NASA CR-

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

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SECOND QUARTERLY REPORT

JUNE 1967

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

Goddard Space Flight Center
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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ABSTRACT

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

Absorption isotherms of zincate in eight separators were measured. The distribution coefficient of zincate was measured and found to be less than one in all cases. Cellulosic separators and unplasticized polyvinylalcohol membranes show no variation in zincate absorption with stand temperature. The absorption of zincate ions in Borden Co. C-3 and 9107-5 increases with stand temperature. Additions of Emulphogene BC-610 do not affect the absorption of zincate in cellulosic separators.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

1. INTRODUCTION

This project is a continuation of Contract #NAS 5-3873, "Investigation and Improvement of Zinc Electrodes for Electrochemical Cells". The aim of this project is to determine the causes and to evolve methods for control of zinc penetration through separators.

Previous work indicates that zinc penetration occurs when zincate diffusion becomes limiting during charge. When zincate is not available in the vicinity of the negative plate, zinc deposition then occurs in the separator. This process eventually leads to shorting of the cell. In a stationary system the important parameter governing zincate availability at the negative plate is the diffusion coefficient of zincate in the electrolyte. If zinc is to plate in a membrane, there must be a source of zincate in the membrane that is available for deposition as zinc. The ease with which zinc growth occurs in a membrane is a function of the concentration and diffusivity of zincate in the membrane. The possibility also exists that adsorption effects may alter the nature of zincate in a membrane, thus increasing the overvoltage necessary to deposit zinc inside the membrane. During the present report period, the diffusivity of zincate in KOH solutions was studied as a function of temperature and KOH concentration. Further analytical work was carried out on absorption isotherms of zincate in separators.

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 coefficients. 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

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

and F the Faraday.

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.

Figures 1 - 8 show the polarographic waves together with the blanks for the various KOH concentrations and temperatures. It can be seen that in all cases a single wave is obtained for the zincate ion discharge. The masking of the zincate wave by the potassium wave is 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 tabulated in Table I. Figure 9 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 μA	D x 10^6	i_d μA	D x 10^6	i_d μA	D x 10^6	i_d μA	D x 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	39.9	9.06	42.0	9.55
35%	14.7	1.34	29.1	4.82	38.7	8.50	44.0	10.5
40%	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 10 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

Curve A, Figure 10 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)[1]. 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 reciprocral viscosity.

Figure 11 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

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

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.

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

Having a complete picture of the diffusion of zincate in KOH electrolytes, one is in a position to analyze the deposition of zinc under various conditions. Furthermore, this study will form the basis for analysis of the effects of the separator on zincate diffusion.

2.2 Absorption Isotherms of Zincate in Separators

The following separators were tested for absorption of zincate: Du Pont - 300 PUDO, YEC - Ag treated 300 PUDO (C-19), Borden Chemical co. - C-3, 9107-5, Film 9107/22, Film 9107/21, Film 9107/27, and unplasticized polyvinyl alcohol (Mono-Sol PVA). Table III gives the conditions under which the separators were tested for absorption of zincate.

Table III Zincate Distribution Coefficients, K. amd Conditions for Absorption Studies on Separators

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 Emulphogene at 25°C
PUDO-300	0.84 **	0.94 *	0.86 *	
C-19	0.81 **	0.84 *	0.79 *	0.83 *
PVA	0.592**		0.610 *	
C-3	0.155**		0.420 *	
9107-5	0.455**		0.75 *	
9107/22	0.84 *			
9107/21	0.91 *			
9107/27	1.06 *			

*Covered in this report period.

**Given in previous report.

The above separators were cut into pieces 3" x 3", weighed, soaked for three days at the given temperature in the pertinent KOH solution containing zincate. The separators were then dried by toweling, dissolved in 10 cc of 1:1 HNO_3, evaporated in a solution containing 1N NH_3OH + 1N NH_4Cl (50 cc). The ammoniacal zinc solution was then analyzed polarographically.

Figure 12 shows a plot of the absorbed zincate in C-19 versus the concentration of external zincate in terms of moles per liter of KOH. It may be seen that the absorption of zincate is not greatly affected by changes in KOH concentration, temperature or Emulphogene (BC-610-General Aniline Co.) additions.

44% KOH at 60°C is a rather severe ambient for cellophane; however, it appears that any degradation of the cellophane that may occur under these conditions does not affect the zincate adsorption.

Figure 13 gives similar plots for 300 PUDO. All plots give similar results. The results for PVA are given in Figure 14. Here, again, we see that the stand temperature has little effect on the zincate absorption. Figures 15 and 16 give absorption curves for C-3 and 9107-5 in 44% KOH at 25°C and 60°C. It may be seen that the absorption curve differs with temperature in both cases.

The increase of absorption of zincate with stand temperature for these two materials may be due to degradation of the films. 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 recurred in the case of the C-3 material. The fact that the zincate absorption changes with stand temperature indicates that C-3 and 9107-5 materials may function differently as separator materials as the cell ages (i.e., their behavior as "zinc stoppers" may be a function of the time that elapses from activation of the cell. Whether their ability to stop dendritic zinc increases or decreases with chemical attack by KOH awaits further investigation.

Figure 17 gives the absorption curves for the Borden Co. films 9107/22, 9107/22 and 9107/27. Their absorption behavior closely resembles that of cellophane. Table III gives the separation factors for the separators under the various conditions of electrolyte and temperature. Tavles IV, V and VI give the data for the various dimensional parameter measurements on films R, S and T. Column 1 gives the concentration of zincate in moles per liter, Column 2 the dimensions of the separator before soaking and Column 3 gives the dimensions of the separator after soaking.

We have now analyzed a number of separators which show a wide variation in the separation coefficient for zincate. During the next reporting period this analytical work will include Radiation Applications, Inc. grafted polyethylene materials. All separators will be tested for zinc penetration. An attempt will be made to correlate the overvoltage for zinc deposition in the membranes and the separation coefficient for zincate ions.

Table IV Dimensional Parameters for Borden Chemical Co. Film 9107/22 (44% KOH at 25°C)

Concentration of ZnO moles/liter	Thickness		Dimensions	
	Before Soaking	After Soaking	Before Soaking	After Soaking
0.2	1.52 mils	1.8 mils	3" x 3"	3.00" x 3.025"
0.4	1.52 "	1.85 "	3" x 3"	3.02" x 3.02"
0.6	1.52 "	1.65 "	3" x 3"	3.01" x 3.02"
0.8	1.52 "	1.7 "	3" x 3"	3.02" x 3.02"
1.0	1.52 "	1.8 "	3" x 3"	3.02" x 3.02"

Table V Dimensional Parameters for Borden Chemical Co. Film 9107/21 (44% KOH @ 25°C)

Concentration of ZnO moles/liter	Thickness		Dimensions	
	Before Soaking	After Soaking	Before Soaking	After Soaking
0.2	1.62 mils	1.9 mils	3" x 3"	3.03" x 3.03"
0.4	1.62 "	1.85 "	3" x 3"	3.03" x 3.03"
0.6	1.62 "	1.65	3" x 3"	3.03" x 3.03"
0.8	1.62 "	1.75 "	3" x 3"	3.03" x 3.03"
1.0	1.62 "	1.70 "	3" x 3"	3.03" x 3.03"

Table VI Dimensional Parameters for Borden Chemical Co. Film 9107/27 (44% KOH

Concentration of ZnO moles/liter	Thickness		Dimensions	
	Before Soaking	After Soaking	Before Soaking	After Soaking
0.2	1.43 mils	1.8 mils	3" x 3"	3.01" x 3.01"
0.4	1.43 "	1.7 "	3" x 3"	3.00" x 3.01"
0.6	1.43 "	1.6 "	3" x 3"	3.00" x 3.01"
0.8	1.43 "	1.75 "	3" x 3"	2.99" x 3.01"
1.0	1.43 "	1.70 "	3" x 3"	3.00" x 3.00"

3. SUMMARY AND CONCLUSIONS

The diffusivity of zincate 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 diffusing zincate species is a large hydrated ion in low concentrations of KOH and a small anhydrous ion in more concentrated KOH solutions.

The absorption of zincate has been determined for various separators, viz: cellophane PUDO (300) (Du Pont), silver treated PUDO (300) - C-19 (YEC), Mono-Sol PVA, and Borden Co. C-3, 9107-5, Film R, Film S and Film T. Additions of Emulphogene BC-610 (G.A.F.) do not affect the zincate absorption in C-19. The absorption of zincate in PUDO (300), C-19 and PVA is the same for a three-day stand at 25°F and a three-day stand at 60°C. However, a three-day stand at 60°C increases the absorption of zincate in C-3 and 9107-5 above that found at room temperature. This increase apparently is due to degradation of the film in 44% KOH at 60°C. No noticeable change in the absorption of zincate occurs in C-19 and 300 PUDO in going from 44% KOH to 31% KOH. The separation coefficient varies by almost an order of magnitude in going from C-3 to C-19. This parameter should be correlated with the overvoltage necessary to deposit zinc in the separator.

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

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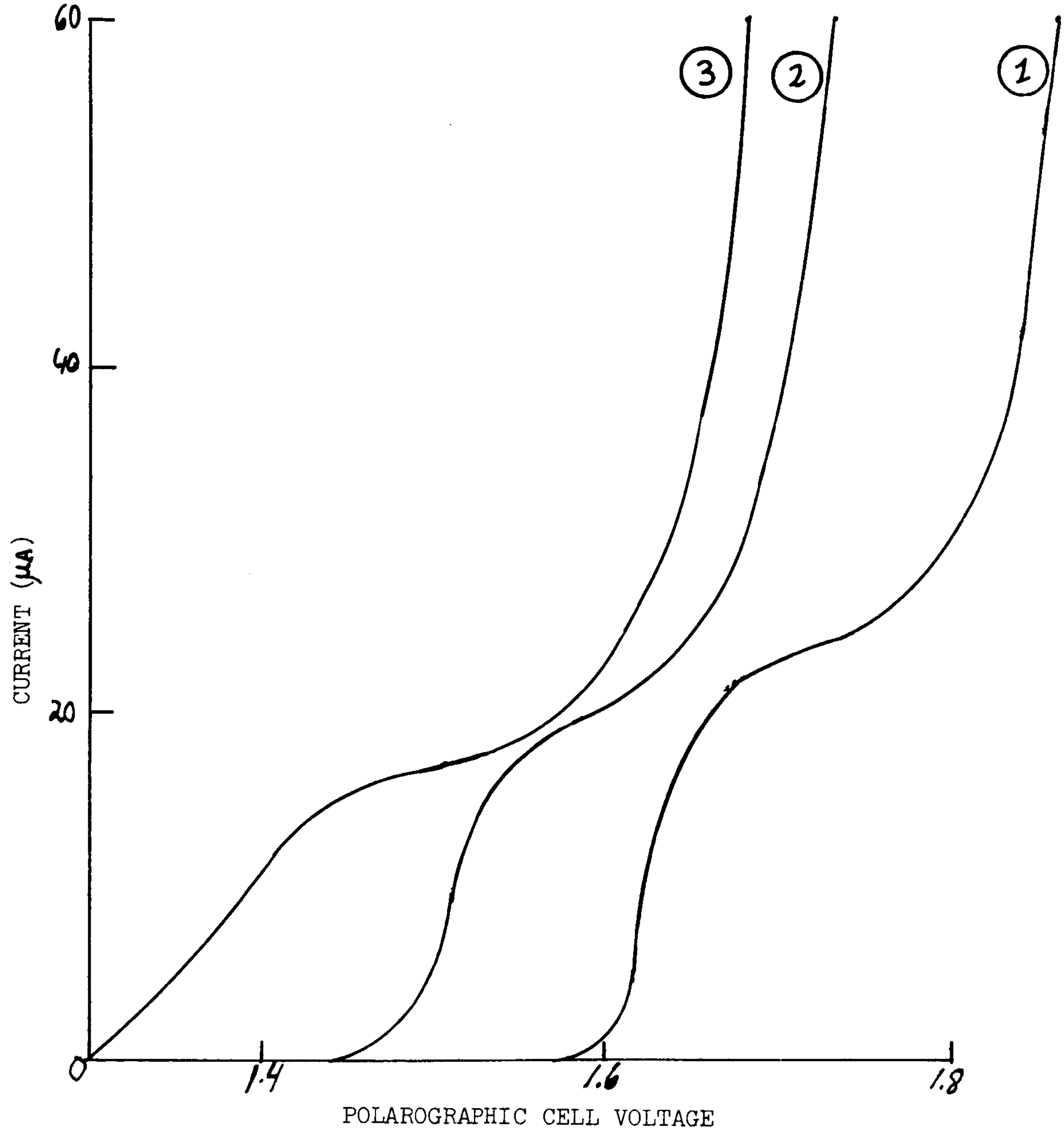
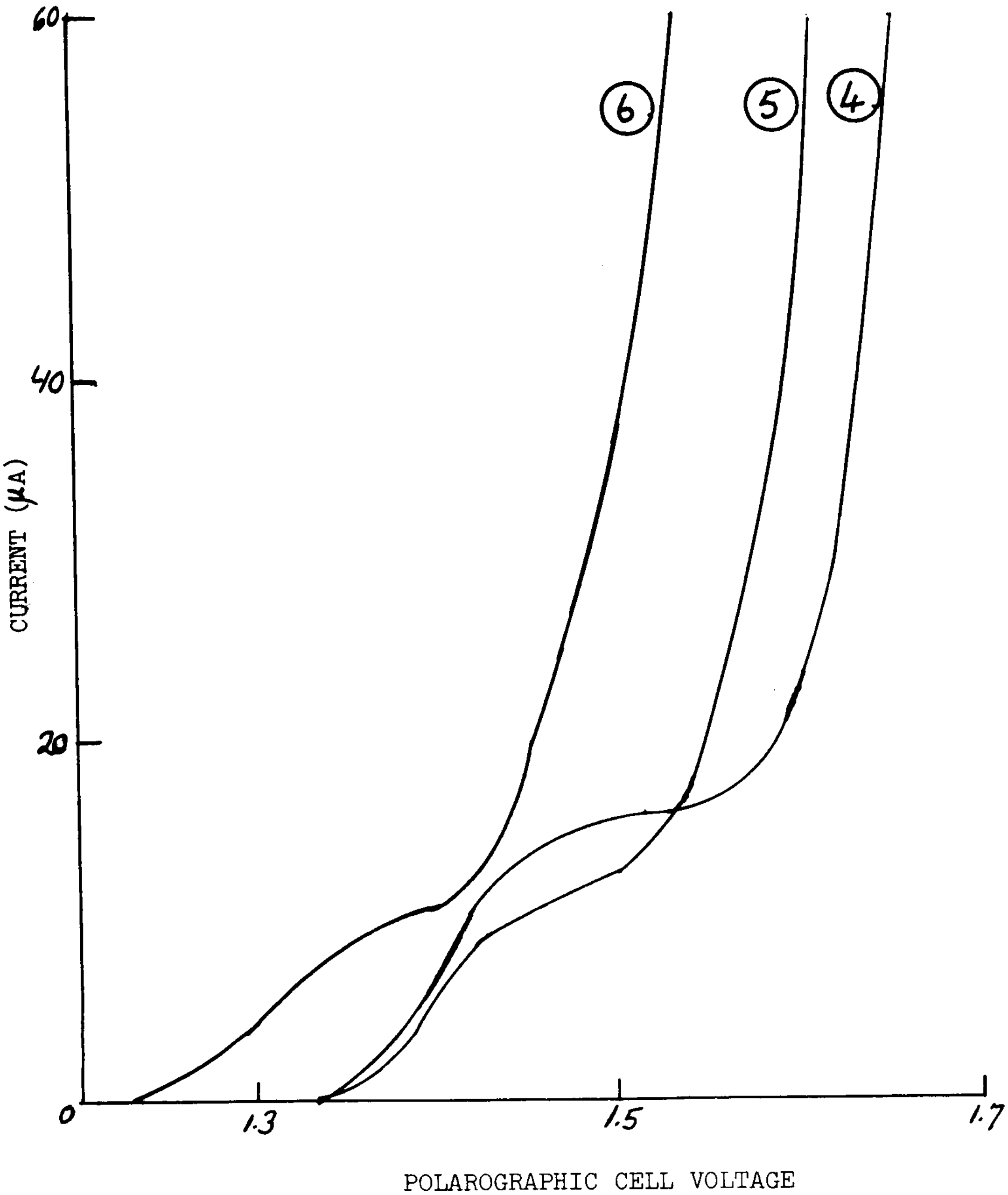


1 5% KOH
2 25% KOH
3 30% KOH

FIGURE 1 ZINCATE POLAROGRAPHS

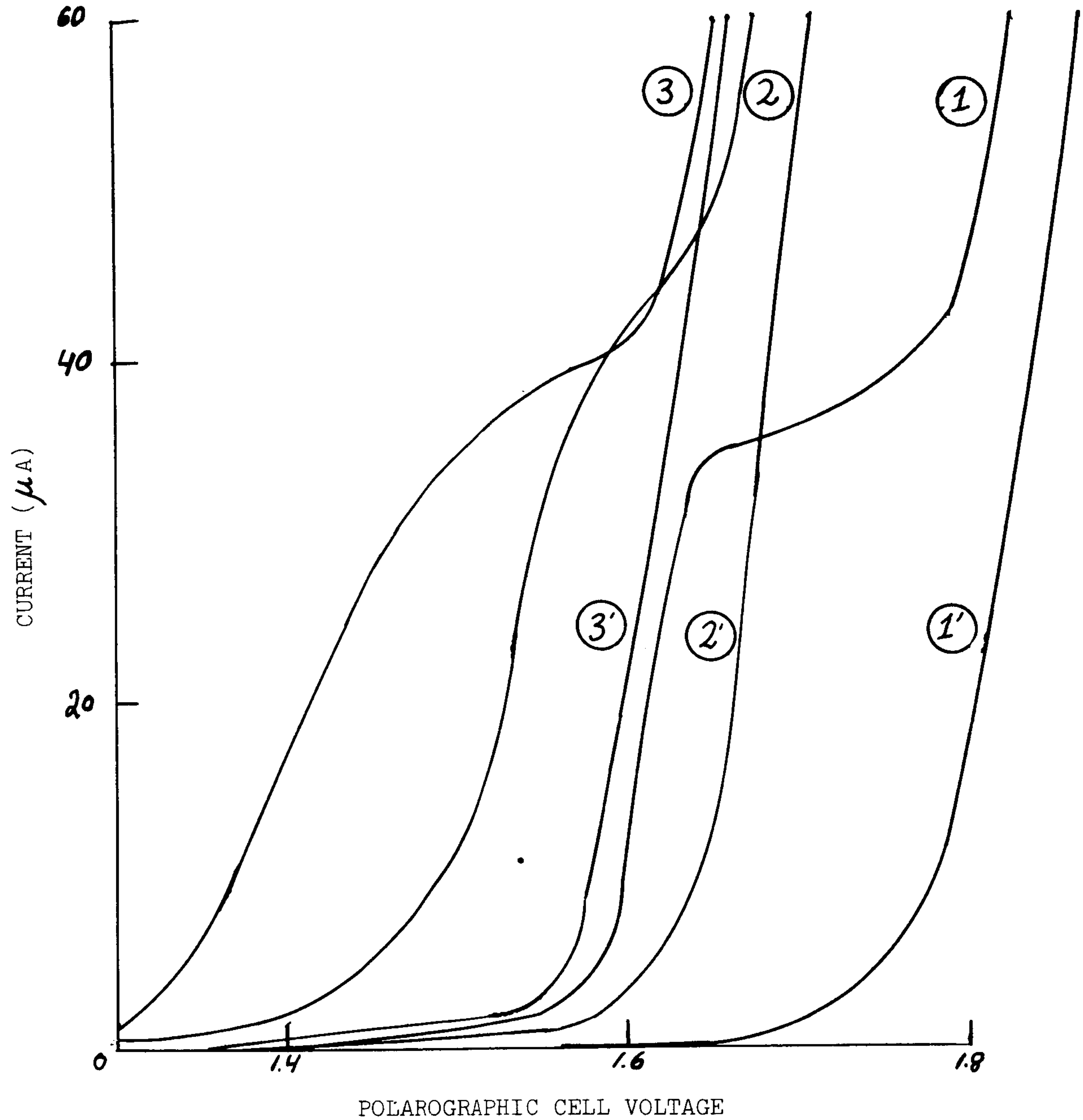
5 x 10^{-3} M ZnO in Conc. KOH, 0°C



4 35% KOH
5 40% KOH
6 44% KOH

FIGURE 2 ZINCATE POLAROGRAPHS

5 x 10^{-3} M ZnO in Conc. KOH, 0°C

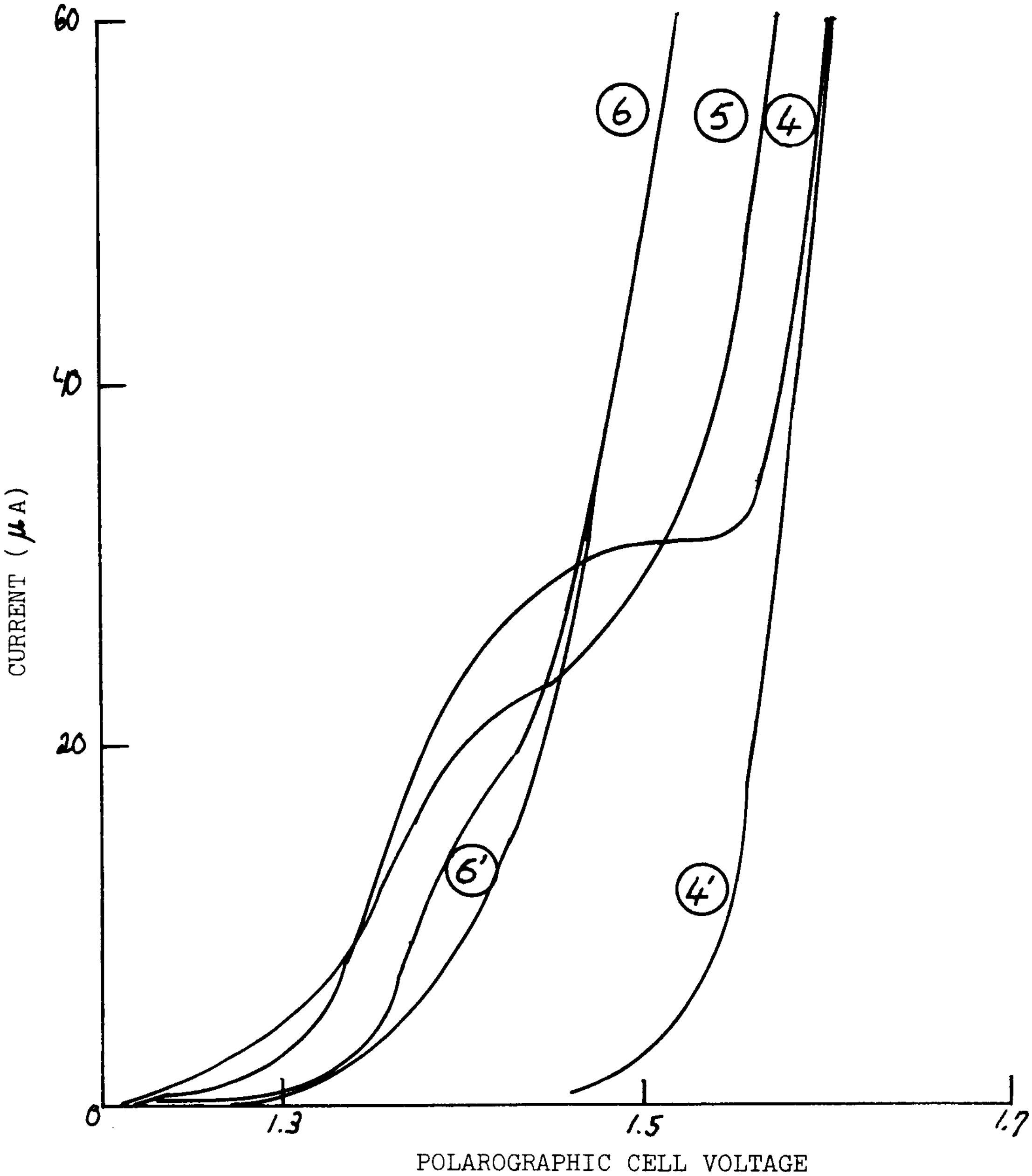


1 5% KOH
2 25% KOH
3 30% KOH

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

FIGURE 3 ZINCATE POLAROGRAPHS

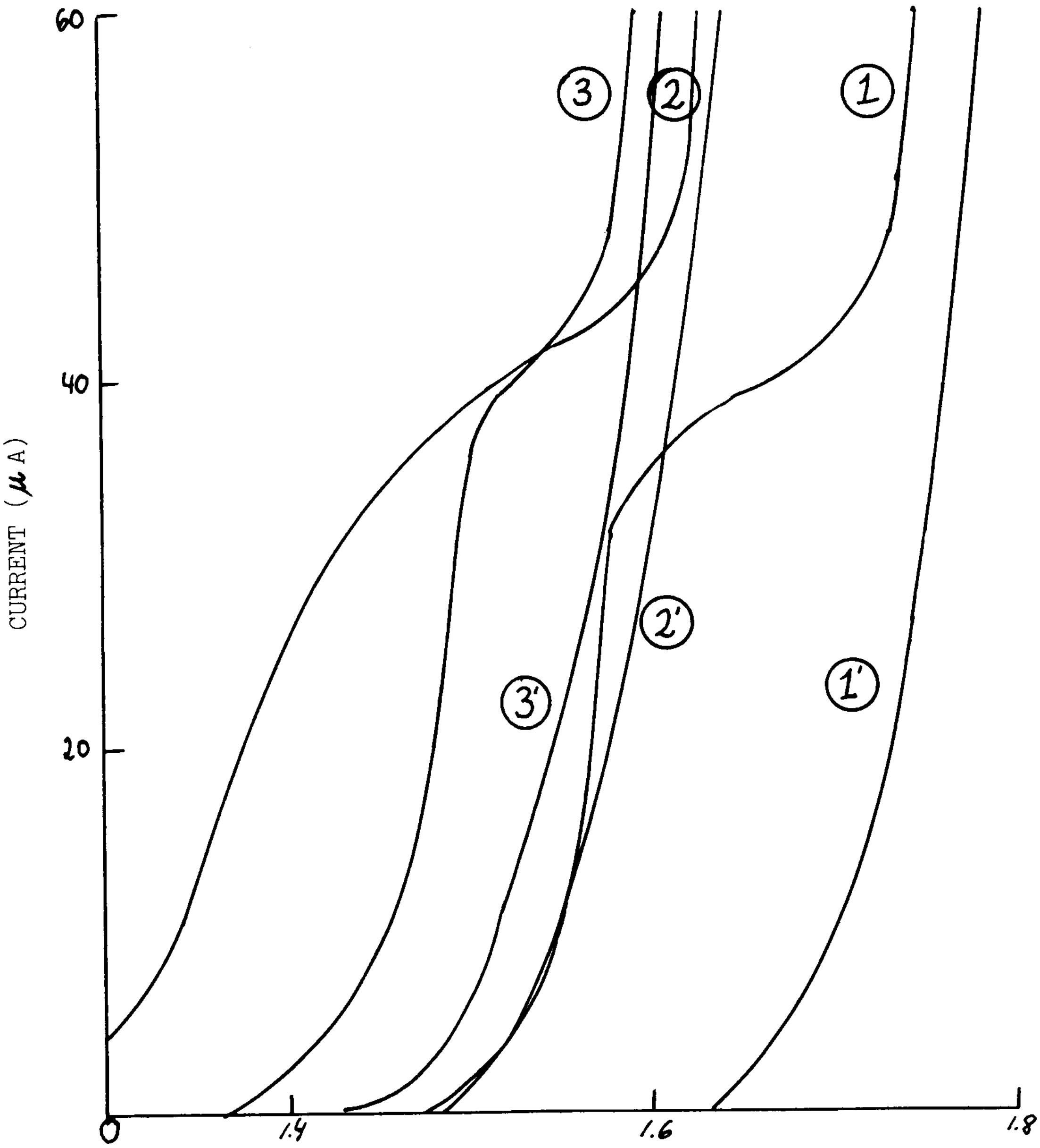
5×10^{-3} M ZnO in Conc. KOH, 25°C



4 35% KOH
5 40% KOH
6 44% KOH
Superscript indicates blanks

FIGURE 4 ZINCATE POLAROGRAPHS

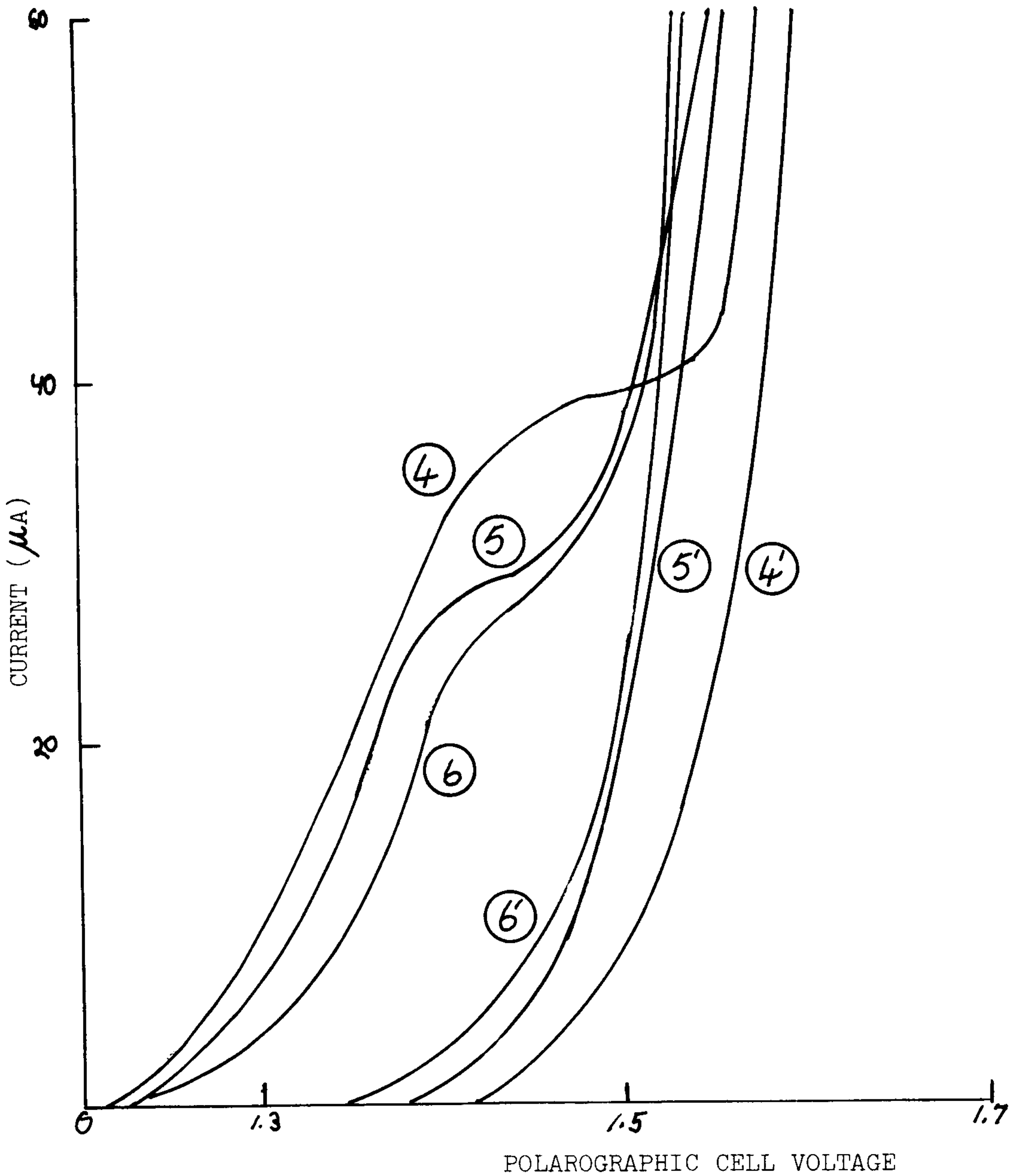
5×10^{-3} M ZnO in Conc. KOH, Room Temp. 25°C



1 5% KOH
2 25% KOH
3 30% KOH
Superscript indicates blanks

FIGURE 5 ZINCATE POLAROGRAPHS

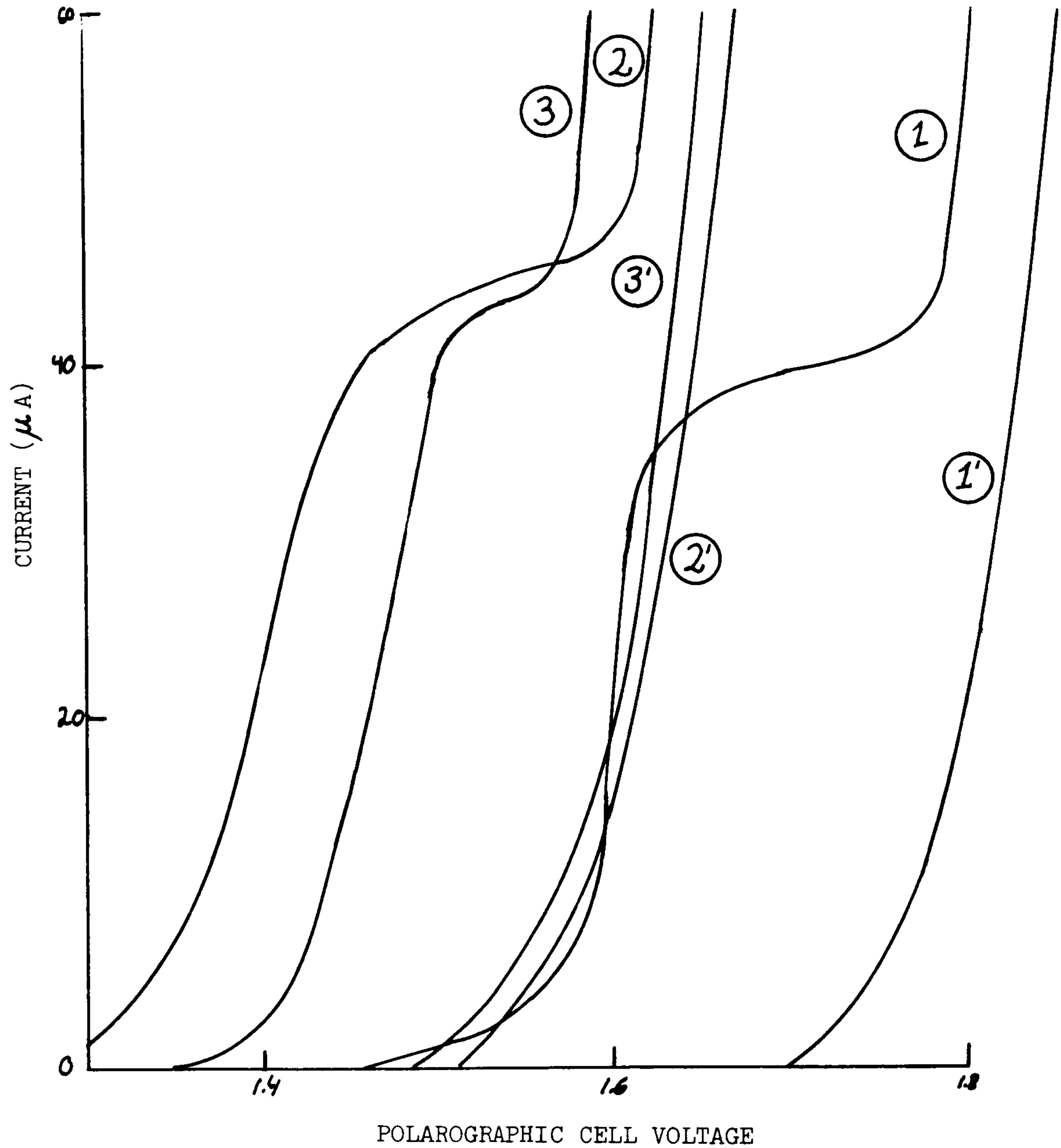
5 x 10^{-3} M ZnO in Conc. KOH, 35°C



4 35% KOH
5 40% KOH
6 44% KOH
Superscript indicates blanks

FIGURE 6 ZINCATE POLAROGRAPHS

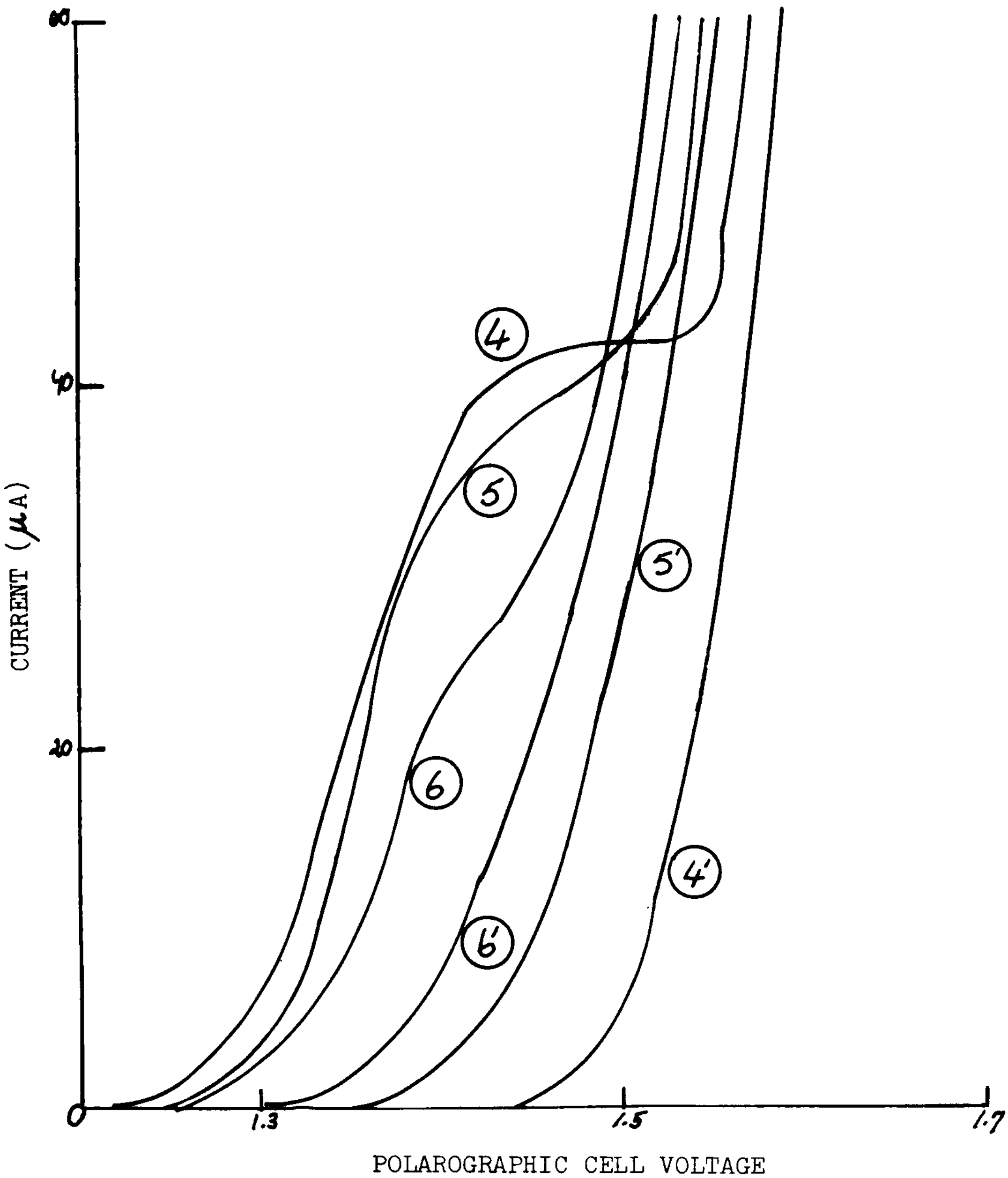
5×10^{-3} M ZnO in Conc. KOH, 35°C



1 5% KOH
2 25% KOH
3 30% KOH
Superscript indicates blanks

FIGURE 7 ZINCATE POLAROGRAPHS

5×10^{-3} M ZnO in Conc. KOH, 50°C



4 35% KOH
5 40% KOH
6 44% KOH
Superscript indicates blanks

FIGURE 8 ZINC POLAROGRAPHS

5 x 10^{-3} M ZnO in Conc. KOH, 50°C

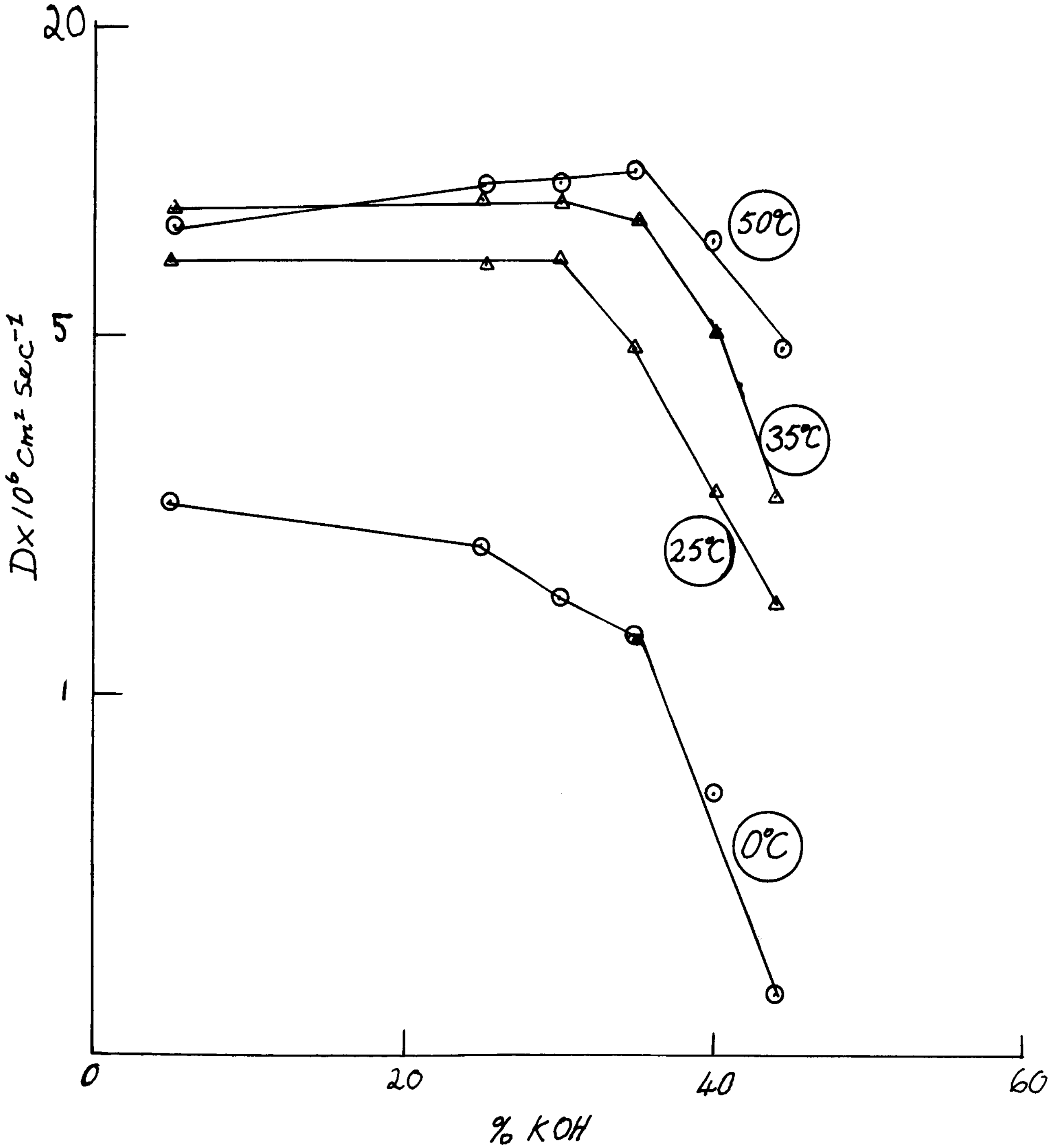


FIGURE 9 DIFFUSION COEFFICIENT FOR ZINCATE VS. KOH CONCENTRATION FOR VARIOUS TEMPERATURES

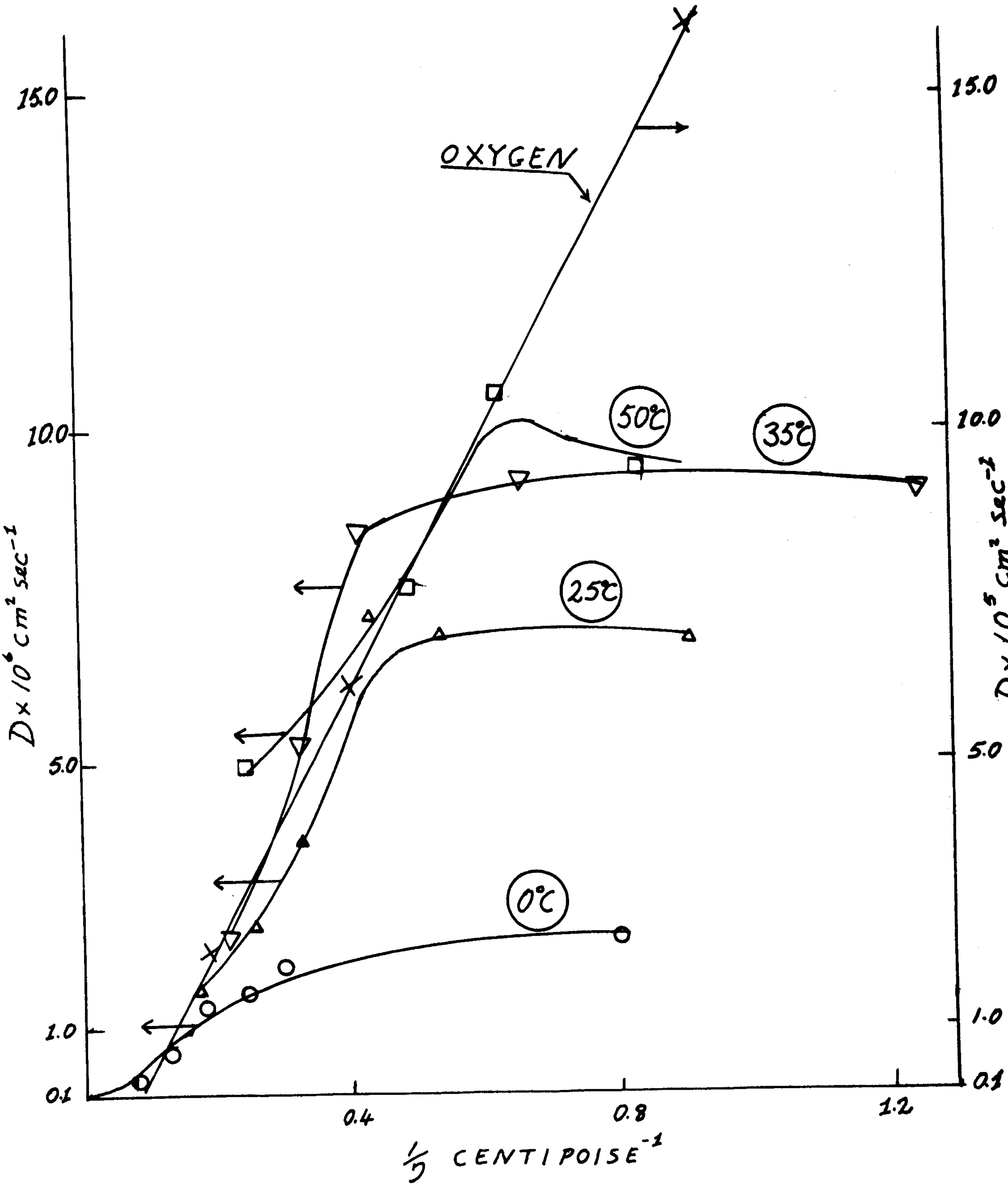


FIGURE 10 DIFFUSION COEFFICIENT FOR ZINCATE VS. RECIPROCAL VISCOSITY

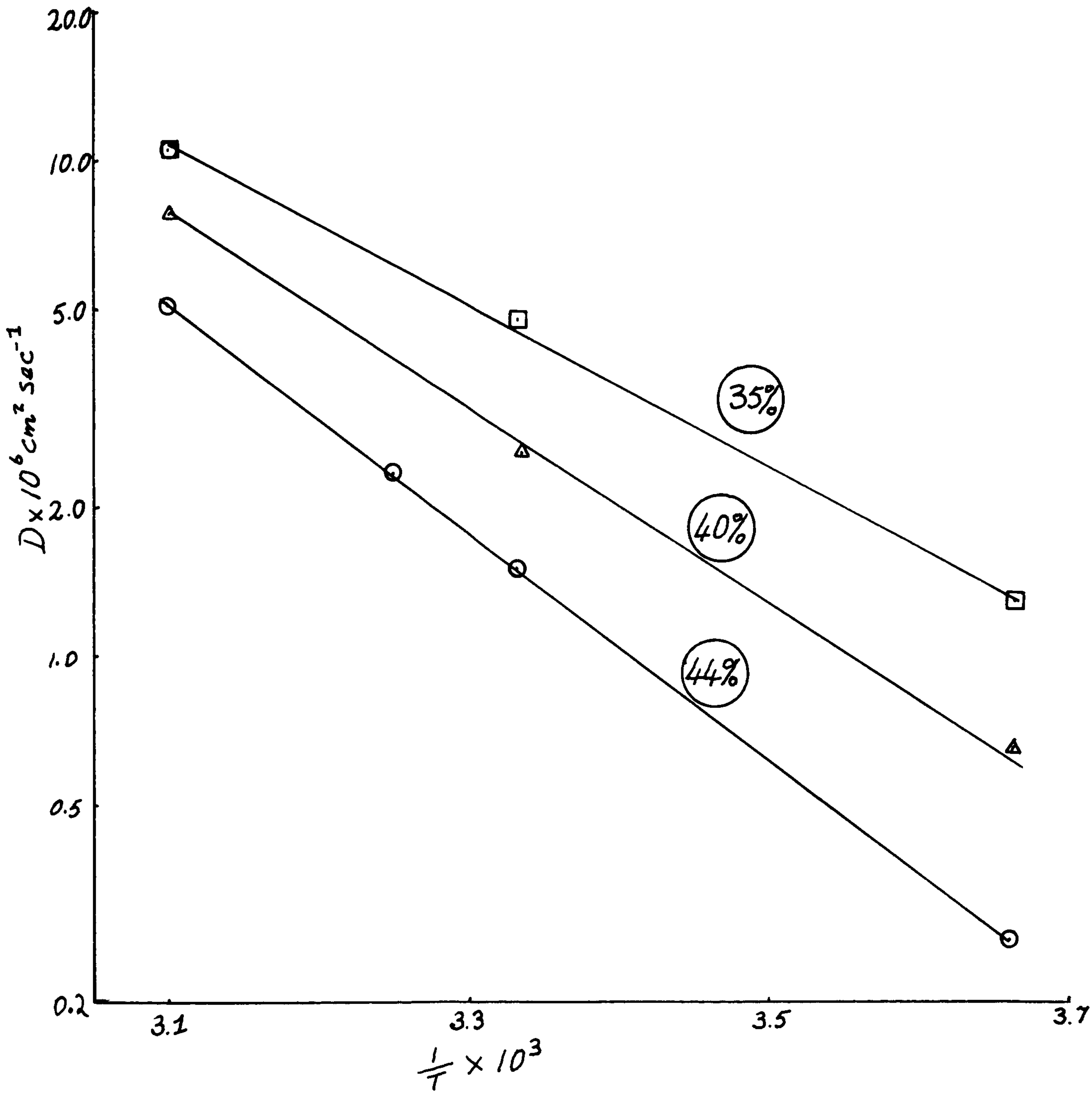
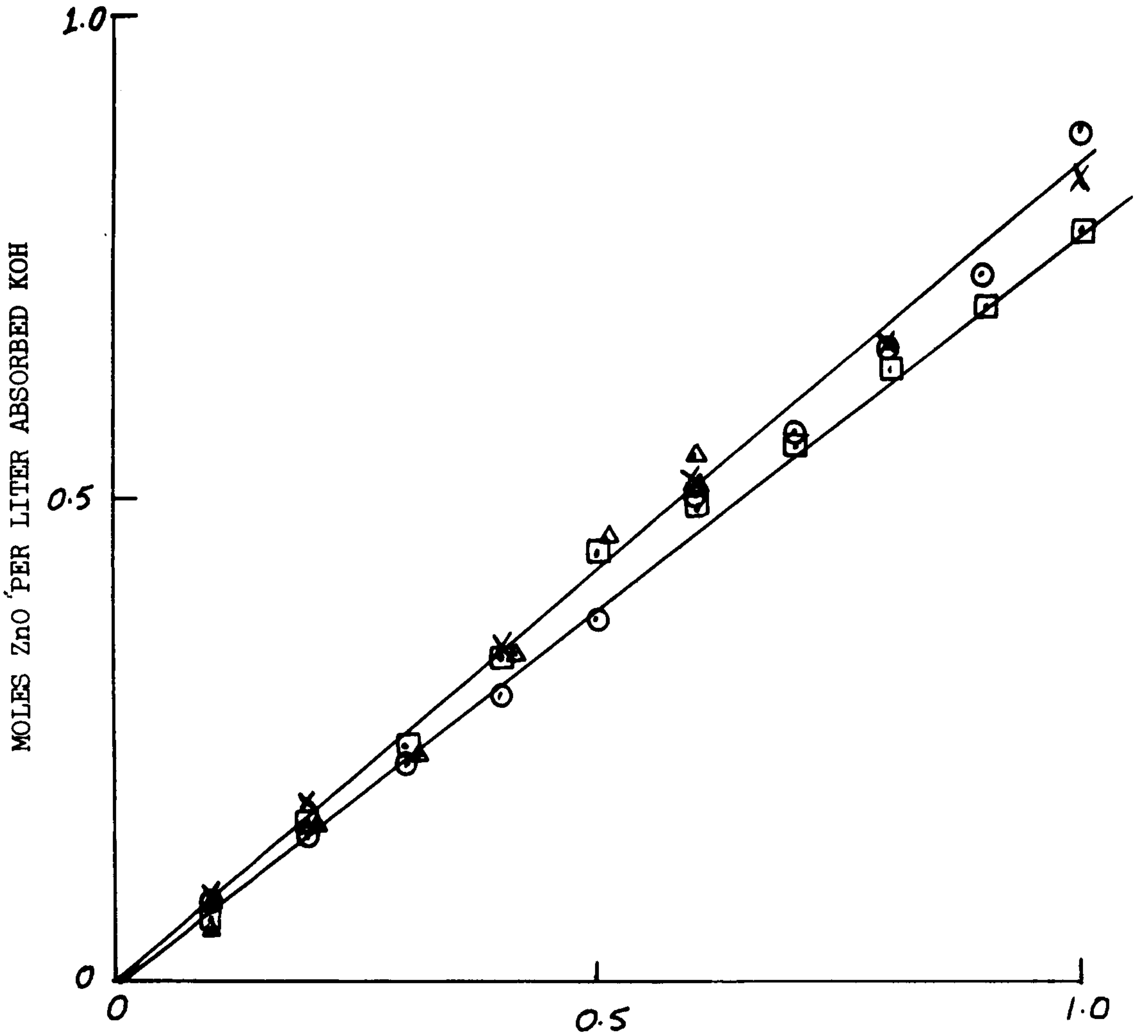


FIGURE 11 ARRHENIUS PLOTS FOR ZINCATE DIFFUSIVITY



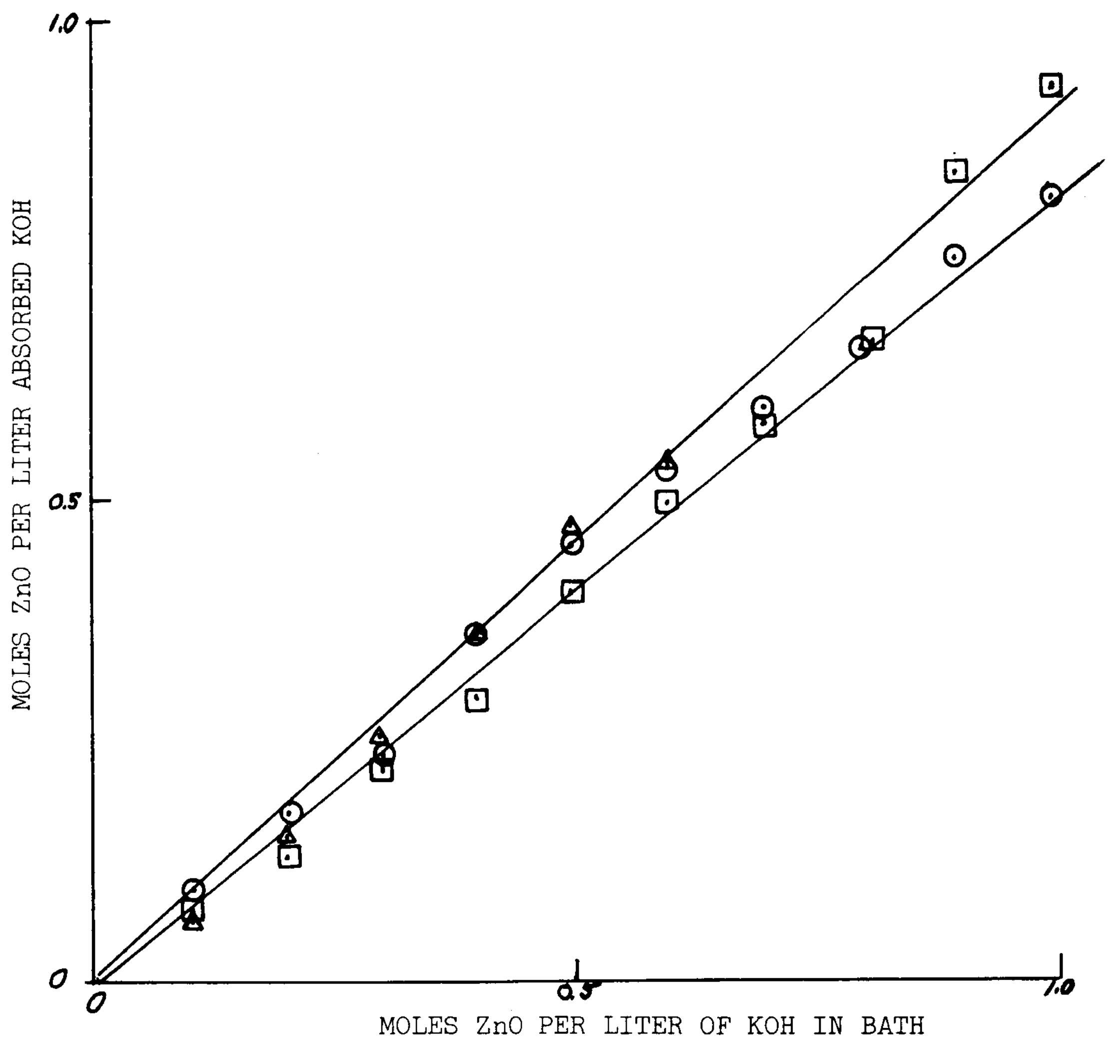
⊙ TEMP = 25°C 44% KOH K = 0.81

⊡ TEMP = 60°C 44% KOH K = 0.79

▲ TEMP = 25°C 31% KOH K = 0.89

✕ TEMP = 25°C 44% KOH SAT'D EMULPHOGENE BC-610

FIGURE 12 ABSORPTION ISOTHERMS FOR YARDNEY C-19



⊙ Temp = 25°C 44% KOH K = 0.84

⊡ Temp = 60°C 44% KOH K = 0.86

Δ Temp = 25°C 31% KOH K = 0.94

FIGURE 13 ABSORPTION ISOTHERMS FOR DU PONT PUDO 300

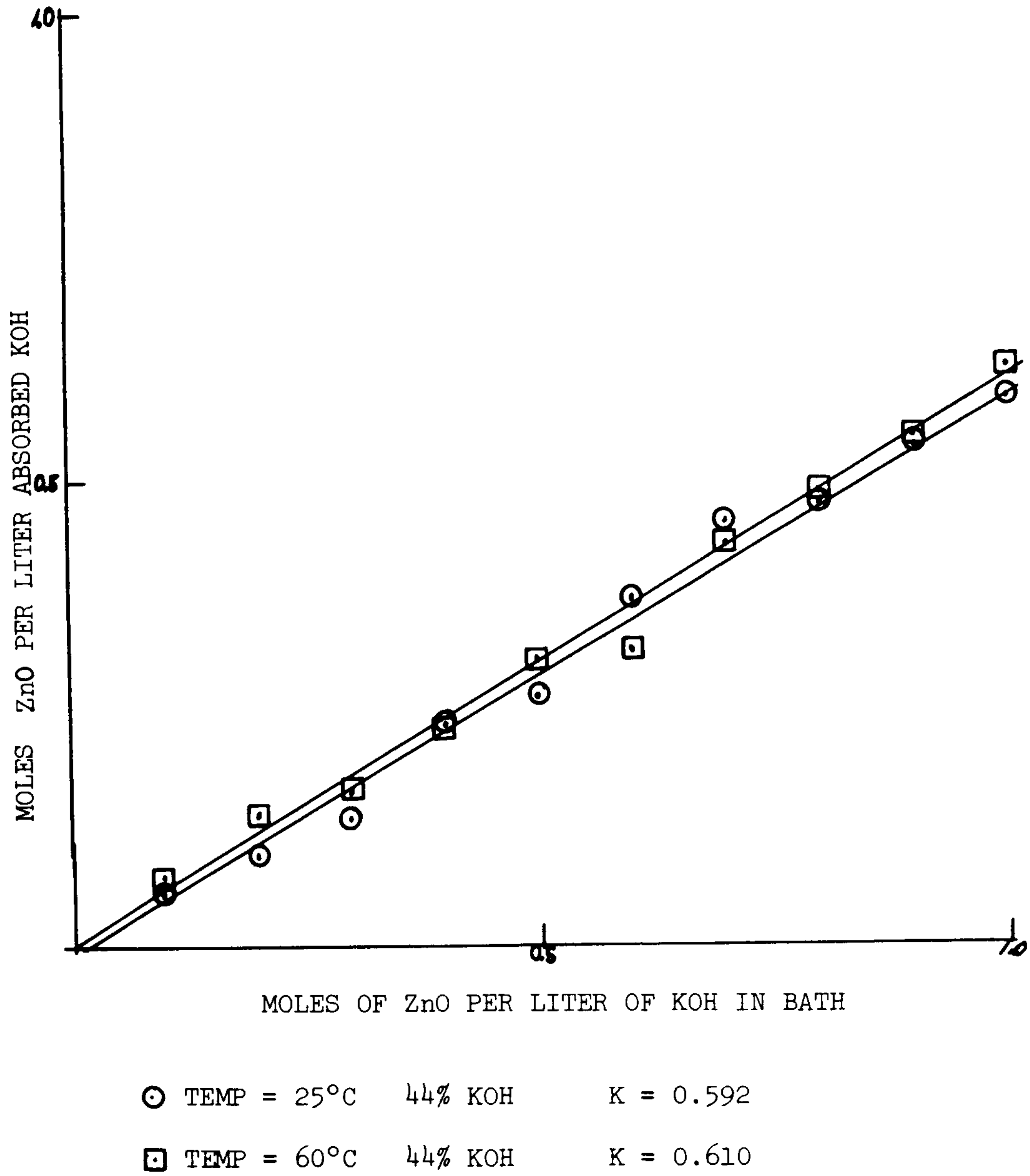
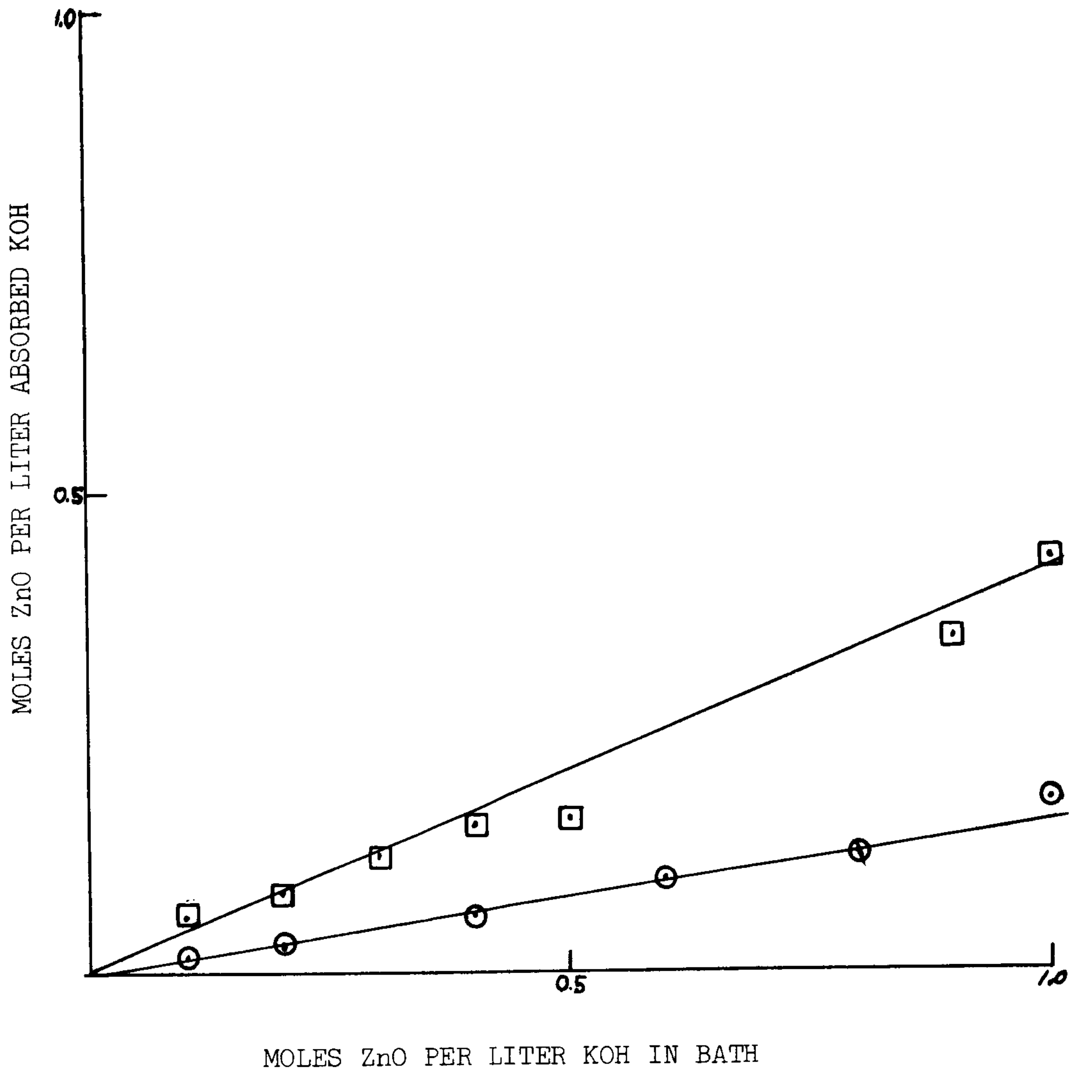


FIGURE 14 ABSORPTION ISOTHERMS FOR MONSANTO PVA



⊙ TEMP = 25°C 44% KOH K = 0.155

⊡ TEMP = 60°C 44% KOH K = 0.420

FIGURE 15 ABSORPTION ISOTHERMS FOR BORDEN C-3

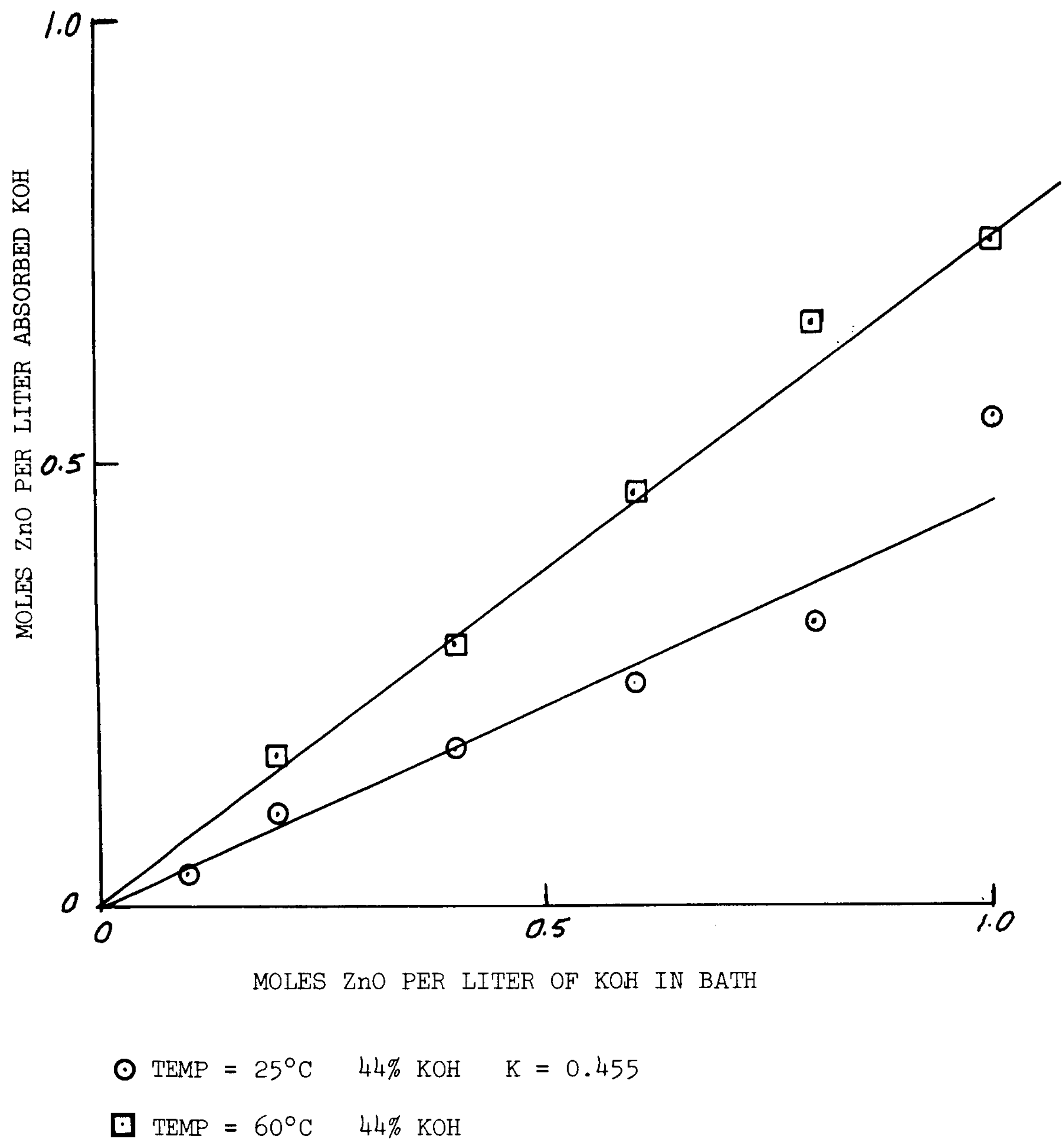
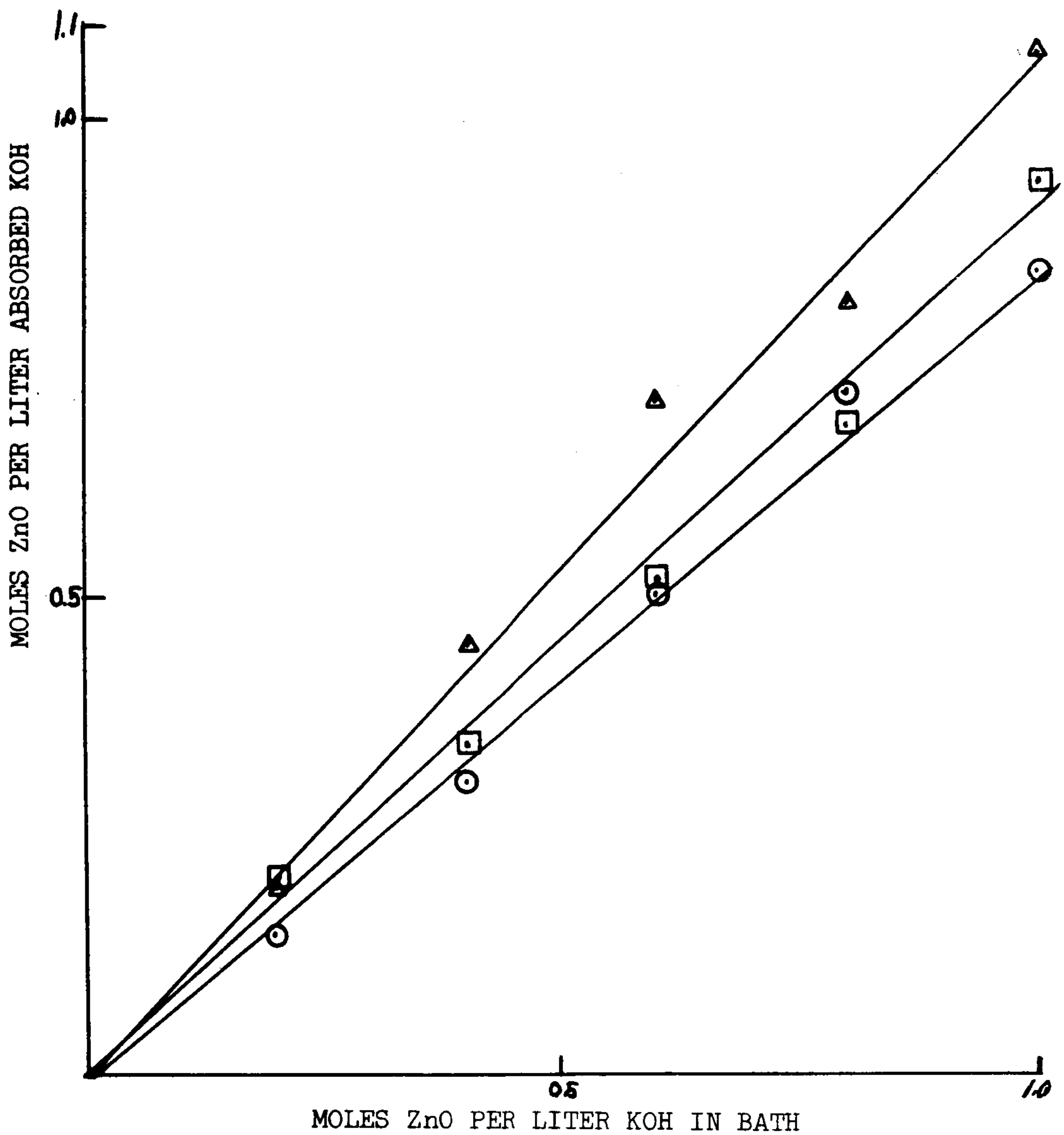


FIGURE 16 ABSORPTION ISOTHERMS FOR BORDEN 9107-5



⊙ BORDEN FILM 9107/22 0.84 TEMP = 25°C

⊡ BORDEN FILM 9107/21 0.91

▲ BORDEN FILM 9107/27 K = 1.06

FIGURE 17 ABSORPTION ISOTHERMS FOR BORDEN FILM 9107/22, FILM 9107/21, and FILM 9107/27