

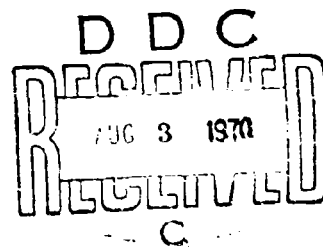
AD 709468



INTERFACE EFFECTS IN MASS
TRANSFER CONTROLLED CORROSION
REACTIONS

by

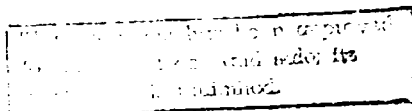
I. Cornet and D. W. Fuerstenau



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OFFICE OF NAVAL RESEARCH

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ONR Technical Report

University of California
College of Engineering
Berkeley, California

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INTRODUCTION

The purpose of the present investigation has been to delineate the role played by surface active agents in mass transfer-controlled corrosion reactions in a saline environment. Major effort has been directed toward dynamic systems where the metal surface moves relative to the saline solution. Research on corrosion inhibition by adsorbed surface-active materials in such dynamic systems has been largely neglected despite the fact that corrosion and corrosion inhibition in numerous Naval applications involves motion of a metal surface relative to sea water environment.

The interfacial region between metal and solution is clearly the site of the corrosion reaction and rate processes are controlled by mass transfer to and through the interfacial film, and which, in turn, will be controlled by the dynamic shear conditions imposed by relative flow of metal and solution. While there has been very little work reported on the performance of corrosion inhibitors in rotating systems, there are several related areas of investigation that are important to the present study.

Several workers have considered the adsorption of simple organics^(1 - 6) and long chain organic surfactants on polarized nickel and copper^(7, 8, 9) surfaces and the mercury-water interface^(10, 11). Hackerman^(8, 9) has summarized the observed relationships between inhibition and molecular structure. Specific effects of organic inhibitors on the corrosion of mild steel in acid solution^(12, 13, 14) have

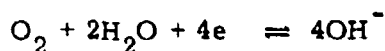
also been reported. The analysis given in two detailed reviews^(8, 15) suggests that the effectiveness of organic and inorganic inhibitors for a given metal depends on the inhibitor concentration, the pH of the system, the velocity of the metal relative to the solution, time, surface preparation, surfactant chain length, temperature, cross-sectional area of the organic molecules and nature of the functional groups on the inhibitor. Reviews have also appeared on the suitability of several electrochemical techniques for analysis of the fundamental aspects of the adsorption of organic inhibitors on solid electrodes^(16, 17, 18).

Analysis of basic mass transfer-controlled reactions at the surface of rotating discs and cylinders and at static surfaces has received considerable attention^(19 - 26). The initial work of Cornet and co-workers^(22, 23, 24) was the starting basis for the experimental approach taken in this work.

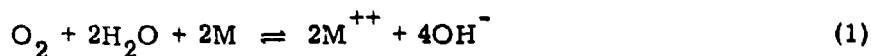
In this report are summarized the results of our research and our understanding of the processes that control corrosion and particularly their sensitivity to relative motion and to the presence of inhibitors. The results should eventually allow for more efficient use and selection of corrosion inhibitors in dynamic systems of immediate concern to operators attempting to control corrosion of marine metal surfaces.

OUTLINE OF EXPERIMENTAL PROGRAM

The fundamental corrosion (i. e. redox) reaction for metal-aqueous aerated solution systems is given by



to yield overall,



where M represents, for example, a metal which yields divalent cations, M^{++} , in solution.

In order to isolate the role of oxygen, a galvanostatic slow-rise polarization technique was used where the metal (Monel, copper or nickel) is operated as a cathode. This metal cylinder can be rotated at constant but variable speed in a bath of 4% NaCl (0.685 molar) solution of known oxygen content.

The alkyl amine surfactants of from C_{10} to C_{16} chain length were selected as model corrosion inhibitors in view of the key role of nitrogen centers discussed by Hackerman⁽⁸⁾ and of increasing chain length⁽⁹⁾ in the action of surfactant inhibitors.

Furthermore, the quantitative hemi-micelle model of surfactant adsorption at solid-liquid interfaces developed by Fuerstenau, et al^(27, 28), has been tested in detail for alkyl amines at negatively charged oxide surfaces. The extension to cathodically polarized metal surfaces is therefore well served by this earlier quantitative adsorption work.

The form of the "ideal" polarization curve in the galvanostatic slow-rise polarization technique is shown schematically in Figure 1.

The measured potential at any point of the experiment is comprised of

- i) Equilibrium redox potential (Open-circuit potential), i. e.

$$E^{\circ} + \frac{RT}{nF} \ln \left[\frac{(\text{OH}^-)^4 (\text{M}^{++})^2}{(\text{O}_2)} \right]$$

where E° is the standard redox potential and (OH^-) and (M^{++}) are concentrations (strictly activities) of hydroxide and metal ions respectively and (O_2) is the concentration of oxygen in the system.

- ii) Activation overvoltage (non-equilibrium term), i. e.

$$\beta \log i/i_0$$

where i = applied current, i_0 = exchange current, and β = constant.

- iii) Liquid junction potential.

- iv) IR drop in solution.

- v) Potential drop due to other secondary reactions.

- vi) Diffusion overvoltage, i. e.

$$\frac{RT}{nF} \ln \left[\frac{i_l}{i_l - i} \right]$$

where i_l = Diffusion limiting current.

In the present system contributions of (iii), (iv) and (v) are assumed to be negligible. Region 1 represents the electrochemical

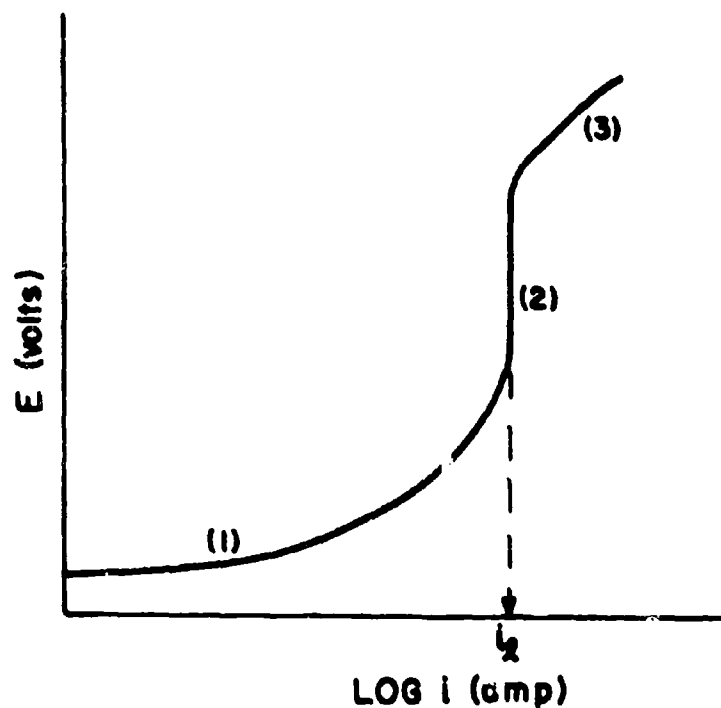
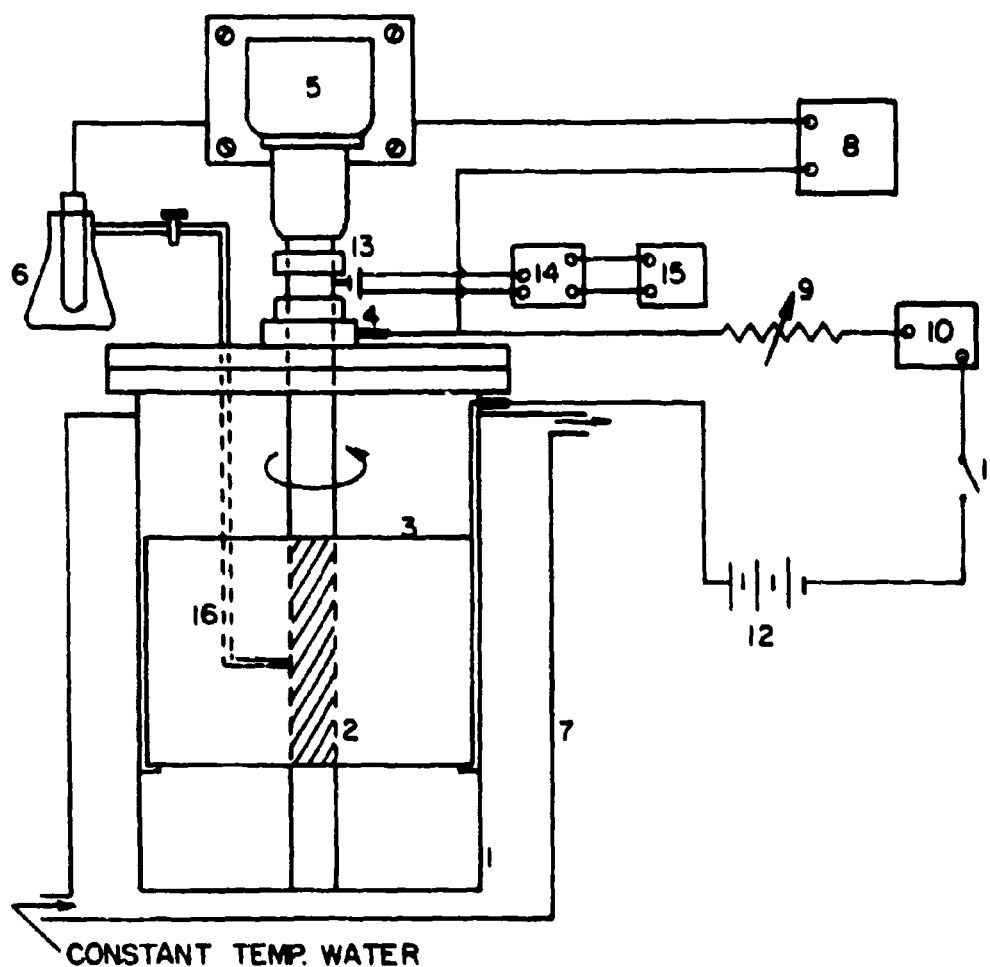


Figure 1. Schematic representation of a polarization curve. In Region 1 electrochemical reactions are rate controlling; in Region 2 mass transfer (i.e. oxygen mass transfer) is rate controlling (i_1 = mass transfer limiting current; Region 3 is controlled by hydrogen evolution.

part of the polarization curve. Diffusion overvoltage, represented by a sharp rise in potential (Region 2 on the curve in Figure 1) is predominant as the applied current approaches the diffusion limiting current. In the region where i is greater than i_l (Region 3 in Figure 1), the shape of the polarization curve is primarily due to hydrogen evolution and its activation overvoltage. Since the diffusion limiting current is in effect the amount of current necessary to protect the cathode from being corroded by oxygen, it is necessary to study the effect of various parameters on the limiting current. The variables being considered in the present study can be divided into physical variables and chemical variables. The physical or mechanical variables, for example speed of rotation of the electrode, must be examined in order to separate out strictly mass transfer effects on O_2 reduction at the electrode surface. Then the chemical variables such as inhibitor concentration and chain length can be expressed in terms of the reactions at the moving surface.

EXPERIMENTAL METHOD

In order to incorporate effects due to mass transfer between the metal surface and the liquid into polarization phenomena, an apparatus with a rotating cylindrical cathode was designed and constructed. The general layout of the experimental assembly and its electrical circuits is shown schematically in Figure 2. The major



- | | |
|--------------------------------|---|
| 1. CELL | 10. MILLIAMETER |
| 2. CATHODE (TEST ELECTRODE) | 11. SWITCH |
| 3. ANODE (PLATINIZED TITANIUM) | 12. 6V BATTERY |
| 4. MERCURY WELL CONTACT | 13. MAGNETIC PICK UP POINT FOR ELECTRODE R.P.M. DETERMINATION |
| 5. MOTOR-VARIABLE SPEED | 14. AMPLIFIER |
| 6. REFERENCE ELECTRODE | 15. FREQUENCY COUNTER |
| 7. CONSTANT TEMPERATURE BATH | 16. CAPILLARY PROBE |
| 8. VACUUM TUBE VOLTMETER | |
| 9. VARIABLE DECADE RESISTOR | |

Figure 2. Apparatus for polarization studies.

part of the research program to date has been concerned with Monel metal as the rotating electrode. The Monel (67% Ni, 33% Cu) electrode is cleaned mechanically, etched with concentrated hydrochloric acid, and washed repeatedly before immersion in the 4% NaCl solution. The cleaning procedure yields a reproducible surface in that under a given set of solution conditions the observed limiting current is constant.

The alkyl amine corrosion inhibitors were used as ammonium acetate salts. These were prepared by dissolving primary amines obtained from Armour Industrial Chemical Company in benzene and adding an equimolar quantity of glacial acetic acid. The acetate salt was recrystallized from benzene by cooling and excess benzene was removed in a vacuum desiccator.

The oxygen content was varied by controlled exposure of air-saturated water to helium gas for various time periods. In most experiments the oxygen content was maintained reasonably constant by exposing the electrolyte solution to atmosphere for a day for oxygen saturation. During the entire experiment the electrolyte is left open to atmosphere. Bubbling oxygen through the solution caused uncontrollable supersaturation and subsequent scatter in experimental results. The oxygen content of the saline solutions was determined by the standard Winkler method.

RESULTS AND DISCUSSION

Physical Variables

In order to delineate the role of mass transfer reactions in rotating systems, the polarization behavior of Monel in the absence of inhibitor, at fixed O_2 content (6.2 ± 0.2 ppm) and fixed pH (6.0 ± 0.2) has been determined as a function of speed of rotation. The results are shown in Figure 3. As the speed of rotation increases the thickness of the hydrodynamic boundary layer decreases thereby increasing the oxygen concentration gradient. In order to achieve protection of the metal surface, larger currents are required at higher R.P.M.

The present experiments represent turbulent flow conditions and are amenable to analysis by the method developed by Eisenberg, et al.⁽²⁹⁾ and given in detail in Appendix I. In Figure 4 the present data are compared to that calculated by the method of Eisenberg, et al., and the close agreement confirms that O_2 reduction at the Monel electrode is a typical mass transfer, diffusion-limited reaction

A further indication of the importance of limiting diffusion current in corrosion is provided by the results of Figure 5. For each of the three separate polarization curves the oxygen content was the same (6.3 to 6.4 ppm), but because of deliberate differences in electrode preparation, the rest potentials (not shown in the figure) were not the same. Despite this difference in rest potential and difference in behavior in Region 1, the limiting diffusion current (i_l) was the same in each experiment.

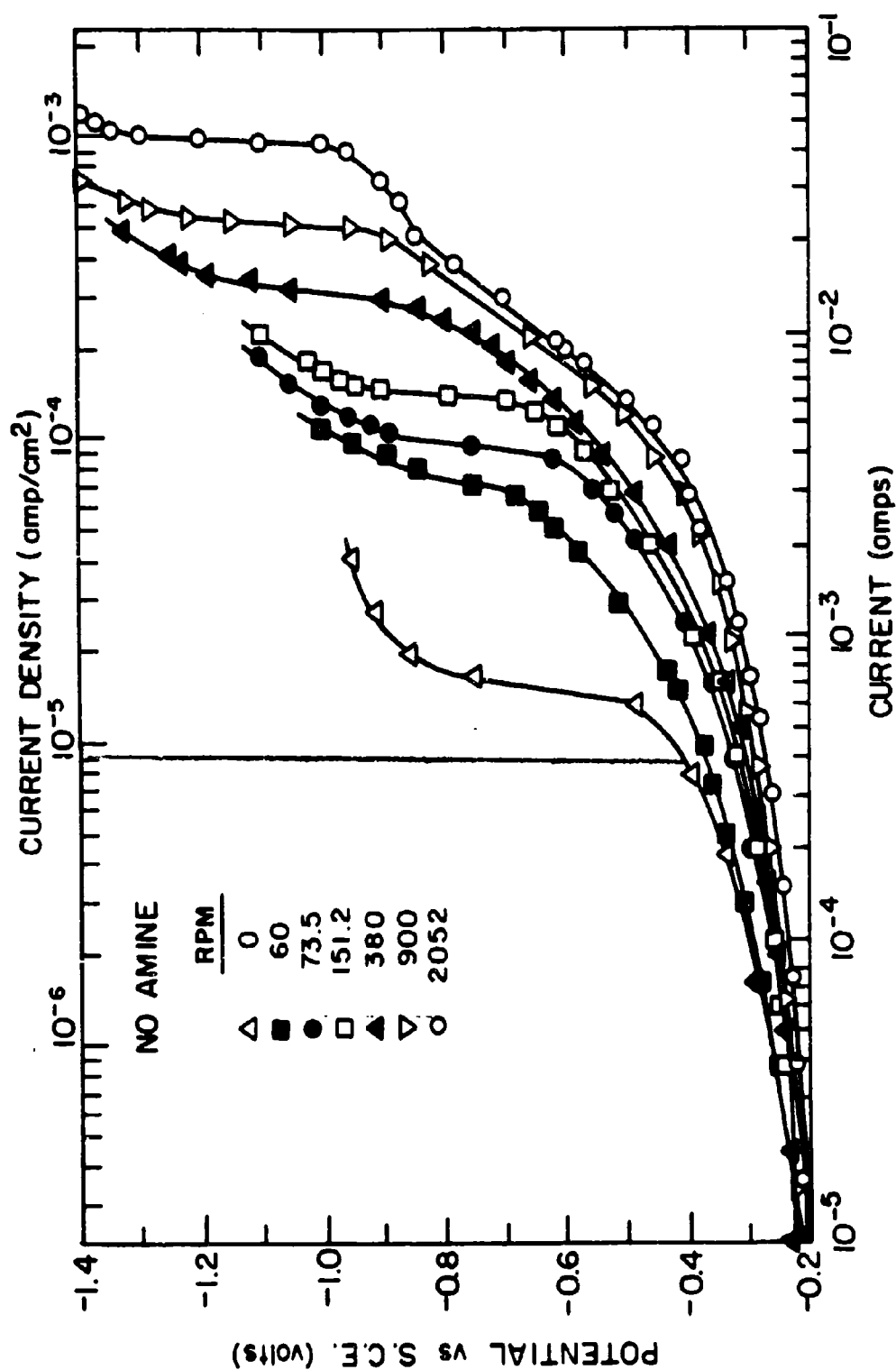


Figure 3. Polarization curves for a rotating Monel cathode in air-saturated 0.685 M NaCl, at 20°C, at various R.P.M.'s.

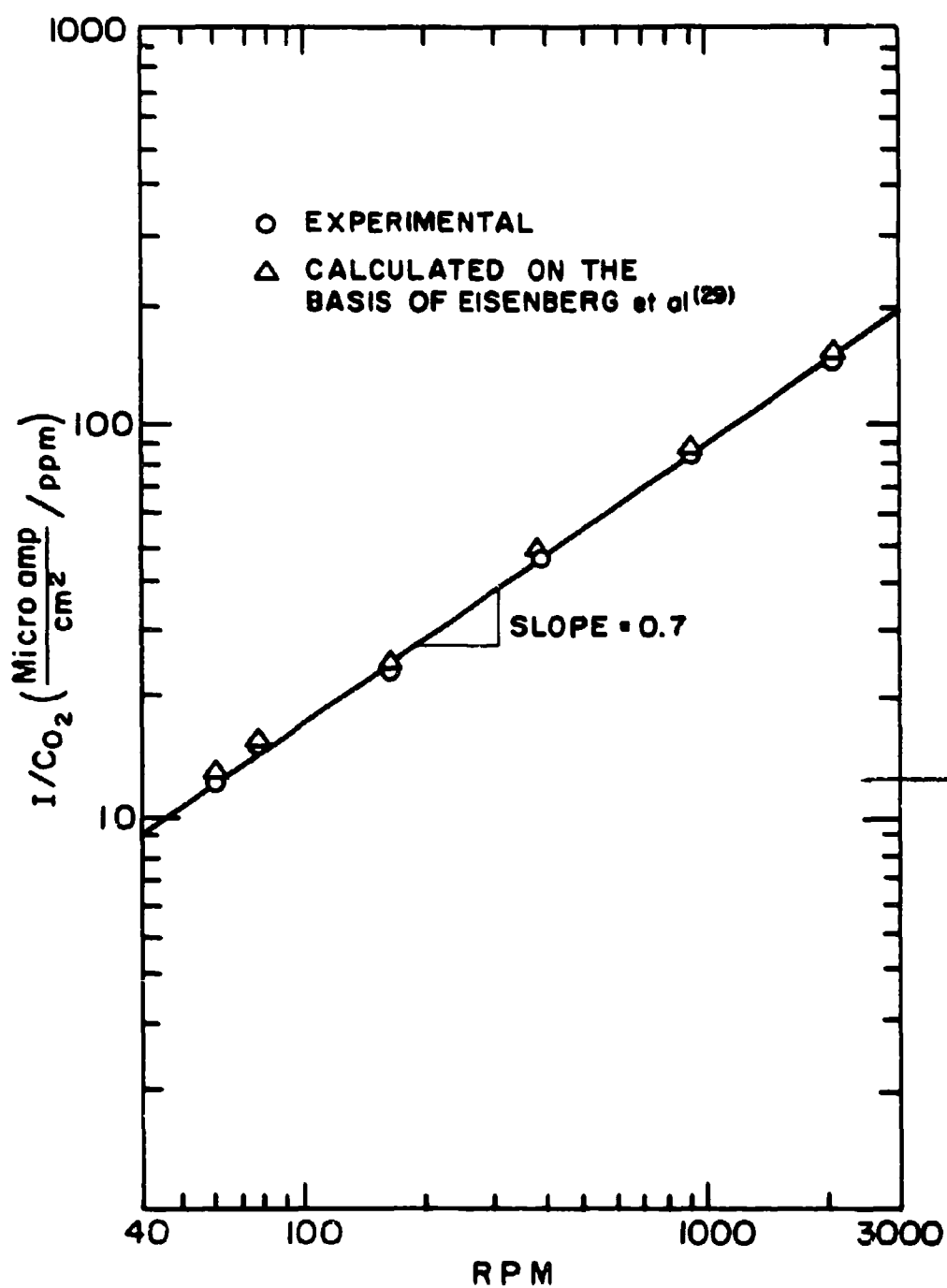


Figure 4. R.P.M. vs I/CO_2 for Monel in 4% NaCl aqueous solution at 20°C.

This is of considerable assistance in analysis of chemical effects at the rotating electrode since it is not always possible to obtain identical starting surfaces. The wide range of rest potentials, -0.165 to -0.207v , (not shown in Figure 5) is not usually encountered and was obtained in the present study by allowing the freshly prepared electrode to stand undisturbed in the 4% NaCl solution for periods up to 84 hours.

The effect of increasing the temperature is shown in Figure 6 for a static Monel electrode. Temperature has several separate effects, the summation of which is that the limiting diffusion current increases with increase in temperature. Experiments are now in progress where a wider temperature range is being used. Separate effects of temperature on the diffusion coefficient and on the oxygen solubility will be calculated and separated out in order to measure the activation energy for the mass-transfer process.

The general effect of increased limiting diffusion current with increased temperature is in agreement with recent work⁽²⁶⁾ on cupric ion reduction at a rotating copper cathode where an activation energy of 5.06 kcal for Cu reduction per mole was obtained.

It is especially important to examine quantitatively the limiting diffusion current and thus the cathodic protection as a function of temperature, rotation and inhibitor concentration. Optimum protection of metal components in marine environments must be adjusted as the sea water temperature changes. Current experiments should

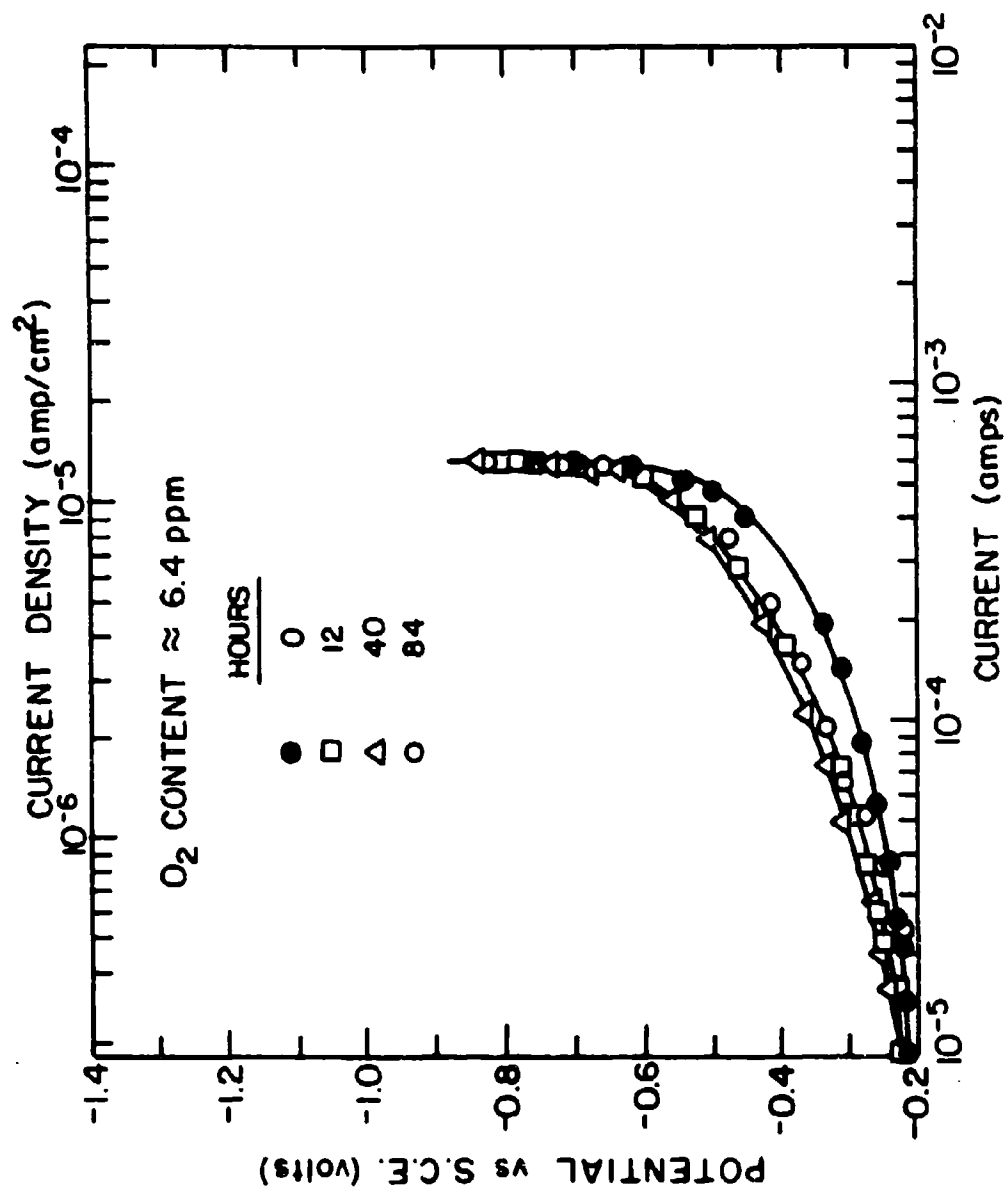


Figure 5. Polarization curves for the Monel cathode in air-saturated 0.685 M NaCl, 0 R.P.M., for various exposure time to the solution.

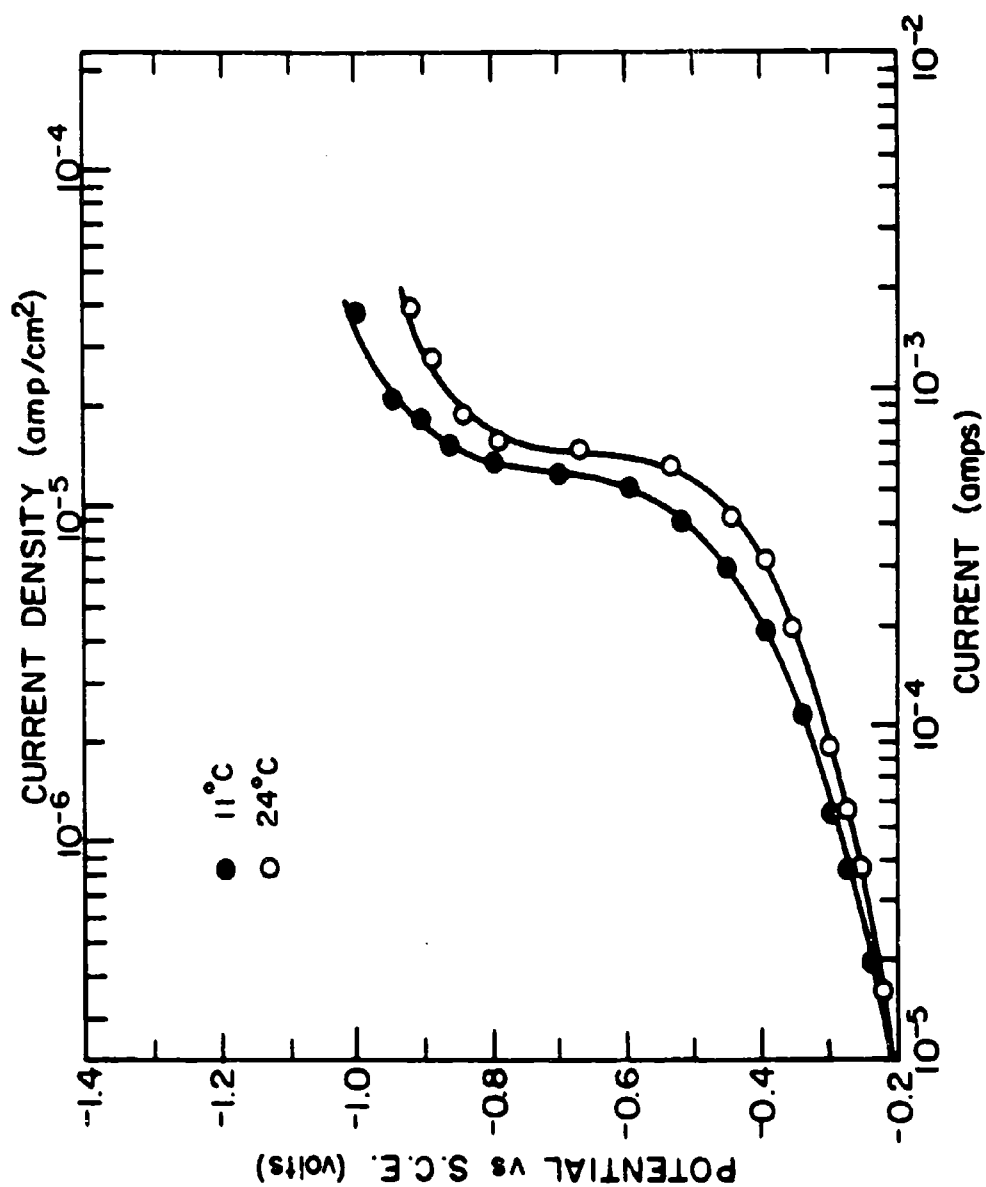


Figure 6. Polarization curves for the Monel cathode in air-saturated 0.685 M NaCl, 0 R.P.M., at different temperatures.

provide a better understanding of the effect of temperature on protection of moving metal components in sea water in the presence of inhibitors.

Chemical Variables

In this research, we have considered two different chemical variables -- the effect of adsorbed surfactants and the effect of oxygen content.

Organic Surfactants: When alkylamine surfactants are present in the system, drastic reductions in the diffusion limiting current are obtained at concentrations as low as 10^{-6} M. This is shown in detail in Figures 7, 8, 9 and 10, representing the effect of 10, 12, 14 and 16, respectively, carbon amine surfactants.

Several important points can be raised immediately. Firstly, the decrease in current requirements for effective protection are very large for such small concentrations of organic additive. In this regard, for example, a concentration of 10^{-5} M of the C_{16} amine for the Monel electrode rotating at 1400 R.P.M. almost recovers the low protection current of a static Monel electrode (compare Figures 3 and 10). It is therefore realistic to think in terms of removing almost completely the deleterious effect on corrosion due to increased speed of rotation by addition of amine-type surfactants. This conclusion is considered to be valid whether one considers the amines as corrosion inhibitors themselves or as surfactants that have synergistic action when used with conventional inhibitors. The synergistic action of

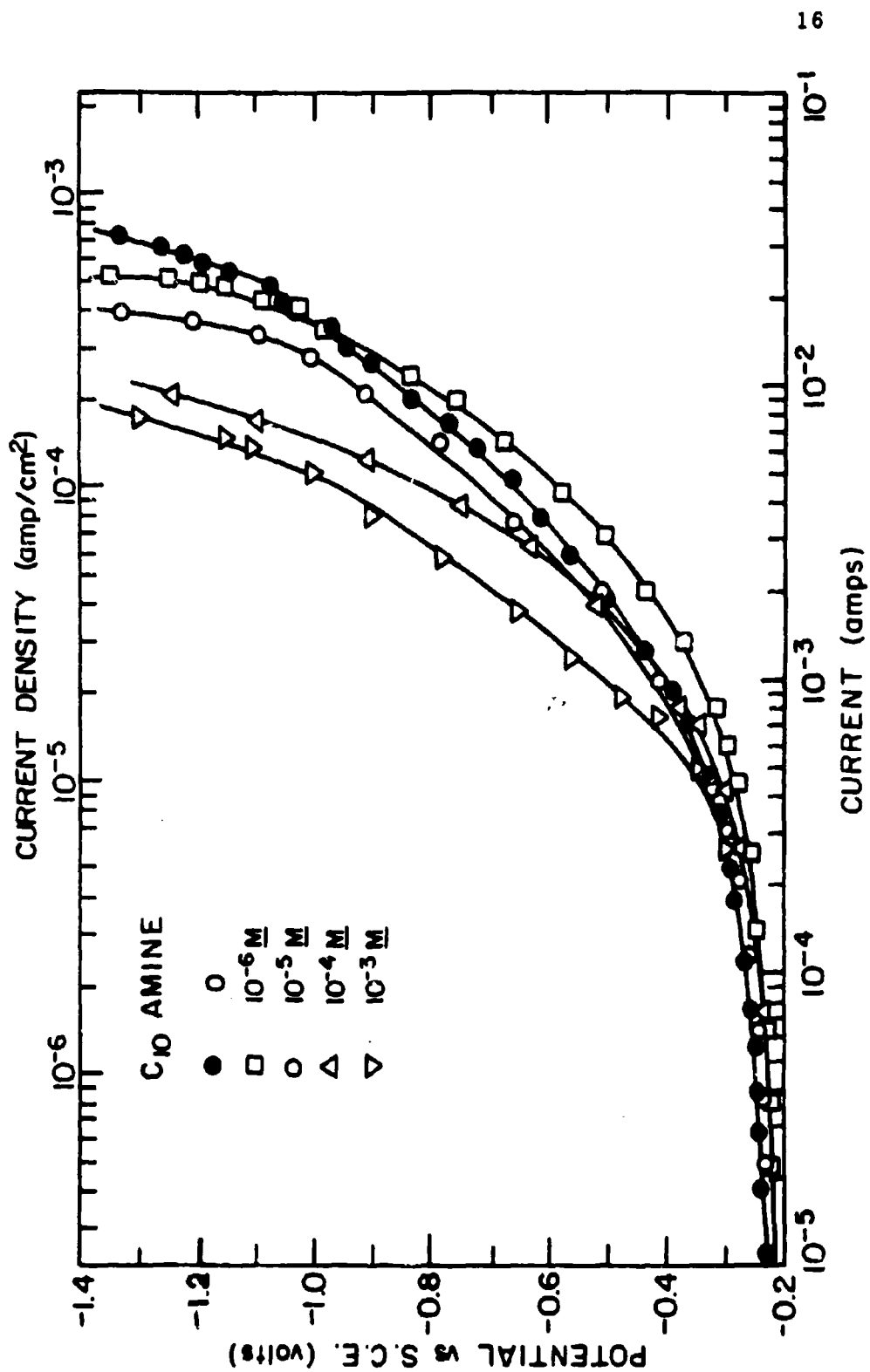


Figure 7. Polarization curves for the Monel cathode in air-saturated 0.685 M NaCl, at 20°C, 1400 R.P.M. (Re = 26,500) as a function of C_{10} amine concentrations.

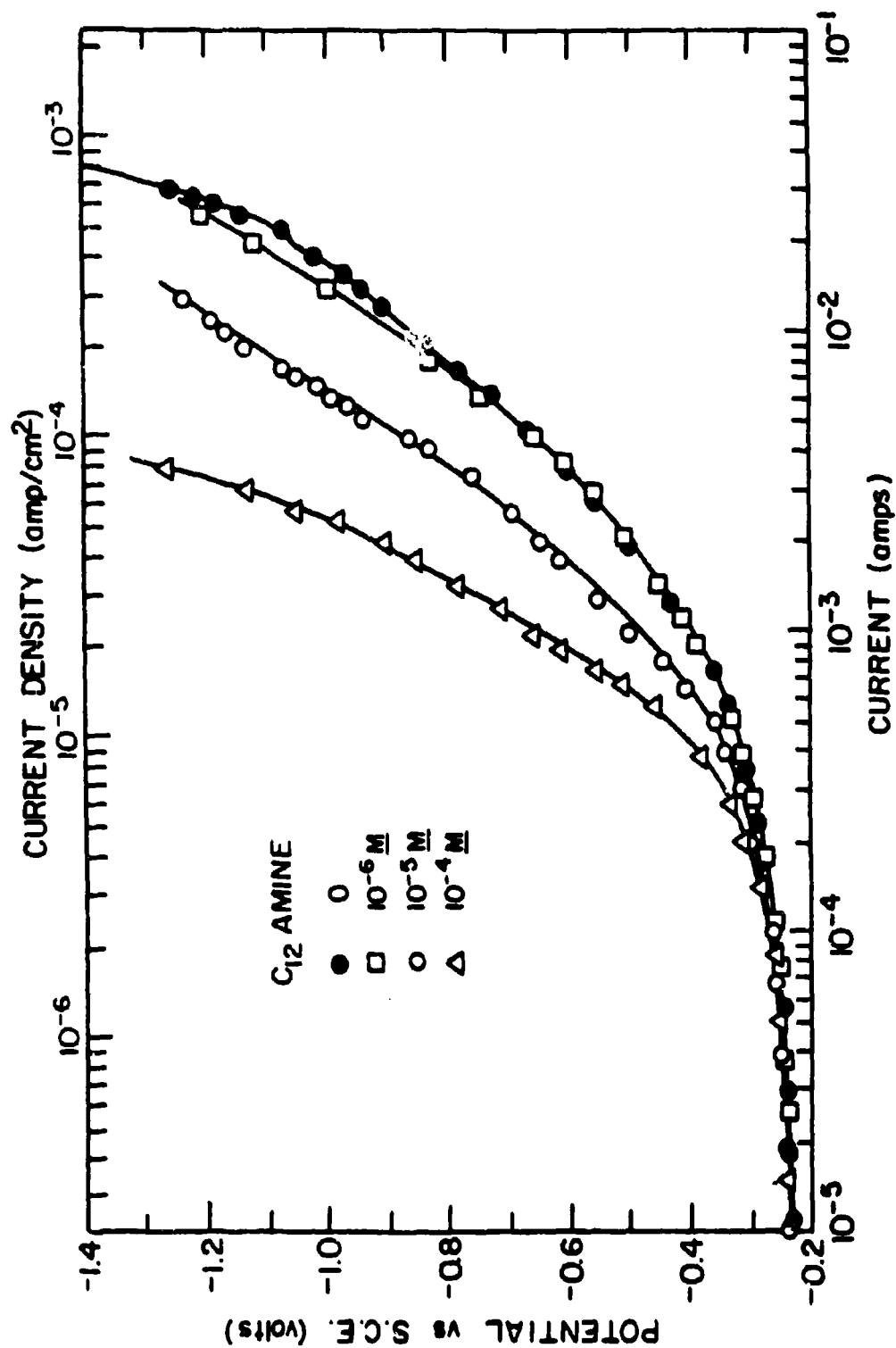


Figure 8. Polarization curves for the Monel cathode in air-saturated 0.585 M NaCl, at 20°C, 1400 R.P.M. (Re = 26,500) as a function of C₁₂ amine concentrations.

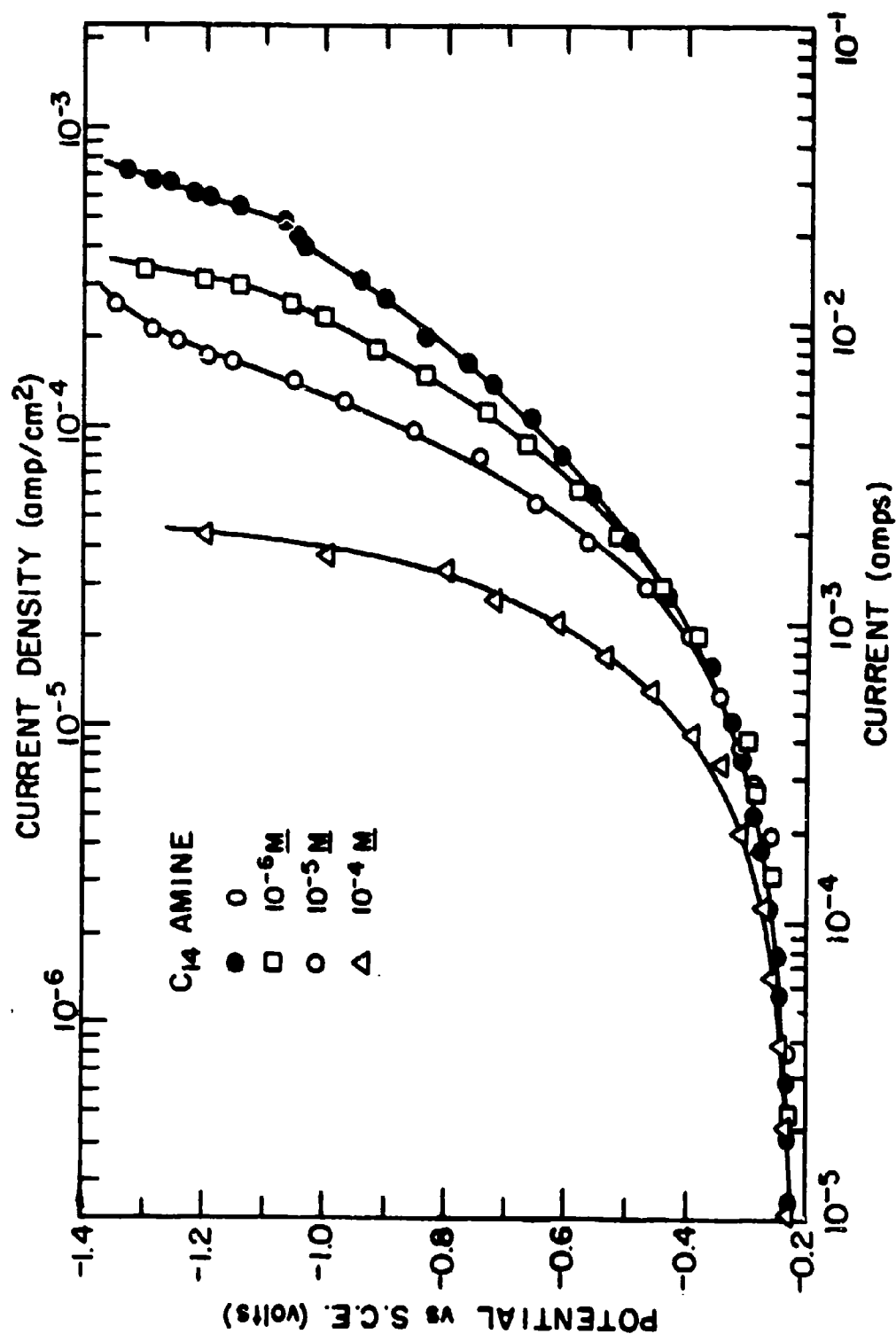


Figure 9. Polarization curves for the Monel cathode in air-saturated 0.685 M NaCl, at 20°C, 1400 R.P.M. (Re = 26,500) as a function of C₁₄ amine concentrations.

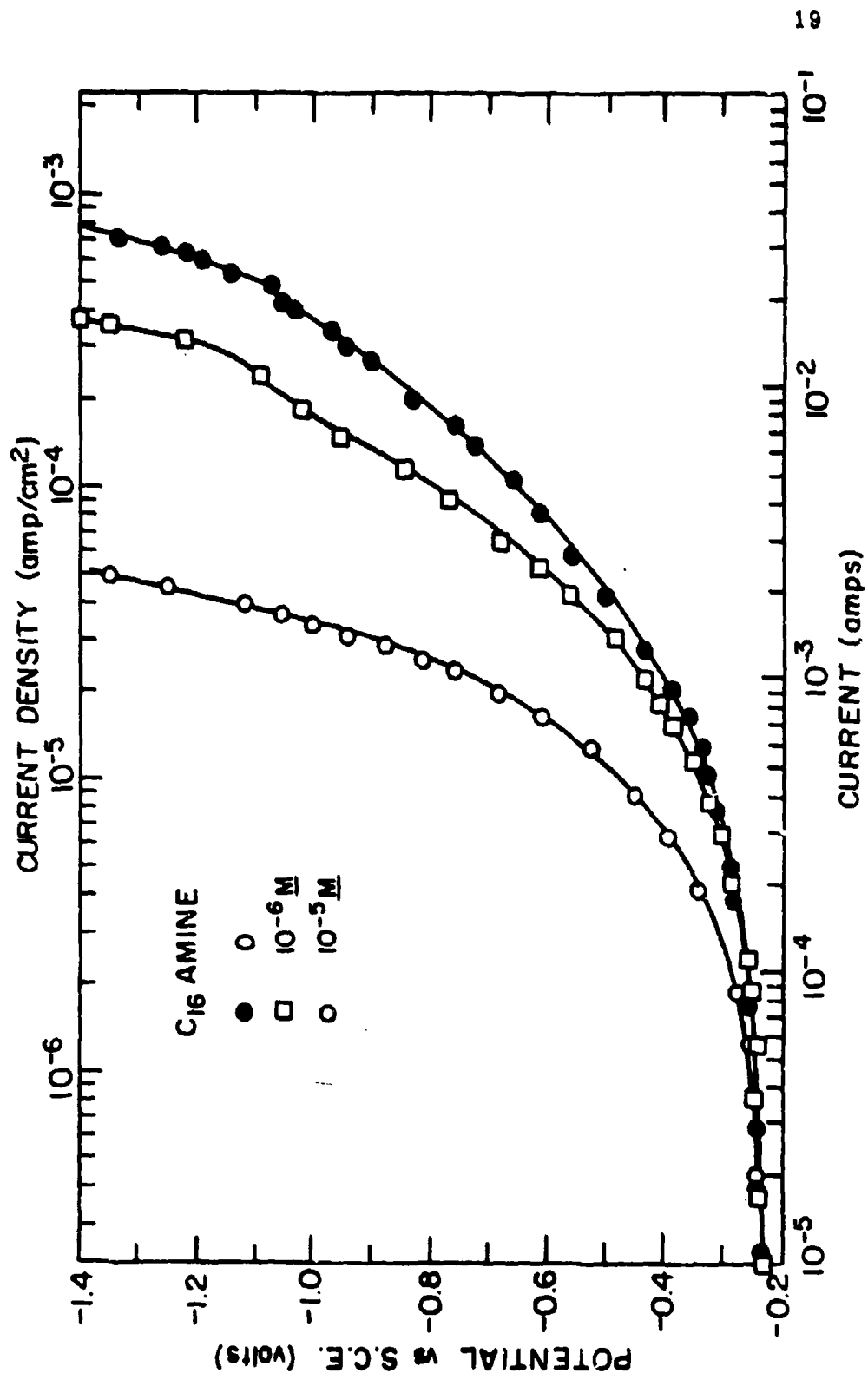


Figure 10. Polarization curves for the Monel cathode in air-saturated 0.685 M NaCl, at 20°C, 1400 R.P.M. (Re = 26,500) as a function of C₁₆ amine concentrations.

amines can be likened to the co-operative adsorption phenomena described by Yamada and Fuerstenau⁽³⁰⁾.

The second general feature of the results shown in Figures 7 to 10 is that there is usually no clearcut (vertical rise) limiting current for systems with the amines present. However, the polarization curves and the tendency to a diffusion limiting current are clearly shifted to lower current densities. The absence of a definite i_L value is thought to be related to the heterogeneity of the system in that amine diffusion to the surface may interfere in a variety of as yet unknown ways with the O_2 diffusion to the electrode.

A third feature of the curves is that although there is some cross-over of the curves in Region 1 with increase in amine concentration, the limiting current region decreases uniformly with concentration. Vetter⁽³¹⁾ has commented on the variability that is sometimes observed in the reaction-controlled region and apparently the present amine surfactants may interfere with these various reaction steps.

If the amine surfactants act as inhibitors by a strictly adsorption role, i.e. the adsorbed amine presents a diffusion barrier to the reacting O_2 molecules, then the well-established hemi-micelle theory of surfactant adsorption^(27, 28) should apply to the corrosion system. In outline, the hemi-micelle model is

- i) At low concentration, the surfactant ions adsorb at isolated sites on the metal surface such that adsorption is not markedly dependent on alkyl chain length.

- ii) With increasing concentration, an abrupt increase in adsorption is observed due to the formation of two-dimensional aggregates analogous to micelle formation in bulk solution. In this region, the surface adsorption density (Γ_i moles cm^{-2}) at a given bulk solution equilibrium concentration (C_b moles cm^{-3}) is strongly dependent on chain length. Thus^(27, 28)

$$\Gamma_i = 2r_i C_r \exp \left[\frac{-Z_i e \psi_s + n \phi_{\text{CH}_2}}{kT} \right]$$

where r_i is radius of the polar head group of the surfactant, k is Boltzmann's constant, T is the temperature, Z_i is the charge of the polar group, e is the electronic charge, ψ_s is the potential at the adsorption plane, n is the number of carbons in the chain and ϕ_{CH_2} is the hydrophobic bonding energy per CH_2 group; ϕ_{CH_2} is approximately $1 \text{ kcal. mole}^{-1}$. For the present saline solution, the ψ_s term is probably constant and small, and the major adsorption energy is the hydrophobic bonding contribution $n\phi_{\text{CH}_2}$.

That the hemi-micelle adsorption concept applies to the action of alkyl amine surfactants in saline solutions for a rotating Monel electrode is illustrated in Figure 11. In this figure, the current density at an applied voltage of -1.2 volts vs S.C.E. (the potential at which limiting current was obtained in the absence of surfactants) is plotted as a function of the alkyl amine concentration for each of the four different chain lengths. Two features of these curves are that there is an abrupt decrease in current requirements over a narrow concentration range for each surfactant and there is a

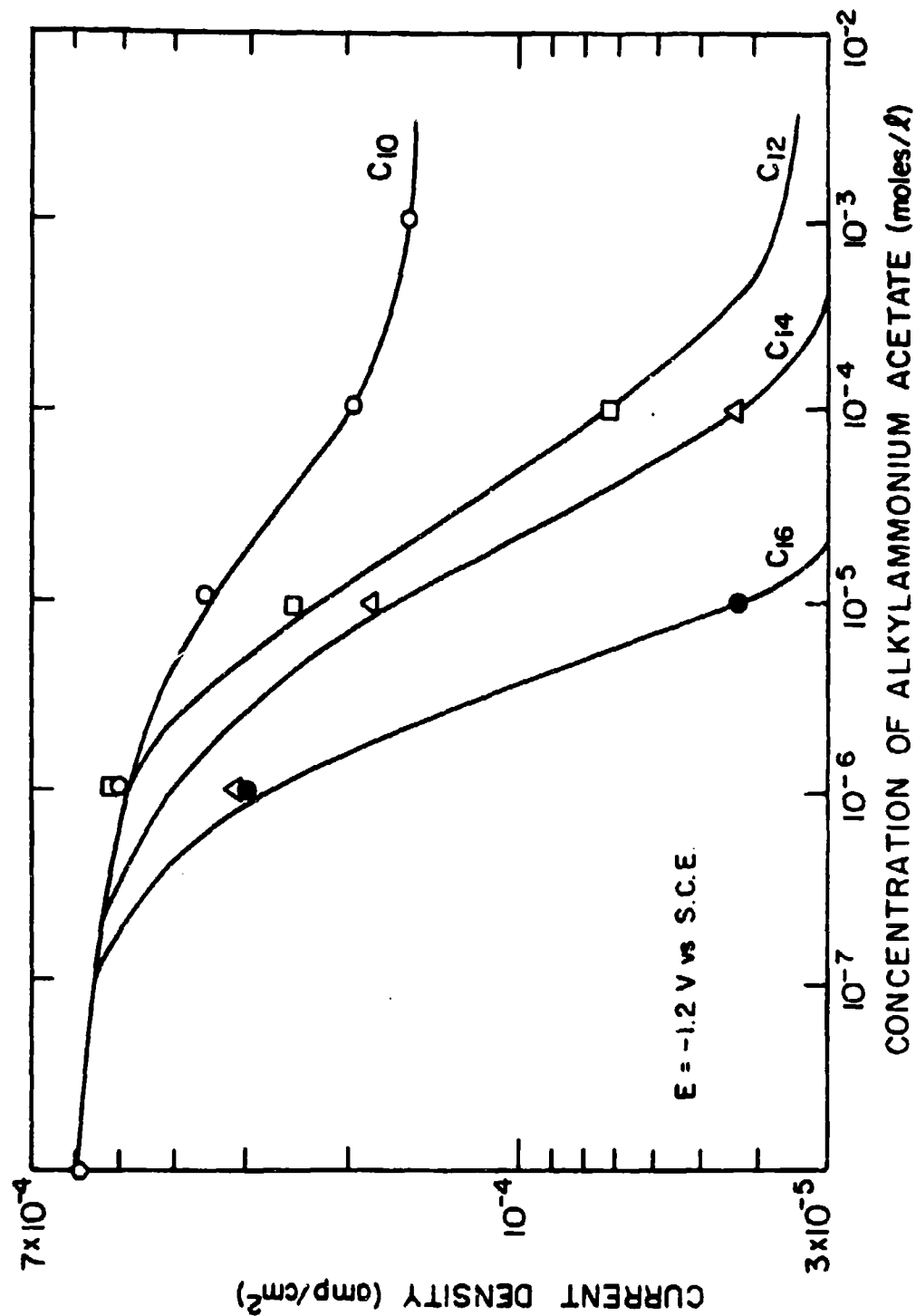


Figure 11. Effect of hydrocarbon chain length on the current density at $E = -1.2 \text{ V vs S.C.E.}$

strong chain length dependence.

The continuing experimental program is designed to test further the application of hemi-micelle theory to the action of surfactants on reducing oxygen transfer to the metal surface. The data of Figure 11 summarize the observed concentration and chain length effects and the similarity to the hemi-micelle phenomenon offers strong qualitative evidence that inhibition of oxygen transfer is due to adsorption processes.

The effect of oxygen content: In the previous sections of this report, the oxygen content was kept constant so that attention could be focused on such variables as speed of rotation and surfactant concentration. However, since O_2 is clearly the species upon which attention must be focused it is necessary to characterize the redox reaction, i.e., oxygen reduction at the electrode surface.

In Figure 12 is shown the effect of variable oxygen content on the polarization curve for a static Monel electrode and one rotating at 1400 RPM. No surfactant was present and the solution was 4% NaCl at $pH\ 6.0 \pm 0.2$ in all cases.

The oxygen diffusion limiting current decreases uniformly in each case with the layer decrease being observed with the rotating system. This is expected in view of the fact that the hypothetical diffusion layer is much thinner in the rotating system and diffusion gradients are much steeper. The relation between O_2 oxygen content in the solution at the limiting current and the limiting current density

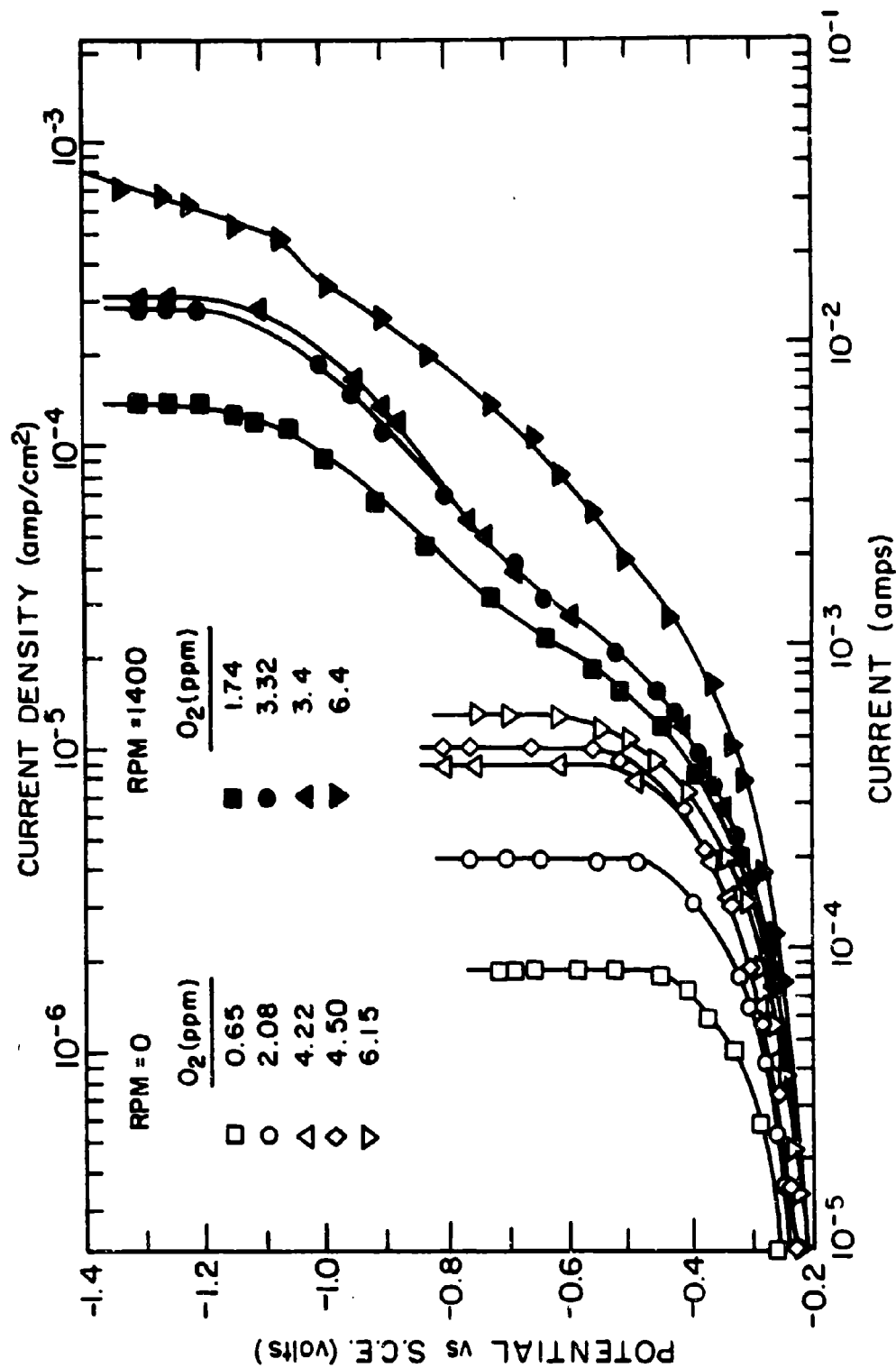


Figure 12. Effect of oxygen content on the limiting current density for a static and rotating Monel cathode in 0.685 NaCl at 20°C.

itself is shown in Figure 13(a) and (b). When the metal cylinder is static no exact relationship can be predicted. However, for turbulent flow case at 1400 RPM the proportionality constant between current density and O_2 content (ppm) of 1.2×10^{-4} of the experimental plot compares very well with that calculated (1.18×10^{-4}) based on the method of Eisenberg, et al. (29).

From these experimental results it can be concluded that the presence of the amine-surfactants in the system is analogous to having lower oxygen contents, as indicated by the shift of the diffusion-limiting currents to lower values in the case of increasing surfactant concentration or decreasing oxygen content.

SUMMARY AND CONCLUSIONS

The galvanostatic polarization technique has been used to detect the specific role of concentration and chain length of amine surfactants in the corrosion reaction at the metal-aqueous solution interface, specifically at the Monel-saline solution interface.

The chain length effect, i. e. increased corrosion inhibition with increased chain length, is considered to be related to hemi-micelle formation or two-dimensional condensation of adsorbed surfactant.

These effects are observed for a rotating system and the deleterious effect of rotation (i. e., the need to increase the cathodic protection) can be offset by selecting a concentration and chain length of surfactant.

In this continuing program, efforts have already begun to

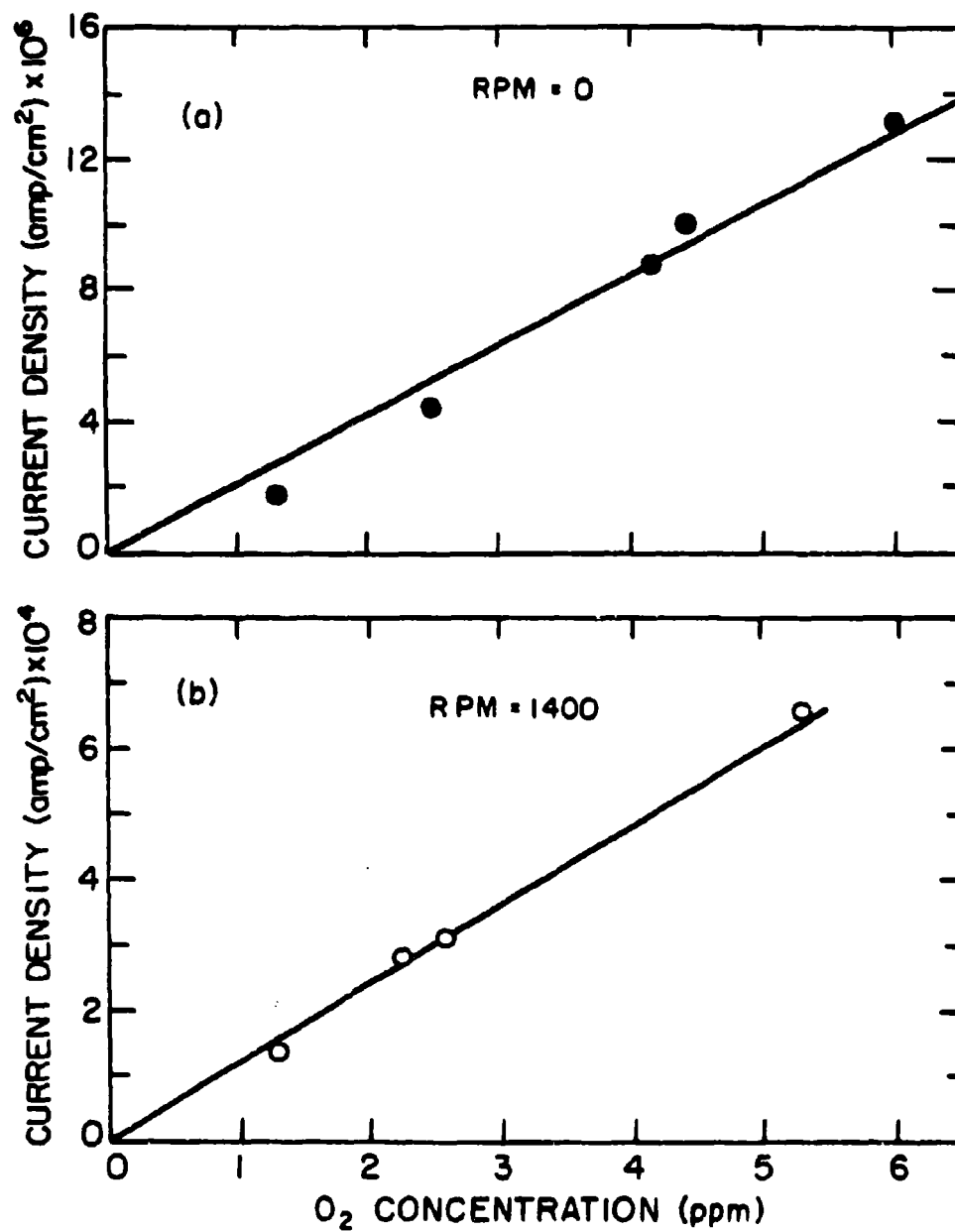


Figure 13a,b. Oxygen concentration vs limiting current density plot.

characterize such effects on rotating electrodes in more reactive systems. Actual adsorption densities will be obtained in order to seek quantitative relationships between corrosion inhibitor efficiency and the structure of the surfactant.

The role of adsorbed surfactant in controlling the oxygen diffusion limiting current will be examined quantitatively so as to relate inhibitor effects to the oxygen reaction in the rotating system. The effect of temperature will also be considered quantitatively so that meaningful assessments can be made of inhibitor efficiency for given conditions of

- (a) oxygen concentration
- (b) temperature of saline solution
- (c) speed of rotation.

Such results should eventually be of application to the problem of the control of corrosion by the use of cathodic protection and corrosion inhibitors in a variety of conditions in the marine environment.

ACKNOWLEDGEMENTS

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APPENDIX I

CALCULATION OF THE LIMITING CURRENT

Diffusion Coefficient, D , for O_2 at $20^\circ C$ = $2.07 \times 10^{-5} \text{ cm}^2 / \text{Sec.}$

Kinematic viscosity, ν , for O_2 at $20^\circ C$ = $10.1 \times 10^{-3} \text{ cm}^2 / \text{Sec.}$

$$\text{Schmidt No.} = \frac{\nu}{D} = 488$$

$$\text{Reynolds No., } Re, = \frac{U \times d}{\nu} = \frac{\pi \times d \times R.P.M.}{60} \times \frac{d}{\nu}$$

where d = characteristic diameter of the cylinder = 1.91 cm

and U = the speed of rotation of the cylinder

$$\begin{aligned} Re &= \frac{\pi d^2 R.P.M.}{60 \nu} \\ &= \frac{3.14 \times (1.91)^2 \times R.P.M.}{10.1 \times 10^{-3} \times 60} \\ &= 18.9 \text{ R.P.M.} \end{aligned}$$

The experimental Sherwood No.,

$$Sh = \frac{i}{A} \times \frac{d}{nF \Delta C \times D}$$

where $\frac{i}{A}$ = current density, $\frac{\text{ampere}}{\text{cm}^2}$

n = number of electrons taking part in the reaction

F = Faraday constant, $\frac{\text{amp. Sec.}}{\text{eqvt. mole}}$

ΔC = concentration gradient

= bulk concentration of reacting species, since at the mass transfer limiting current concentration of reacting species at the surface of the metal is assumed to be zero

D = Diffusion constant for reacting species in $\frac{\text{cm}^2}{\text{Sec.}}$

$$\begin{aligned}
 Sh &= \frac{1 \times 1.91}{45.6 \times 4 \times 98500 \times C_{O_2} \times 2.07 \times 10^{-5}} \\
 &= \left[5.24 \times 10^{-3} \frac{i}{C_{O_2}} \right] \text{amp}^{-1} \text{mole cm}^3 \\
 &= \left[5.24 \times 10^{-3} \times 32 \times 10^6 \frac{i}{C_{O_2}} \right] \text{amp}^{-1} \cdot \text{ppm} \\
 &= \left[1.65 \times 10^5 \frac{i}{C_{O_2}} \right] \text{amp}^{-1} \cdot \text{ppm}
 \end{aligned}$$

The Sherwood No., obtained on the basis of the expression given by Eisenberg, et al

$$\begin{aligned}
 Sh &= 0.079 \times S_c^{0.356} \times Re^{0.7} \\
 &= 5.55 \times \text{R.P.M.}^{0.7}
 \end{aligned}$$

Comparing (1) and (2)

$$\begin{aligned}
 \left[1.65 \times 10^5 \frac{i}{C_{O_2}} \right] \text{amp}^{-1} \times \text{ppm} &= 5.55 \times \text{R.P.M.}^{0.7} \\
 \therefore i &= \left[\frac{5.55}{1.65 \times 10^5} \text{R.P.M.}^{0.7} \times C_{O_2} (\text{ppm}) \right] \text{amp} \\
 &= \left[3.38 \times 10^{-5} \times \text{R.P.M.}^{0.7} \times C_{O_2} (\text{ppm}) \right] \text{amp}
 \end{aligned}$$

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13. ABSTRACT

The galvanostatic polarization technique has been used to detect the specific role of concentration and chain length of amine surfactants in the corrosion reaction at the metal-aqueous solution interface, specifically at the Monel-saline solution interface.

The chain length effect, i.e. increased corrosion inhibition with increased chain length, is considered to be related to hemi-micelle formation or two-dimensional condensation of adsorbed surfactant.

These effects are observed for a rotating system and the deleterious effect of rotation (i.e., the need to increase the cathodic protection) can be offset by selecting a concentration and chain length of surfactant.

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14. KEY WORDS	LINK A		LINK B		LINK C	
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