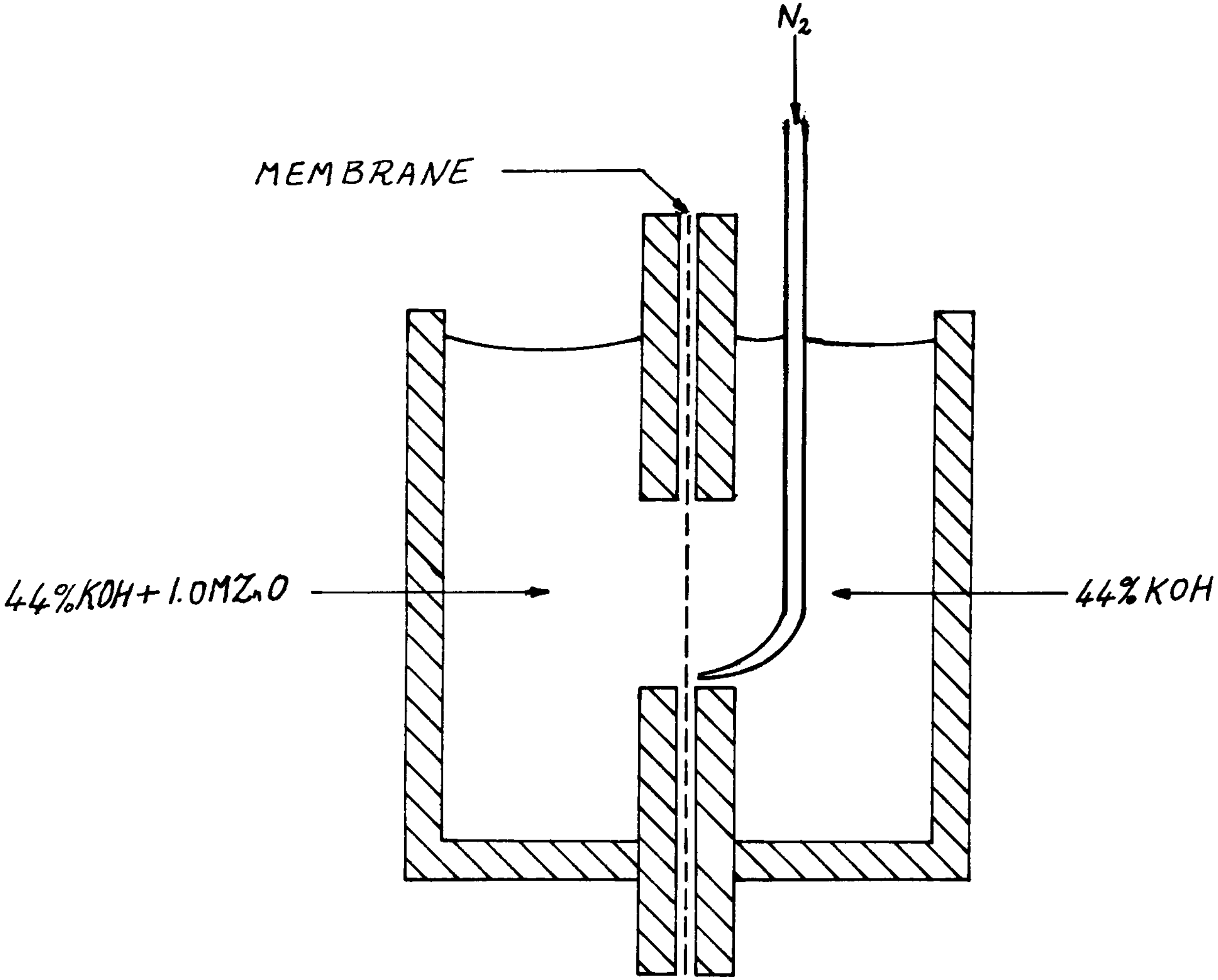


Figure 15. Apparatus for Zinc Diffusion Measurements

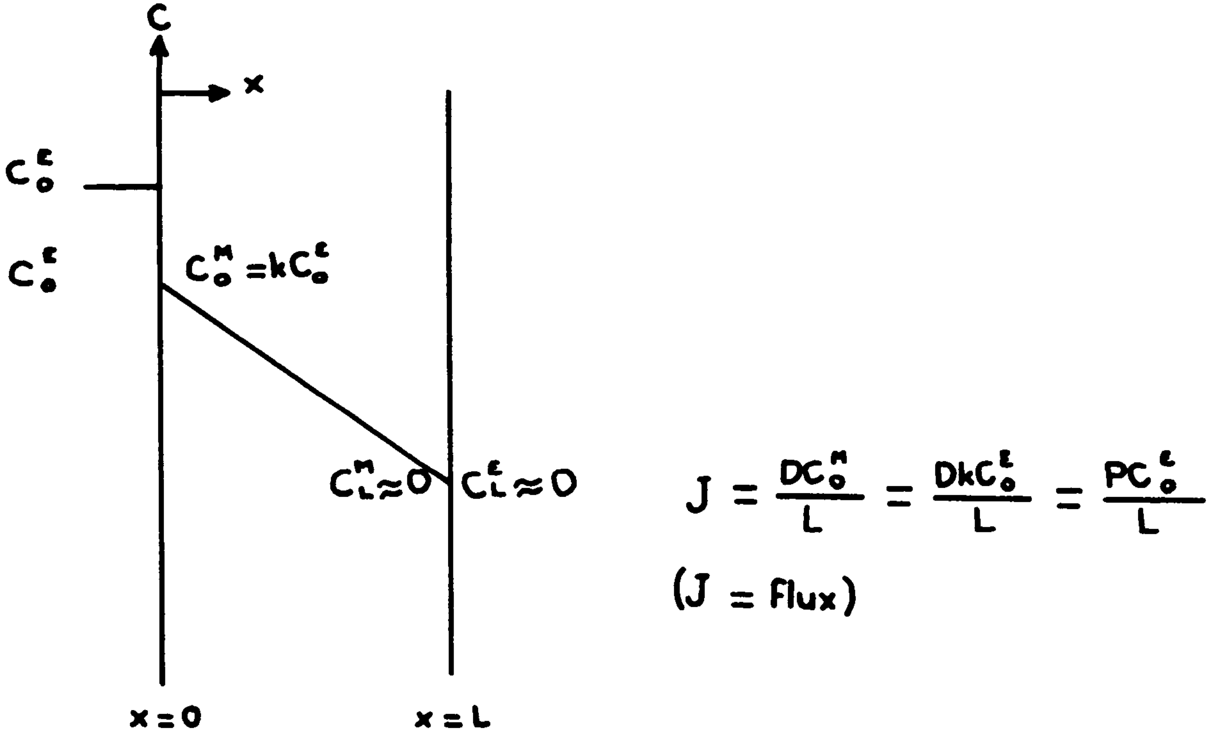


Figure 16. Schematic Representation of the Concentration Profile For Zincate in the Membrane

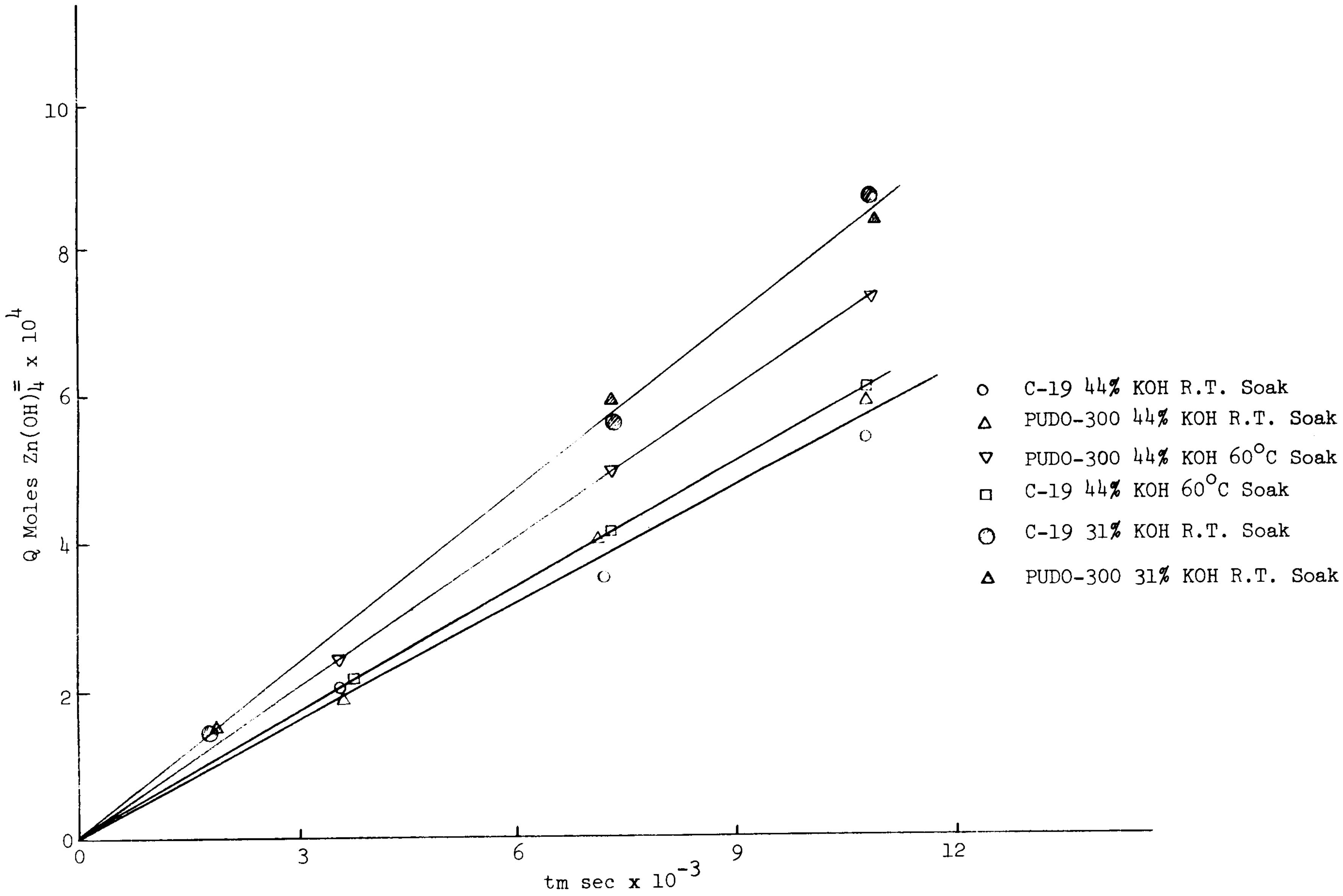


FIGURE 17 Permeation of Zincate through PUDO-300 (DuPont) and C-19 (YEC)

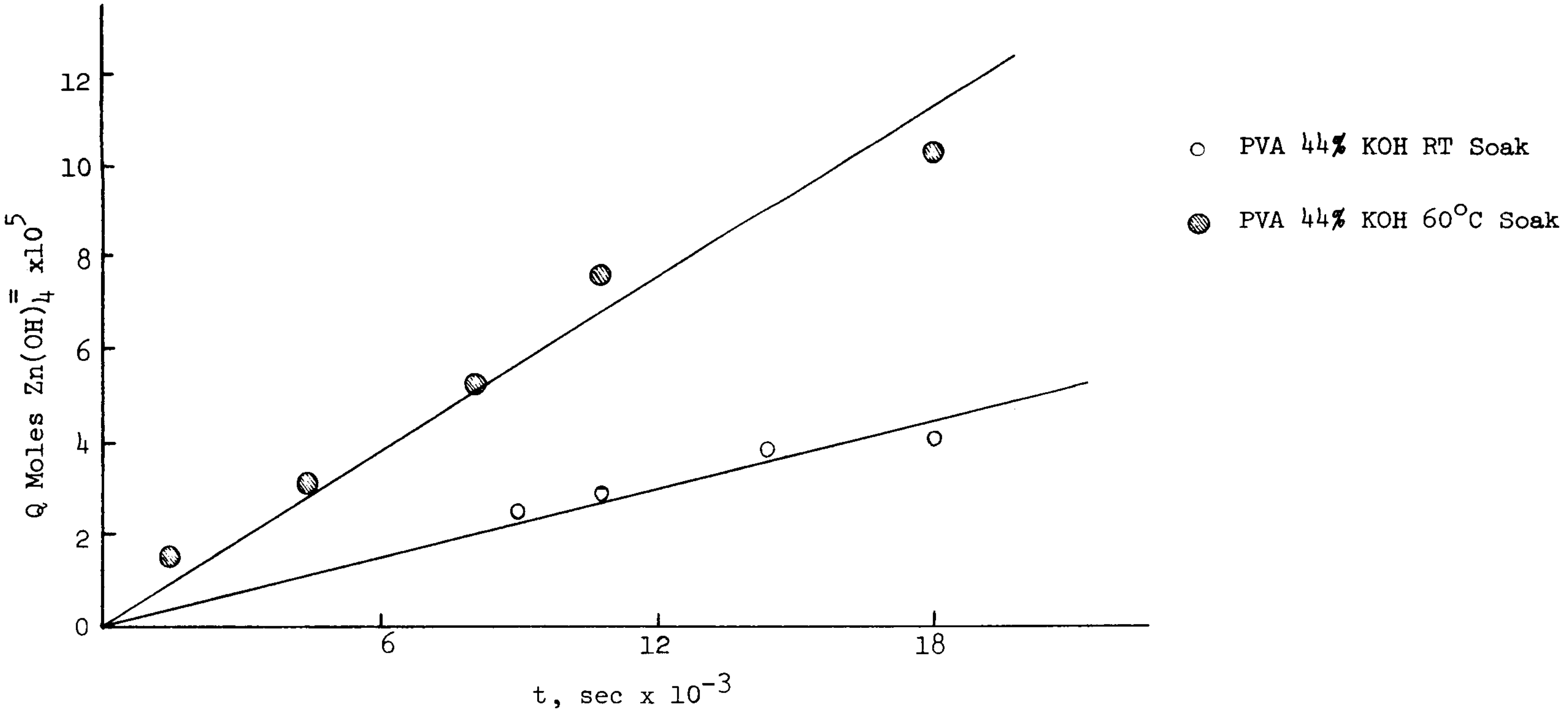


FIGURE 18 Permeation of Zincate through Polyvinyl Alcohol (Monosol PVA)

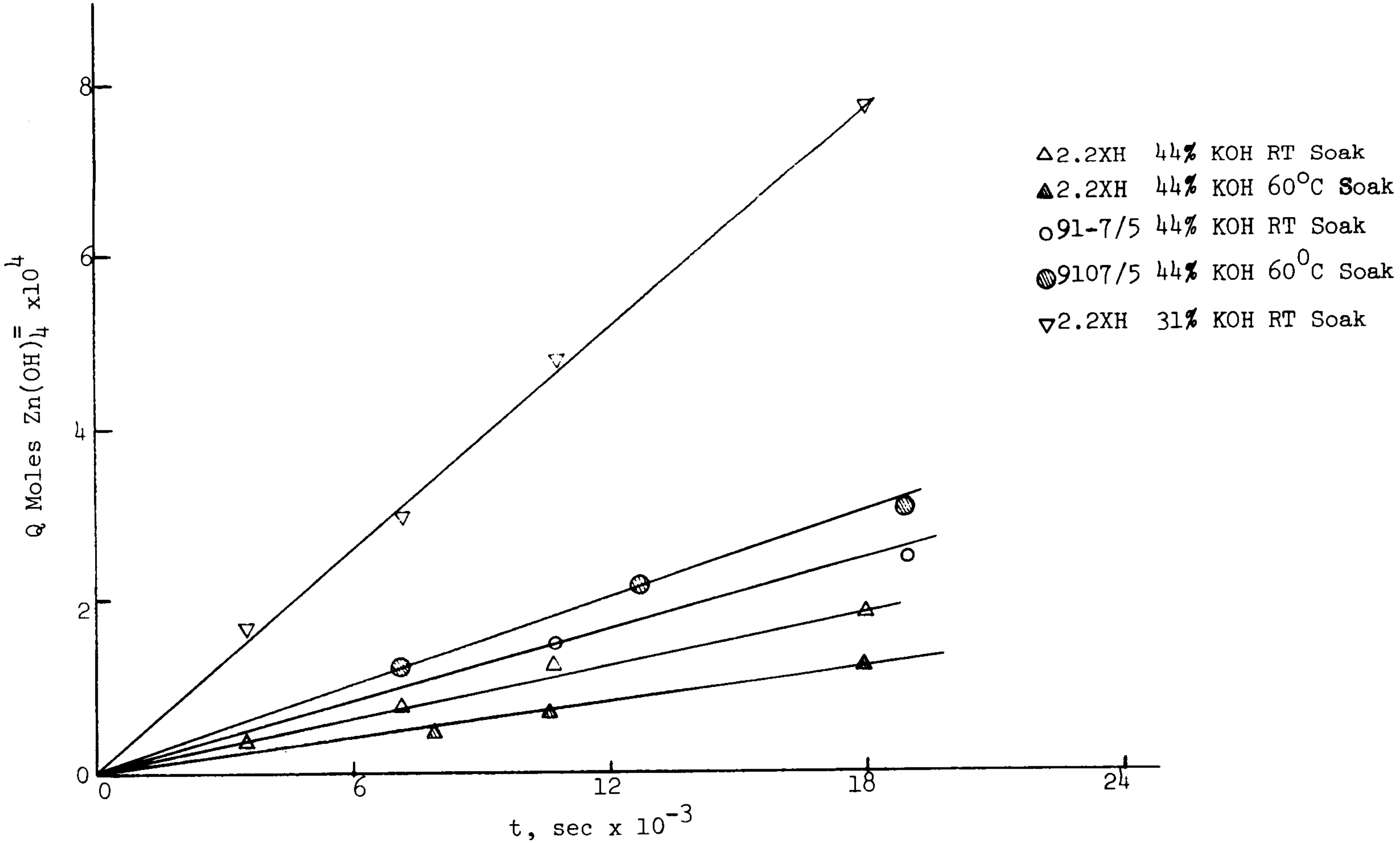


FIGURE 19 Permeation of Zincate through 2.2XH Series 2 (Radiations Applications Inc.) and 9107/5 (Borden Chemical Co.)

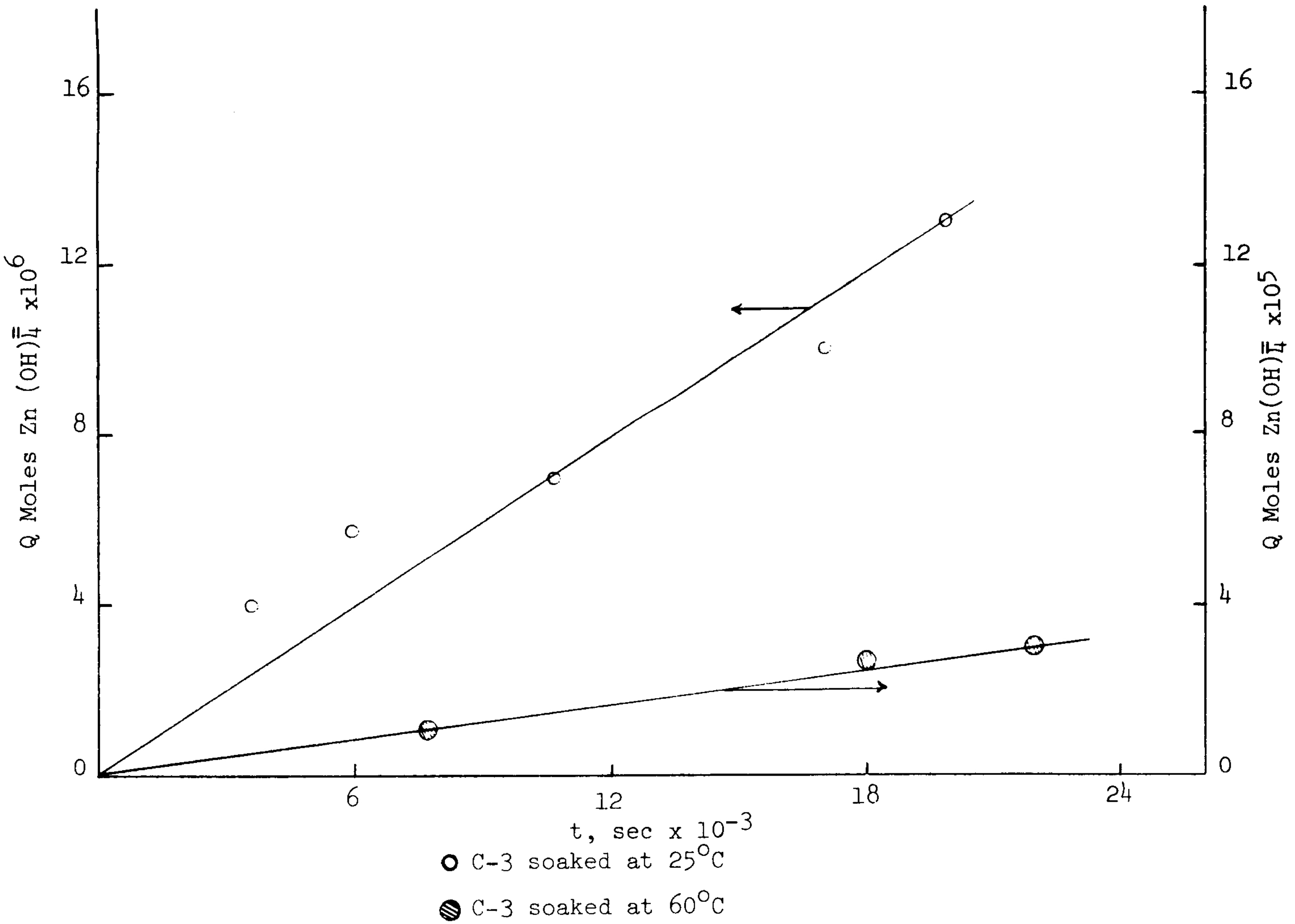


FIGURE 20 Permeation of Zincate through C-3 (Borden Chemical Co.)

where A is the area through which the penetration takes place and t is the time for the quantity (Q) to penetrate. Also,

$$J = \frac{P}{L}\left(C_o^E - C_L^E\right) \qquad \underline{\text{Equation 3}}$$

where C_L^E is the concentration of zincate in the electrolyte at x=L, L, the membrane thickness, and P, the permeation constant for the membrane. For the experimental conditions chosen $C_L^E << C_o^E$

$$J = \frac{PC_o^E}{L} \qquad \underline{\text{Equation 4}}$$

Also

$$J = \frac{DC_o^M}{L} \qquad \underline{\text{Equation 5}}$$

$$= \frac{DkC_o^E}{L} \qquad \underline{\text{Equation 6}}$$

Combining Equation 2 and Equation 6 gives

$$D = \frac{QL}{AtC_o^E k} \qquad \underline{\text{Equation 7}}$$

Figures 17-20 give plots of Q versus t for the various membranes. Table IV gives values of J, P, k and D for the various membranes. D and k values are not given for the Borden Co. material #9107/5. This membrane is a triple laminate and k values are not known for the various components of the laminate.

The zincate diffusivities in the membranes are one to three orders of magnitude lower than the diffusivity in free electrolyte. Figure 21 gives a plot of the diffusivity of zincate in the various membranes versus the membrane conductivities in the electrolyte. It can be seen that the relationship between zincate diffusivity and membrane conductivity is roughly linear. Both parameters are related to the pore size in the membranes; hence, the direct relationship. In the case of zincate diffusion in free electrolyte, the ratio of the zincate diffusivity in 31% KOH to that in 44% KOH was 4.65. In the case of cellulosic membranes (PUDO 300 and C-19) the ratio is 2.26, and for 2.2XH the ratio is 6.8. This result demonstrates the importance of the membrane properties in determining the zincate diffusivity.

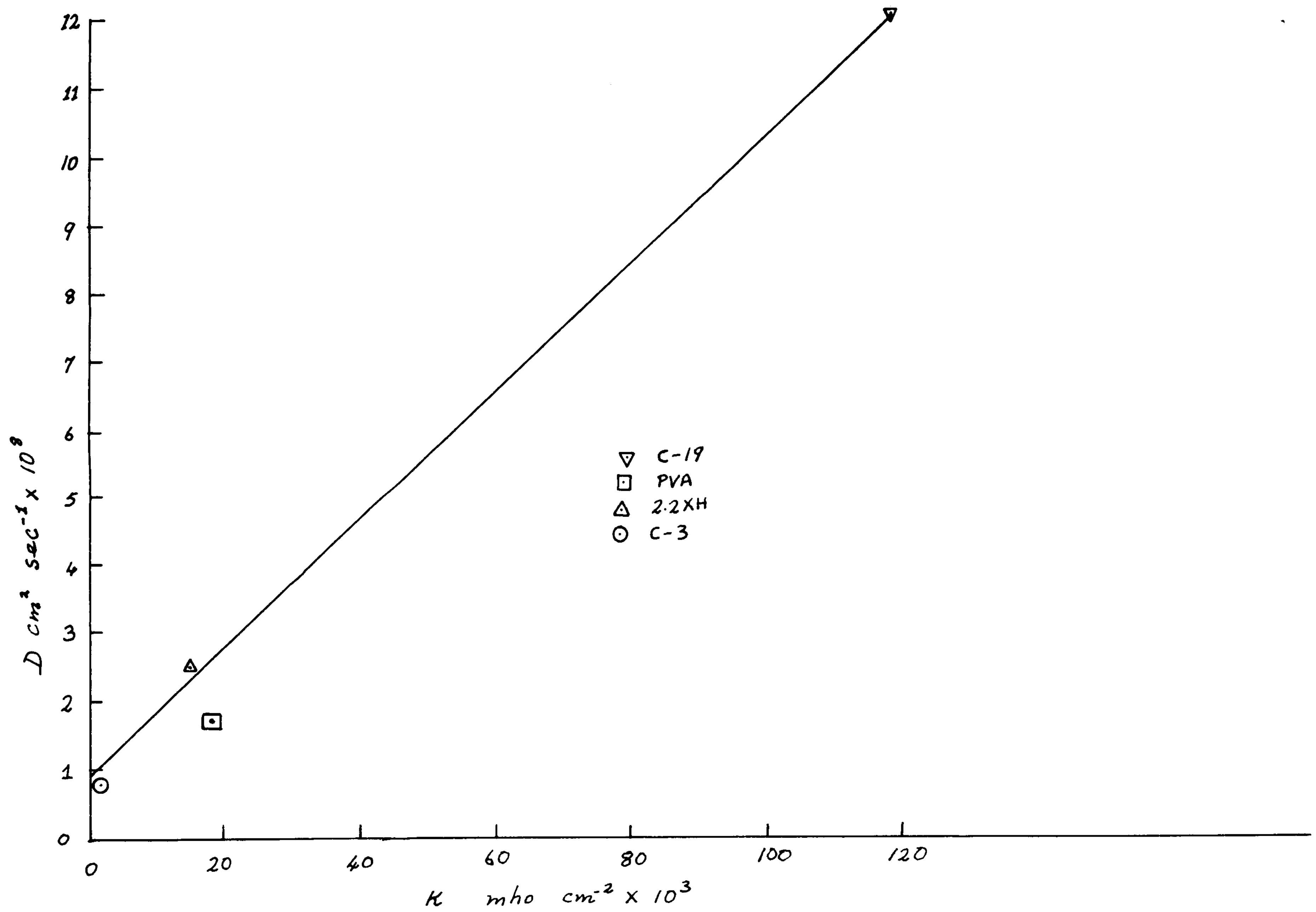


Figure 21. The Diffusivity of Zincate in Separators Versus the Conductivity of the Separator in Electrolyte

Table IV Zincate Transport Parameters in Separator Membranes

	Separator	J moles/cm/sec	L cmx10	P cm /sec	k	D cm /sec
44% KOH; R.T. Soak	C-19	1.04×10^{-8}	7.61	7.8×10^{-8}	0.65	1.2×10^{-7}
	PUDO-300	1.04×10^{-8}	7.61	7.85×10^{-8}	0.69	1.13×10^{-7}
	PVA	7.1×10^{-10}	5.59	3.58×10^{-9}	0.27	1.33×10^{-8}
	C-3	1.53×10^{-10}	5.08	7.56×10^{-10}	0.09	8.4×10^{-9}
	2.2XH	1.74×10^{-9}	3.81	7.4×10^{-9}	0.28	2.63×10^{-8}
	9107/5	2.63×10^{-9}	5.08	1.34×10^{-8}	-	-
31% KOH R.T. Soak	C-19	1.53×10^{-8}	7.61	1.95×10^{-7}	0.72	2.71×10^{-7}
	PUDO-300	1.53×10^{-8}	7.61	1.95×10^{-7}	0.72	2.71×10^{-7}
	2.2XH	8.54×10^{-8}	3.81	5.38×10^{-8}	0.30	1.79×10^{-7}
44% KOH; 60°C Soak	PUDO-300	1.33×10^{-8}	7.61	1.03×10^{7}	0.77	1.32×10^{-7}
	C-19	1.1×10^{-8}	7.61	8.3×10^{-8}	0.77	1.08×10^{-7}
	PVA	1.25×10^{-9}	5.59	7.1×10^{-9}	0.37	1.92×10^{-8}
	C-3	2.52×10^{-10}	5.08	1.28×10^{-9}	0.145	8.85×10^{-9}
	2.2XH	1.375×10^{-9}	3.81	5.25×10^{-9}	0.3	1.75×10^{-8}
	9107/5	3.32×10^{-9}	5.08	1.69×10^{-8}	-	-

Figures 17-20 also give plots of Q versus t for the various membranes that were soaked for three days in 44% KOH + 110 M ZnO at 60°C. Table IV gives values of T, P, K and D for the various membranes.

It can be seen that soaking the membranes at 60°C in KOH increases the flux of zincate through all membranes except 2.2XH and C-19. The flux through C-19 does not change and the flux through 2.2XH is reduced. The slight increase in PUDO-300 as opposed to C-19 may be due to electrolyte attack of the separator which is prevented by silver treatment of the separators. The reduction of the flux through 2.2XH may be due to a slight leaching of the grafted material in the hot caustic electrolyte. The flux increase in the other materials is due in part to the increased diffusivity for zincate in the membranes and in part to the increased separation coefficient for zincate in membranes soaked in hot electrolyte.

2.5 Zinc Penetration of Separators Under Potentiostatic Conditions

Zinc penetration of separator membranes was investigated under potentiostatic conditions. Figure 22 shows an exploded view of the zinc penetration test cell. The electrical circuit is shown in Figure 23.

The test procedure was as follows.

The separator under test and a sheet of Viskon paper were soaked for least 24 hours in 44% KOH containing 81 grams of ZnO per liter. The cell was assembled as shown in Figure 22. Electrolyte (44% KOH + 1M ZnO) was added and the zinc electrode potentiostatted at the desired potential. The voltage between the platinum screen prior to penetration of the membrane was 1.3V to 1.5 V. At penetration, the voltage drops by 0.1V to 0.5V. The separators tested by this method were as follows: PUDO-300 (Du Pont), Silver treated PUDO-300 (YEC C-19), C-3 and 9107/5 (Borden Chemical Co.)(1), 2.2XH Series 2 (RAI) and PVA (Monosol polyvinylalcohol). In the initial tests using this method irreproducible results were found. These results were caused by oxygen depolarization of the zinc reference electrode. Modifications were made to eliminate access of oxygen to the zinc reference. Once this was done the results were found to be reproducible. This accounts for the differences in the results reported here and those reported in the third quarterly report.

The times for zinc penetration to occur in various membranes at different overpotentials are tabulated in Table V. If penetration had not occurred after 55 hours the run was terminated. The only test carried out in excess of 55 hours was for PVA at 100 mV. In this run no penetration occurred after 92 hours. At an overpotential of 75 mV the zinc deposit consisted entirely of mossy zinc.

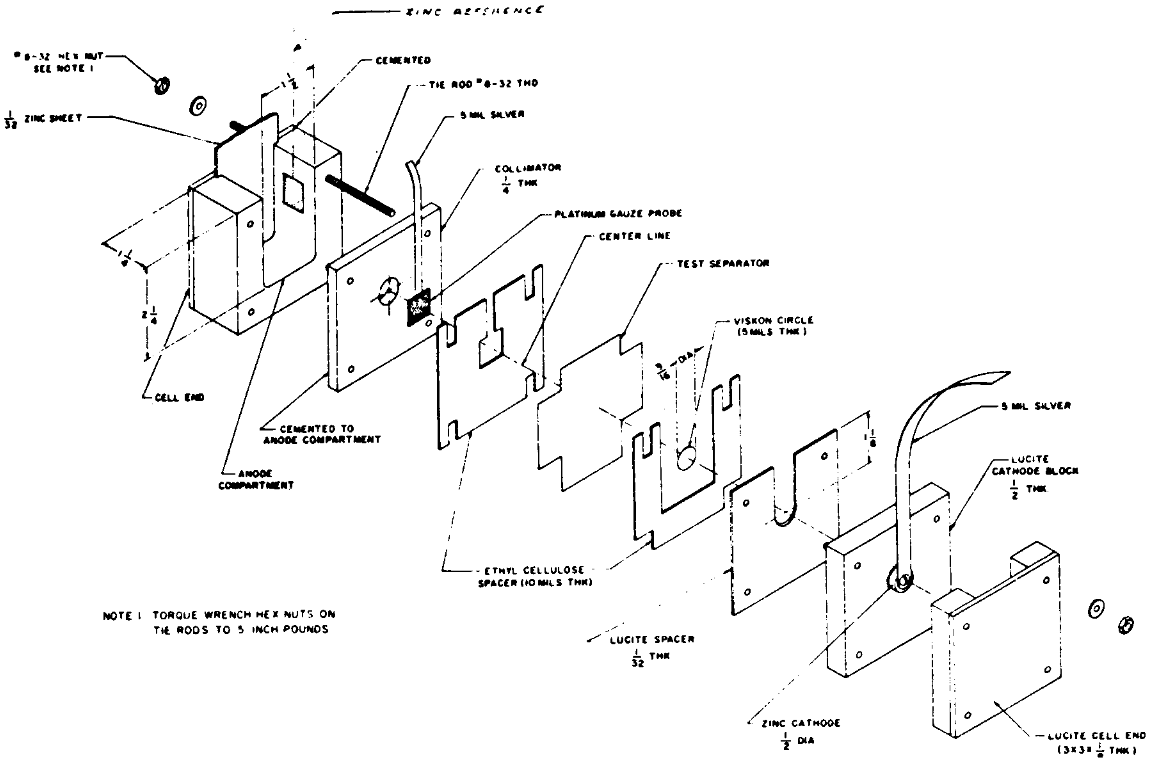


Figure 12 Zinc Penetration Test Cell (Exploded View)

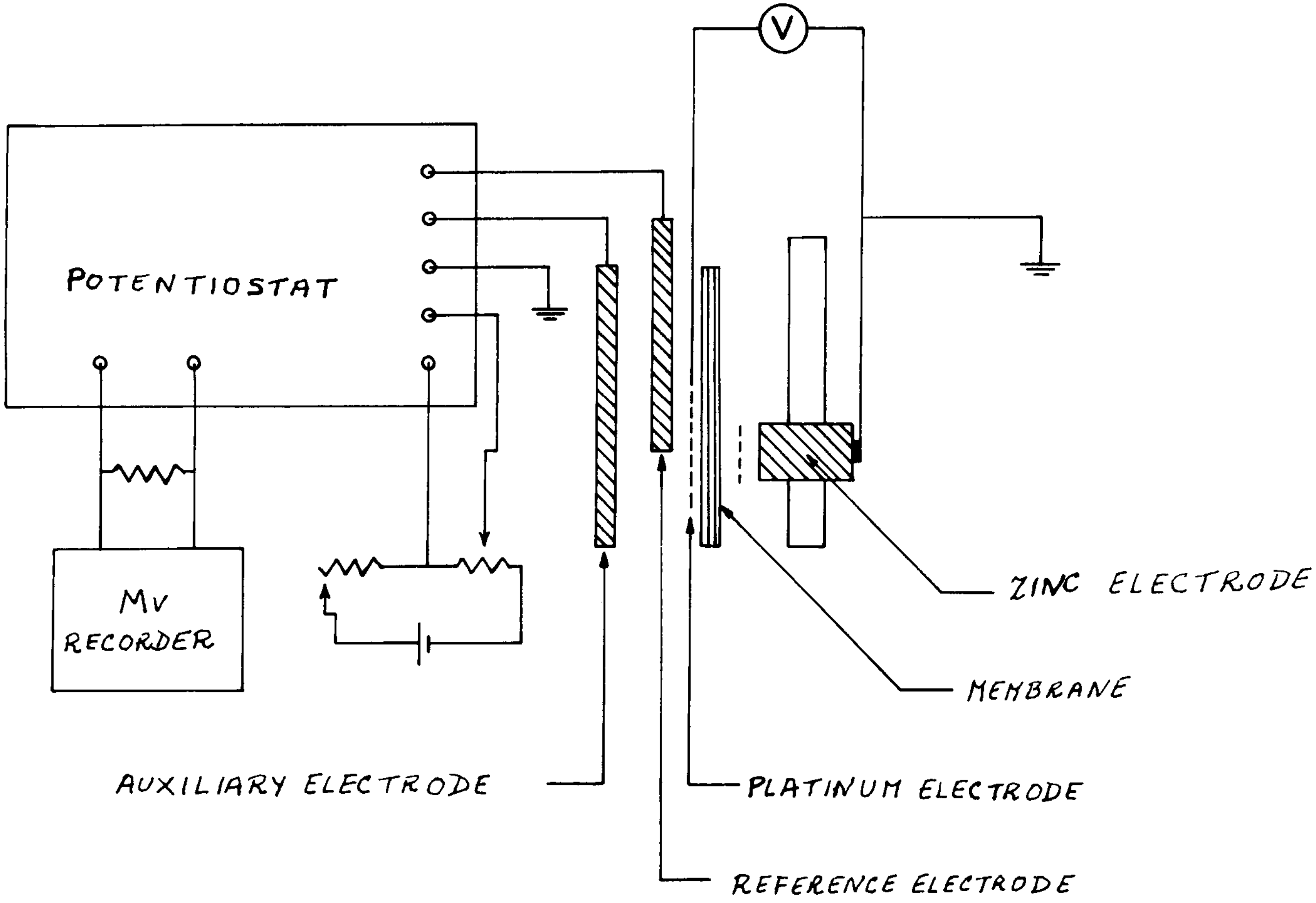


Figure 23. Schematic Representation of the Electrical Set-Up for the Zinc Penetration Test

	Time in Hours to Zinc Penetration					
Overvoltage Separator	75 mV	100 mV	125 mV	150 mV	175 mV	200 mV
C-19	>55	14				3.5
PUDO-30	>55	12				3.5
PVA		>92	50			6.0
2.2XH		30	10			2.0
C-3		>55	>55	>55	>55	34
9107/5		>55	12			8.0

Table V Zinc Penetration Time for Separator Membranes and Overpotential

Copious quantities of moss were deposited and the zinc deposit pushed the cellulosic membrane against the platinum screen. The imprint of the platinum screen could be seen on the zinc deposit and on the membrane. However, no penetration of the membrane occurred at 75 mV overpotential.

Since no dendrites were found, it is evident that the deposition occurred under activation-controlled conditions. At a potential where zinc deposition is activation controlled, the rate of zinc deposition will depend on the activity of zincate in the ambient electrolyte and the energy of activation for the zinc deposition process. The absorption tests indicate that the activity of zinc in the membranes is lower than that in the free electrolyte. Furthermore, there is a possibility that the initial state of the zincate ion in the membrane differs from that in the free electrolyte. In such a case, the activation energy for the deposition process would be different in the separator than in the free electrolyte. These two factors would explain the absence of zinc penetration in C-19 and PUDO 300 under activation-controlled conditions.

The fact that zinc penetration occurred in C-19 and PUDO-300 at -100 mV after a short time indicates that cellulosic materials have a low resistance to dendrite growth. It is in the overvoltage interval of 75-100 mV that zinc dendrites start to form in 44% KOH.

Polyvinylalcohol and 9107/5 were not penetrated at 100 mV during the runs. The C-3 membrane did not undergo zinc penetration in 55 hours until an overpotential of 200 mV was reached. In all of these runs with PVA, 9107/5 and C-3 the deposit was dendritic and zinc deposition occurred under diffusion-controlled conditions. The diffusivity measurements show that the flux of zincate in these membranes is smaller than in the case of cellulosic membranes. The zincate flux decreases as follows--9107/5 PVA C-3. This order is the inverse of the order of the times required to achieve penetration at an overpotential of 125 mV. This order does not prevail at 200 mV. However, at an overpotential of 200 mV considerable hydrogen evolution occurs which may affect the results. However, C-3, which has the lowest permeability for zincate did not penetrate at 200 mV until 34 hours.

These results would indicate that the membranes can tolerate an overpotential on the zinc electrode in excess of the overpotential necessary to form dendrites before zinc growth is initiated in the membrane. The magnitude of this excess overpotential depends on the transport properties of the membrane. Thus cellulosic materials which can transport zincate at an appreciable rate can tolerate only a very small overpotential in excess of the overpotential necessary to form dendrites on the electrode before zinc penetration occurs. A material such as C-3, which transports zincate at a very low rate requires a large excess of overpotential above that necessary to form dendrites on the electrode to initiate zinc deposition in the membrane.

2.6 Controlled Potential Cut-Off for Silver-Zinc Cells

The fact that it appears that there is a critical potential below which no zinc penetration through the separator will occur, offers interesting possibilities for the charge control of silver-zinc cells. During the year we procured a scanner which cuts off cells on charge, either when the cell voltage reaches a particular value or when the zinc overvoltage reaches a certain preset value.

A total of 36 10 AH based on 4g Ag/AH silver-zinc cells was constructed for test on this program. The cells consisted of four positives and five negatives. The positives were enclosed in a bag of non-woven nylon, wrapped with five turns of separator and incorporated in the cell packs with the negatives in a normal "U" wrap. The zinc to silver weight ratio was 0.6:1, actual weight ratio. The cell pack was contained in a plastic case. A separate "U" (a reference electrode "U"), consisting of three turns of separator, was also incorporated in the case. A silver electrode was inserted in one arm of this "U" and a dry charged zinc electrode was inserted in the other arm of the "U". The completed cell case had four terminals: a positive, a negative, a zinc reference terminal, and a terminal for the silver electrode in the reference electrode "U". This silver electrode was incorporated to charge up the reference electrode if it self-discharged. This cell group consisted of six groups of six cells each. All factors in each cell were constant except the separator. The separators incorporated in these cells were PUDO-300 (Du Pont), C-19 (YEC), Polyvinylalcohol ("Monosol" PVA), C-3 and 9107/5 (Borden Chemical Co.), and 2.2XH grafted polyethylene (Radiation Applications, Inc.).

Preliminary tests were made with this scanner on 12 cells (two from each group). The cells were cut off at -150 mV with respect to the zinc reference. The cells were charged at the C/10 rate to this cut-off and discharged at the C/2 rate for one hour. The zinc polarization was the only cut-off used on charge. No arrangements were made to cut off the cell at a particular cell voltage. After 14 cycles, penetration of the separator had occurred in all cells. When the cells were cycled on this regime the cell voltage always exceeded 2.1 volts before the zinc reached -150 mV. Gassing occurred on both positives and negatives before the cut-off was reached. A second batch of 12 cells (two from each group) was tested using -75 mV as the cut-off on the zinc electrode. In the first cycle the cell voltage exceeded 2.1 V before the cut-off was reached on the zinc electrode. However on subsequent cycles the zinc cut-off was reached before the cell voltage reached 2.0 V. The cells with C-3 and 9107/5 separator foamed on the first cycle. This was apparently due to some decomposition products of the separators which gave a detergent action. After seven and ten cycles respectively the cells with C-3 and 9107/5 came up to 2.1 V on charge. The zinc electrodes started to gas and charging was stopped. The cells were then taken apart. Holes were found in the separator at the fold of the reference electrode "U". This had caused the reference electrode to short to the working electrode, thus preventing cut-off. Cracks were also found in some separator layers surrounding the positives at the "U" folds. However, no zinc growth was found in the body of the separator. These cracks and holes in the separator were purely mechanical and apparently were due either to a loss of the flexing properties of the separators on being left in a room of low humidity prior to fabrication of the cells, or to handling the membranes on making the "U" wraps. The remaining eight cells were cycled for 25 cycles. The cells were then taken apart in the charged state. No growth of zinc had occurred in any of the membranes. In all cases the membrane layer in abuttal to the zinc electrode was clear and devoid of holes and zinc. The zinc deposit on the electrode consisted entirely of mossy zinc. The zinc plates in the cells with C-19 and PUDO-300 underwent no shape change during cycling. However the cells with PVA and 2.2XH underwent considerable shape change. The plate area in each case was reduced by about 30T. The cells with 9107/5 and C-3 separators had undergone about 15% shape change before the zinc electrode had shorted to the reference electrode. Apparently membranes with high resistivities and low permeation rates for zincate accelerate shape change. This has been noted before in this laboratory. However, here we have a clear cut case since due to the nature of the cycling regime the zinc electrode was charged to the same potential in all cells. When using the cell voltage as cut-off the zinc electrode may be charged to different potentials in different cells, thus making a comparison of the zinc electrode behavior more difficult. The use of this cycling regime enables us to eliminate all variables and thus observe the effect of the separator on the zinc electrode behavior.

It should also be pointed out that use of the zinc overvoltage as a cut-off in cycling cells gives rise to vastly different conditions than those which usually prevail in a secondary silver zinc cell. In the first cycle we charge up all the available zinc oxide to zinc. Thus, the silver electrode is overcharged on the first cycle. On subsequent cycling we discharge some of the zinc and again charge it up. After the first cycle the silver electrode does not come up to the oxygen evolution potential on charge. The cell is essentially cycled on a zinc cycle with the end point of charge of the zinc electrode controlled. The good charge - discharge efficiency of the silver positive makes such cycling possible, and gives no reason to expect losses in capacity of the silver electrode on such a regime. The fact that the zinc electrode operates for the most part in a highly charged condition (i.e., largely zinc metal instead of zinc oxide) ensures an adequate supply of zinc to discharge the silver electrode when power has to be drawn from the cell.

3. SUMMARY AND CONCLUSIONS

The diffusivity of zincate in the alkaline electrolyte has been determined as a function of KOH concentration and temperature. The diffusion coefficient-reciprocal viscosity plot does not follow the Einstein-Stokes equation. A qualitative explanation for this deviation from the Einstein-Stokes law is that the zincate species is a large hydrated ion in low concentrations of KOH and a small anhydrous ion in more concentrated KOH solutions.

The zincate diffusivity - KOH concentration dependence and the zincate solubility - KOH concentration dependence is such that the product of the zincate diffusivity and zincate solubility goes through a maximum at about 31% KOH.

Studies of zinc deposition on rotating discs show that dendrites are deposited under diffusion controlled conditions whereas mossy whiskers are deposited under activation controlled conditions.

The absorption of zincate has been determined for various separators -- PUDO 300 cellophane (Du Pont), Ag treated PUDO-300 (Yardney C-19), unplasticized polyvinyl alcohol ("Monosol" PVA), 2.2XH Series 2 (R.A.I. acrylic grafted polyethylene), C-3, 9107/5, 9107/21, 9107/22, 9107/27 (Borden Chemical Co.) (1). Except for film 9107/27 the concentration of zincate in the membrane is always less than that in the ambient electrolyte. The membranes in the alkali zincate electrolyte act as a separate phase which have a separation coefficient for zincate. This separation coefficient varies by a factor of seven for the membranes tested and is lowest for C-3. This separation coefficient does not change for cellulosic membranes and 2.2XH in going from 44% KOH to 31% KOH. Addition of Emulphogene BC-610 (General Aniline & Film) does not affect this separation coefficient in cellulosic membranes in 44% KOH. When the soak temperature was increased from room temperature to 60°C the separation coefficient increased markedly for C-3 and 9107/5. This apparently was due to chemical attack of these membranes in the hot caustic solutions. In the case of the 2.2XH material a slight decrease in the separation coefficient occurred when the soak temperature was increased to 60°C.

Diffusivity measurements for. zincate were carried out on the various membranes. The diffusivity of zincate in the membranes was found to be one to three orders of magnitude lower than the zincate diffusivity in the free electrolyte. The zincate diffusivity in the membranes is directly related to the conductivity of the membranes in the electrolyte. Both parameters are apparently related to the pore size of the membranes. These results indicate that the likelihood of finding a membrane which will not allow zincate ions to diffuse and at the same time conduct OH ions at a reasonable rate is rather remote. When the membranes were soaked in electrolyte for three days at 60°C a marked increase in the zincate diffusivity occurred for all membranes except cellulosic membranes and 2.2XH grafted polyethylene.

The membranes were tested to determine the overpotential required for zinc deposition in the membranes. Zinc growth occurs in cellulosic materials whenever the overpotential exceeds that necessary to form dendrites (75 mV). Membranes such as C-3 can tolerate an overpotential of 175 mV on a zinc electrode in close abuttal with the separator without zinc growth occurring in the separator. The overpotential necessary to initiate the growth of zinc is a function of the separation coefficient and zincate diffusivity in the membrane. Membranes with low zincate diffusivities and low separation coefficients (e.g. C-3) can tolerate high overpotentials on the zinc electrode without zinc penetration occurring. Since some membranes such as C-3, 9107/5 and polyvinylalcohol transport zincate at an increased rate when soaked for three days in KOH at 60°C it is reasonable to assume that similar changes in their transport properties would occur on prolonged stand in KOH solutions at ambient temperatures. Furthermore, the efficacy of these membranes as zinc stoppers will change as the cell ages. Membranes such as C-19 and 2.2XH which do not undergo such changes in zincate transport properties on stand at 60°C should continue to behave equally well as zinc stoppers as the cell ages.

Tests on silver zinc cells show that if cells are cut off on charge when the zinc electrode reaches an overpotential of 75 mV with respect to a zinc reference no zinc penetration of the separator membranes occur.

Membranes with high resistivities accelerate shape change when used in silver zinc cells. The best shape retention was found with low resistivity cellulosic membranes.

4. REFERENCES

1. Improved Separators for Silver Oxide-Zinc and Silver Oxide-Cadmium Cells for Spacecraft Application. Contract No. NAS5-9107 Borden Chemical Co. 1965.

2. Gubbins, K. E., Walker, R. D. J. Electrochem. Soc. 112, 469(1965).

5. NEW TECHNOLOGY

1. A potentiostatic method for screening separator membranes for zinc penetration.

2. A method of charging silver zinc cells whereby the cell is cut off on charge when the zinc overvoltage reaches a pre-set value.