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POLAROGRAPHIC DETERMINATION OF MICELLAR DIFFUSION COEFFICIENTS

by

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ABSTRACT

ADVISOR: DR. HORST W. HOYER

A polarographic method for the determination of micellar diffusion coefficients was developed and the diffusion coefficients of the sodium decyl sulfate, sodium dodecyl sulfate and the sodium tetradecyl sulfate micelles were determined. In order to determine its diffusion coefficient, the micelle must be specifically tagged with an electro-reducible species.

Two methods were used for tagging: Solubilization within the micelle of a water insoluble divalent metal soap and divalent cation tagging of the micelle surface. Cadmium was chosen as the tagging metal ion since its reduction wave is in an area which was free from any interfering surfactant waves.

The diffusion current obtained from the tagged surfactant solutions were compared with the current obtained from an ionic solution of cadmium whose concentration corresponds to the cadmium concentration in the surfactant solution. This ratio is related to the diffusion coefficients of the species by the Ilkovic equation. Correction factors for the spherical nature of the mercury drop and for the differences in drop times have been included:

$$(i_{dm}/i_d) \mathrm{x} D \mathrm{x}\ 1.14 = D_m$$

Of the two tagging methods used, doubts were cast on data obtained from the solubilization method since a salt effect on the cadmium soap was observed.

With the divalent cation tagging method, a known concentration of cadmium ions were added to the surfactant solutions. The solutions were run polarographically and the diffusion coefficients calculated. For the sodium decyl sulfate, sodium dodecyl sulfate and sodium tetradecyl sulfate micelles values of $1.66 \times 10^{-6} cm^2/sec$, $0.87 \times 10^{-6} cm^2/sec$ and $0.46 \times 10^{-6} cm^2/sec$, respectively, were obtained as the micellar diffusion coefficients.

The interactions between the cadmium and the micelle were investigated by doing a monolayer study of the interaction of cadmium ions on a spread long chain sodium sulfate ($NaC_{20}SO_4$). It was found that the cadmium ions were probably concentrated in the surface region and that no strong interaction between the cadmium ions and the monolayer was indicated. The activity of a constant amount of cadmium ions in a varying amount of sodium dodecyl sulfate was measured with a cadmium specific ion electrode. There was a large drop in the cadmium ion activity as the surfactant concentration increased indicating that the cadmium ion was adsorbed on the micelle surface. The lack of any precipitation as the cadmium and surfactant concentrations were increased indicates that there is no strong interaction between the cadmium ion and the surfactant.

Thus, since there is no strong interaction between the cadmium ion and the surfactant and that the cadmium ion is on the surface of the micelle, the polarographic method for the determination of micellar diffusion coefficients is valid.

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Key:
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○ – on 8.5 x 10^{-3}M NaOH substrate
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General Introduction to the Problem

Knowledge of the size and shape of macromolecular and colloidal particles allows one to predict many of their physical properties. The measured diffusion coefficients of these moieties will give some insight into their actual physical dimensions. Standard methods for the measurement of diffusion coefficients are rather involved, both technically and theoretically; especially when micellar species are involved.

The problem at hand was to find a method for the rapid determination of micellar diffusion coefficients. The polarographic method is one in which diffusion coefficients can be determined rapidly. The adaption of this technique to the determination of the diffusion coefficients of sodium alkyl sulfate micelles was accomplished. Specific procedures and techniques were developed for this method and used with success. The following is a report on the development of this technique and on the results obtained with it.

CHAPTER I:

Background

Molecules having a hydrocarbon (hydrophobic) tail with an ionic or polar head (hydrophilic) will tend to concentrate at an interface. These amphipatic compounds show sharp changes in the physical properties of their solutions above a certain concentration. Above this concentration, commonly called the critical micelle concentration or cmc, an increase in surfactant concentration leads to the formation of large stable aggregates which, as first named by Von Nageli (1), are called "micelles".

The physical properties of solutions of surface active materials change at the critical micelle concentration. These physical properties include measurements of equivalent conductivity (2,3), high frequency conductivity (4), dye solubilization (2), surface tension (5), osmotic pressure (6), light scattering (2), detergency (7) and density (8). (See figure 1) The leveling off of the osmotic pressure suggests that a phase separation is occurring although no apparent or gross phase separation is noted (9). The sharp increase in light scattering above the cmc indicates the formation of a colloidal species (9,2) as does the sudden increase in the concentration of a water-insoluble dye (2), solubilized by the detergent solution. The leveling off of detergency and surface tension is indicative of the saturation of the solution with alkyl sulfate anions (7) with any additional anions going into micelle formation. A decrease in the equivalent conductivity of the surfactant solution above the cmc is due to the kinetic adsorption of the counterions onto the micellar surface due to its high surface charge; hence reducing the number of counterions available to carry the current and lowering the net charge on the micelle. Also the retardation effect (braking effect) of the ionic atmospheres of the unattached counterions on the micellar migration explains this phenomenon (10,11).

A) Micellar Physical Properties

The physical properties of micelles has long been a subject of investigation. Techniques used to investigate the properties of macromolecules have been used to elucidate the structure of micelles since they are colloidal in nature. A brief discussion of several of these techniques and results obtained from them will follow.

The physical structure of a micelle has been a matter of discussion and dispute by many authors for a number of years. Hartley (12) postulated that the simplest possible micelle in dilute solution is roughly spherical in shape, two ion lengths in diameter. These would be composed of the long chain ions so that the polar heads are outward in contact with the water and their long chains forming a hydrocarbon interior. The micelle would be surrounded by a Coulomb cloud of gegenions in a variable number. McBain (13) believed that there are two types of micelles: a small ionic micelle at low concentrations similar to the one just mentioned, and a large neutral or lamellar type (see figure 2) in which the polar heads line up with polar heads and the hydrocarbon tails align with the hydrocarbon tails. McBain (14) and Harkins et al (15) using X-ray diffraction showed that at high soap concentrations a lamellar structure was found. Corrin (16) by calculating the angular variation in intensity of the scattered X-ray radiation, assuming a spherical micelle, obtained qualitative agreement with observed scattering curves while Harkins (17) stated that a cylindrical model of the micelle at high surfactant concentration is more appropriate. Brady (18) using Fourier analysis of an X-ray diffraction pattern of sodium dodecyl sulfate concluded that the spherical model of the micelle was most compatible with his data. Reiss-Husson et al (19) using absolute small angle X-ray scattering concluded that for sodium dodecyl sulfate the micelle is spherical at low concentrations and is transformed into rod-like micelles at higher concentrations. The rod-like model seems to be consistent with Harkins' (17) cylindrical model. Although the spherical form is the generally accepted shape of the micelle (9), any shape is actually possible since it is a finely despersed second phase.

Measurements of the amount of light scattered by solutions of association colloids provide information about the weight of and charges on the micelle. Debye (20,21) derived an expression which related the turbidity, t, of the solution of macromolecules to its molecular weight, M:

$$HC/t = 1/M + 2Bc \qquad (1)$$

where c is the concentration, B is a constant which is a measure of the deviation from ideality in the van't Hoff osmotic pressure law and

$$H = \frac{32\pi^3}{3} \cdot \frac{n_o^2}{N\lambda^4} \left(\frac{n - n_o}{c}\right)^2 \qquad (2)$$

where N is Avogadro's number, λ is the wavelength of the incident light and n and n_o are the refractive indices of the solution and solvent, respectively. If Hc/t is plotted against c, the intercept at the y-axis when c equals zero is 1/M.

When dealing with micellar solutions there is a slight modification of equation 1. Since it is assumed that there are no micelles below the cmc, the c term is then modified to become (c - cmc) (21), which is representative of the concentration of micelles. Below the cmc the light scattered is independent of the surfactant concentration (22) so that the t term is modified to become $(t - t_o)$, where t_o is the turbidity below the cmc.

Edsall et al (23) showed that the charge of colloidal electrolytes can be calculated from the slope B of the Hc/t vs c curve. Assuming ideal behavior (activity coefficient = 1) for all species the simplified expression for the effective charge, p, was derived (22):

$$P = M\sqrt{Bx} \quad (3)$$

where B is the slope at infinite dilution of the colloidal ion (the cmc for micellar solutions) and x is the concentration of the simple salt at that point (added salt if any plus the cmc).

Mysels and coworkers (22,24) did light scattering measurements on sodium dodecylsulfate solutions. In the earlier paper (22) they obtained a molecular weight of 23,000 with an aggregate number of 80 monomers/micelle with an effective charge of 14.5 electrons/micelle for sodium dodecyl sulfate in water only. In the later paper (24) they modified their light scattering technique and obtained the following: an aggregate number of 62 monomers/micelle and an effective charge of 1 04 electrons per micelle. The value of the molecular weight is that of the unhydrated micelle (25); in other work the micelle is assumed to have a hydration thickness of 1.5A (25).

The use of sedimentation methods to determine physical properties of macromolecules is well documented. The Svedberg (26) did much to advance the field of ultracentrifugation which is a method of producing accelerations up to 300,000 g's. If a particle of mass m falls in a medium of density ρ, then the gravitational force on the particle is $m(1 - \bar{v}\rho)g$, where v is the partial specific volume of the particle. If the velocity of sedimentation is dx/dt, then f(dx/dt) is the friction force where f is the frictional coefficient. Thus at the terminal velocity:

$$f(dx/dt) = (1 - \bar{v}\rho)mg \qquad (4)$$

In a centrifugal field of force, g is replaced by w^2x where w is the angular velocity and x is the distance from the center of rotation. Thus:

$$f(dx/dt) = (1 - \bar{v}\rho)mw^2x \qquad (5)$$

If s, the sedimentation constant, is substituted for $(dx/dt)/w^2x$, then:

$$S = (1 - \bar{v}\rho)/f \qquad (5a)$$

If the sedimentation frictional coefficient is the same as the diffusion frictional coefficient then the Stokes' Einstein equation (see next section) can be substituted, thus:

$$M = RTs/D(1 - \bar{v}\rho) \qquad (6)$$

where M is the molecular weight.

Granath (27) used sedimentation techniques to determine the molecular weights of sodium dodecyl sulfate micelles in the presence of various electrolytes. Also from his sedimentation data, frictional ratios (see next section) for the sodium dodecyl sulfate micelle were calculated.

Electrophoresis, the movement of a charged particle in an electric field, has been used to determine the size, charge and shape of a micelle. The electrophoretic velocity, as a first approximation (28) is:

$$v = E_{app}D_o\zeta / 4\pi\eta_o \qquad (7)$$

where E_{app} is the applied potential, D_o is the dielectric constant of the solvent, ζ is the zeta potential and η_o is the viscosity of the solvent. From the electrophoretic mobility (v/E_{app}) of the micelle and the zeta potential, Stigter and Mysels (29) using a tracer electrophoresis technique suggested by Hoyer (30) determined the micellar charge and degree of ionization for sodium dodecyl sulfate in water and various NaCl solutions. It was found that 28.7% of the counterions move freely. This agrees with Mysels and Dulin (31) who by measuring transport numbers showed 28% of the counterions move independently. Botre' et al (96) and Feinstein et al (98) found, by using electromotive force measurements of sodium ions, a degree of dissociation of cations (sodium ions) from the $NaDDSO_4$ micelle to be 16% and 14%, respectively, while Shedlovsky et al (97), also using emf measurements of sodium ion, found it to be 22%.

From these data, Stigter and Mysels (29) concluded that the micelle surface is not likely to be a smooth one. It is believed that the heads rise above the surface so as to expose the whole polar area to the water. The smaller sodium ions will then be able to penetrate into the surface. This roughness of the micelle may explain its relatively low degree of ionization (29).

In summarizing, the sodium dodecyl sulfate micelle in water, at room temperature, at low concentration is roughly spherical being transformed into a rod-like structure at higher concentrations. Its molecular weight is somewhere between 18,000 - 23,000 with an aggregate number between 60 - 80 monomers/micelle. The degree of ionization is somewhere between 15 - 28% with an effective charge of 10 - 15 electrons/-micelle. The surface of the micelle is rough, with some of the polar heads above the surface.

B) Diffusion Coefficients

1) Fick's Laws

Diffusion is defined as the directed movement of a substance under the influences of forces that arise from differences in the concentration of the substance in various parts of the medium. The direction of diffusion is from regions of higher to lower concentrations (or chemical potential) and its rate is proportional to the magnitude of the concentration difference and to certain characteristic properties of the diffusing substance and the medium.

The diffusion of a substance in one direction, called linear diffusion, is the simplest type. If one considers a cylinder (figure 3) in which the diffusion is proceeding in an upward direction (+x direction), the number of moles of a substance that diffuse across a given cross-section, A cm^2, in an infinitesimal interval of time, dt, is proportional to the concentration gradient, dc/dx, at the plane in question and is expressed as:

$$dN = -DA\,(\partial c/\partial x)dt \qquad (8)$$

where D is a constant of proportionality called the "diffusion coefficient". This relationship was first recognized by Fick (32). D has the units of $length^2/time$, and is the number of moles of substance that diffuses across the unit area in unit time across a unit concentration gradient. Fick's first law is usually expressed as a flux which is the number of moles of substance which flow through a unit area in a given time:

$$f_{x,t} = dN/Adt = -D(\partial c/\partial x) \qquad (9)$$

In order to calculate the total amount of material that diffuses across a given plane in a finite time interval, one must have a knowledge of the change in concentration with time at the plane in question. The change in concentration with time between two planes separated by a distance of dx is equal to the difference between the number of moles entering at plane x and the number leaving at plane x+dx, divided by the volume, Adx, enclosed between the planes:

$$dc/dt = \left[(dN/dt)_x - (dN/dt)_{x+dx}\right] /Adx \tag{10}$$

or:

$$dc/dt = (f_x - f_{x+dx})/dx \tag{10a}$$

but

$$f_{x+dx} = f_x + (\partial f_x/\partial x)dx \tag{11}$$

From equation 9:

$$\partial f_x/\partial x = -D\partial^2 c/\partial x^2 \tag{12}$$

From the above equation the fundamental differential equation for linear diffusion, or Fick's Second Law, is obtained:

$$\partial c/\partial t = D\partial^2 c/\partial x^2 \tag{13}$$

In order to obtain an expression for c as a function of x and t, it is necessary to integrate the above equation. In the integration it is necessary to specify initial and boundary conditions; that is, the concentration at the plane in question at time zero, the method of establishing the diffusion layer, and the restrictions imposed by the geometry of the diffusion field.

The general diffusion equation may be integrated to yield the following equation:

$$c = (c_o/2)\left(1 - \frac{2}{\sqrt{\pi}} \int_0^y e^{-y^2} dy\right) \tag{14}$$

where

$$y = x/2\sqrt{Dt} \tag{15}$$

and c is the concentration at time t and distance x from the original boundary using the following boundary conditions:

at t = 0, for $x > 0$, $c = 0$

$x < 0$, $c = c_o$, where c_o is the initial concentration, and the following assumptions are made: 1) the diffusion coefficient is independent of concentration and 2) there are no cell effects (11). Typical solutions for equation 14 at different t values are shown in figure 4 where a value of D equal to 2.5 x 10^{-7}cm^2/sec is used. A more convenient form of equation 14 is the completely integrated one:

$$c/c_o = \left(\tfrac{1}{2}(Dt)^{-\frac{1}{2}}\right) \exp(-x^2/4Dt) \qquad (33) \quad (16)$$

If ln c versus x^2 is plotted, the slope of the curve is $-1/4Dt$ from which the diffusion coefficient can be calculated.

2) Determination of Physical Properties from Diffusion Coefficients

In the determination of the physical parameters of colloidal particles, a simple geometric model (sphere, ellipsoid or rod) must be assumed in order to apply a hydrodynamic treatment to the particles. Also, it must be assumed that the particles are free to carry out their appropriate motions independently without interacting with like particles; that is, the solutions are sufficiently dilute, and the particle size is much larger than that of the solvent so that the only retarding forces are frictional. Stokes (34) by using the above assumptions and by also assuming that the layer of solvent adjacent to the particle moves with the particle, derived an expression for the frictional coefficient, f, of a spherical particle: $f = 6\pi\eta r$ (17) where η is the viscosity coefficient of the solvent and r is the radius of the particle.

The relationship between the frictional coefficient and the diffusion coefficient of a particle, derived by Einstein (35) in 1905, is:

$D = RT/Nf$ (18), where N is Avogadro's number.

If one assumes that the particles are spherical, then the general frictional coefficient in Einstein's equation becomes identical with Stokes' frictional coefficient and equation 17 and equation 18 can be combined. Thus a relationship between the diffusion coefficient and an equivalent spherical radius is established:

$$D = RT/6\pi\eta Nr \qquad (19)$$

If one is dealing with large spherical molecules which do not polymerize in solution, or undergo solvation, and whose molar volume in solution is the same as in the pure state, the radius can be computed from the molecular weight, M, and the density, d, of the substance in the pure state by:

$$M = (4/3)\pi r^3 Nd \qquad (20)$$

By substituting for r in equation 19, the following relationship is obtained for the diffusion coefficient of a hypothetical unsolvated spherical particle of the same molecular weight and density as that being investigated:

$$D_o = RT(4\pi Nd)^{1/3} / 6\pi\eta N(3M)^{1/3} \qquad (21)$$

The deviation from the "ideal" spherical unsolvated particle is measured as the frictional ratio (11):

$$f/f_o = D_o/D \qquad (22)$$

The two main reasons for D_o/D to be greater than unity are 1) the occurrence of solvation of the particle and 2) the deviation of the particle shape from that of a sphere. Oncley (36) suggested that the frictional ratio could be separated into solvation and asymmetry factors by the following equation:

$$f/f_o = (f/f_e)(f_e/f_o) = (D_e/D)(D_o/D_e) \qquad (23)$$

where f/f_o is the increase in the frictional ratio due to solvation of the particle and f_e/f_o is the effect due to the asymmetry of the particle. Kraemer (37) derived an expression for the frictional factor due to only solvation by assuming the solvating liquid to have the same density as the bulk liquid:

$$f/f_e = D_e D = (1 + w/\bar{v}\rho)^{1/3} \qquad (24)$$

where w is the weight of solvent whose density is ρ solvating one gram of pure solute of partial molar volume $\bar{V}$.

Herzog et al (38) and Perrin (39) deduced an expression relating the asymmetrical frictional factor to the axial ratio of an ellipsoid of rotation. Perrin's relationships are:

for prolate ellipsoids: $(b/a < 1)$

$$f_e/f_o = D_o/D_e = (1-b^2/a^2)^{\frac{1}{2}}/(b/a)^{2/3}\ln(1+(1-b^2/a^2)^{\frac{1}{2}}/(b/a)) \qquad (25)$$

for oblate ellipsoids: $(b/a > 1)$

$$f_e/f_o = D_o/D_e = (b^2/a^2-1)^{\frac{1}{2}}(b/a)^{2/3}\tan^{-1}\left(\frac{b^2}{a^2} - 1\right)^{\frac{1}{2}} \qquad (26)$$

Thus, a knowledge of the diffusion coefficients of a particle allows for the calculation of various molecular parameters of the particle. Size and shape are parameters which permit one to predict various physical properties of macromolecules.

3) Methods of Determining the Diffusion Coefficient

In spite of the fundamental importance of the diffusion coefficient in determinining the physical properties of colloidal electrolytes, only a limited number of values have been reported. The difficulties inherent in the usual experimental methods in the determination of diffusion coefficients seems to account for this lack of micellar diffusion data. A brief description of some of the standard diffusion measurement techniques and their application to micellar diffusion will be given.

a) Interference Method

Longsworth (40) studied the diffusion of various salts by observing the spreading of a boundary using an interference method. When light passes through a boundary separating two solutions, the rays are deflected by the gradients of refractive index.

The image of the illuminated horizontal slit, s, is thus spread over a rectangular area in the focal plane, P. (See figure 5) The upper edge of the area is formed by the light that passes, without deflection, through the homogeneous layers of solvent and solution that are above and below the boundary, respectively. The lower edge of this area is formed by light that undergoes a maximum deflection in the boundary. As the diffusion proceeds, the boundary becomes more diffuse and the area in the image plane contracts upward. At any instant one sees an interference pattern which is qualitatively described by Gouy (41) and quantitatively by Kegeles and Gosting (42). Longsworth used both a Tiselius and Lamm cell to hold the diffusing materials. In the Tiselius cell an initial sharp boundary between the solution and solvent was formed by a shearing mechanism. This cell was not good optically since it distorted the slit image with respect to its length (40).

In the Lamm cell the boundary was formed by removal of a partition between the solution and the solvent. The cell, although optically good, always left the possibility of leakage from the partition (40).

Using the distance of the interference line from the image of the slit, the number of interference fringes and various cell constants to obtain a numerical constant, C_t, and a path difference parameter, j_m, the diffusion coefficient is calculated from:

$$D = j_m^2 \lambda^2 b^2 / 4 \pi C_t t \qquad (27)$$

where λ is the wavelength of light, b is the optical distance from the center of the cell to the photographic plant and t is the run time. In this method a zero time correction is necessary since there is an initial mixing of the solution and solvent and this causes the concentration distribution at any instant to appear as though the boundary had formed at a time before it actually formed.

Using the above method, Brudney and Saunders (43) determined the integral diffusion coefficient for sodium cholate and potassium decanoate and other colloidal systems. The integral diffusion coefficient is applied to a value of D found by allowing a solution to diffuse into pure water. The same authors also determined the diffusion coefficients for potassium laurate below and above the cmc (44) which they found drops off sharply after the cmc and then goes through a minimum (although not found by others) at some concentration above the cmc. Parker and Wasik (45) also using the interference method in conjunction with an IBM 704 computer determined the diffusion coefficients of dodecyl trimethyl ammonium chloride below and above the cmc. They also found that the diffusion coefficient decreases sharply at the cmc in a step type of function.

b) Scale Method

Lamm (46) developed an optical method of following diffusion called the scale method. A uniformly illuminated transparent scale is placed behind the observation cell and the image of the scale is focused on a ground glass or photographic plate. If the cell contains a homogeneous fluid, then an undistorted image of the scale is obtained. If there is a liquid boundary in the cell in which there is a change in refractive index, part of the image of the scale is displaced. By measuring this displacement one is able to calculate diffusion information.

Lamm (47) used this method to determine diffusion coefficients for the potassium salts of lauric and myristic acids in an alkaline medium. Granath, using the scale method also determined diffusion coefficients for potassium laurate and myristate (48) and determined micellar diffusion coefficients for potassium oleate, sodium dodecyl sulfate and cetyl trimethyl ammonium bromide (27).

c) Open End Capillary Method

Another method of determining diffusion coefficients was developed by Anderson and Saddington (49) and Wang (50). In this method, fine uniform capillaries which are filled with a radioactive tracer solution, are held in a vertical position in a large circulating bath of non-radioactive solution (see figure 6). The primary assumption in this general method is that the mass difference between the radioactive tracers and the non-radioactive species will not affect the diffusion coefficient to any large extent, or in other words, the tracer atoms behave exactly the same way as the non-radioactive atoms. If a self-diffusion coefficient is to be determined, then the non-active solution is to be at the same concentration as the tracer solution. The tracer is allowed to diffuse upward, and the concentration of tracer at the open end of the capillaries is kept essentially at zero by stirring the non-active solution. In this case the diffusion is essentially one dimensional and linear so that Fick's second law (equation 13) is followed: The solution to this differential equation becomes (50):

$$c/c_o = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left[-(2n+1)^2\pi^2 Dt/4l^2\right] \cos\left[\frac{(2n+1)nx}{2l}\right] \tag{28}$$

where c_o is the initial concentration of tracer, l is the length of the capillaries and t is the time of the run. In order to facilitate the calculations Wang (50) derived an expression for the average tracer concentration in the capillary:

$$c_{av}/c_o = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-(2n+1)^2\pi^2 Dt/4l^2\right] \tag{29}$$

and then chose values of Dt/l^2 and calculated c_{av}/c_o. A general working curve of c_{av}/c_o vs Dt/l^2 was drawn.

Kolp et al (51) and Courchene (52) used the capillary method to determine the diffusion coefficients of dodecylbenzene sulfonate, dimethyldodecyl amine oxide and a mixture of the two. S^{35} (51,52) and C^{14} (51) were used as tracers. It was also found that the diffusion coefficient is independent of concentration below the cmc and above the cmc it dropped off rapidly, at first and then more and more gradually with increasing concentration.

The diffusion coefficient of a micelle can be determined directly by tagging the micelle with a trace amount of radioactive material that is completely solubilized by it. Lauryl alcohol, tagged with C^{14}, at a level of 10 ppm, was used (51). It was found that this amount of tagging agent left the micellar structure unaffected.

d) Porous Barrier Method

Another general method for diffusion coefficient determination is where the species diffuse through a porous barrier. This method was originally developed by Northrop and Anson (53) and further refined by McBain and Liu (54). This method consists in separating two homogeneous bldies of solution by an indifferent membrane with pores of a visible or microscopic size; thus confining the diffusion gradient to within the membrane (see figure 7).

The material whose diffusion coefficient is to be determined is placed in the cell. Prior to the actual determination, a "steady diffusion column" (54) is established in the membrane. The cell is then placed into a tight fitting beaker and the experiment begins.

Since the diffusion gradient is linear within the membrane, Fick's second law is applicable. Solving the differential equation, McBain et al (54) arrived at the following:

$$Kdt_E = \log c - \log(c_o - 2c) \qquad (30)$$

where K is the cell constant, t_E is the elapsed time and c is the concentration in the beaker. By using a material whose diffusion coefficient is known the cell constant is determined and all values of D are expressed in absolute values.

Using a porous membrane cell McBain and coworkers studied the diffusion of potassium laurate (54), sodium oleate (55), and some sulfonic acids (56, 57). It was found that as the concentration of the soap increased, the diffusion coefficient dropped off sharply after the cmc and then leveled off. Hartley and Runnicles (58) did diffusion measurements on cetyl pyridinium chloride with swamping electrolyte as did Abbot and Tartar (57) on dodecanesulfonic acid. Dean et al (59) used this method to study the diffusion of Aerosol OT micelles tagged with a water insoluble dye, Orange OT.

A method which was specifically for the measurement of diffusion coefficients of macromolecular tracer systems was developed by Mysels and Stigter (60). The tracer and tracerless solutions are immobilized in two fritted glass discs (see figure 8). The discs are clamped together and submerged in mercury to prevent evaporation during the proceedings. After some time they are separated and the amount of tracer in each disc is determined, usually by spectrophotometric methods. Working curves relating the ratio of transport across the plane of separation to $(t_1)^{\frac{1}{2}}$ allows the unknown diffusion coefficient to be determined from:

$$t_1 D_1 = t_2 D_2 \qquad (31)$$

where D_1 is the known diffusion coefficient, and t_2 is the time of the run.

Stigter et al (25) used this method to determine the self-diffusion coefficient for sodium dodecyl sulfate micelles. The diffusion coefficient was found to decrease sharply at the cmc and decrease less sharply as the surfactant concentration is increased.

The previously mentioned methods have several major drawbacks which leave them unfeasible for the rapid determination of micellar diffusion coefficients. They are all experimentally tedious, in that they are time consuming and involve elaborate set-ups and techniques. Calculation of the diffusion coefficients is usually complex with the actual data measurements being difficult.

In the following chapter, a polarographic method for the determination of micellar diffusion coefficients has been developed. This method is experimentally simpler and far less involved in the calculation of the diffusion coefficients.

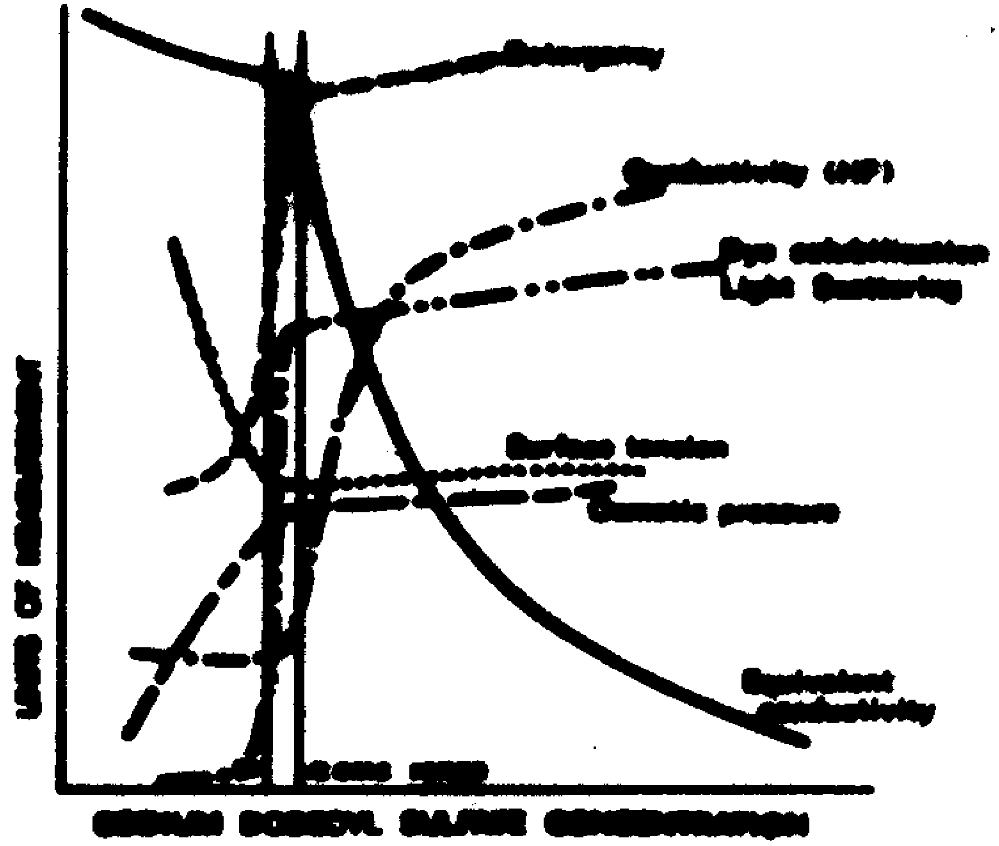


Figure 1

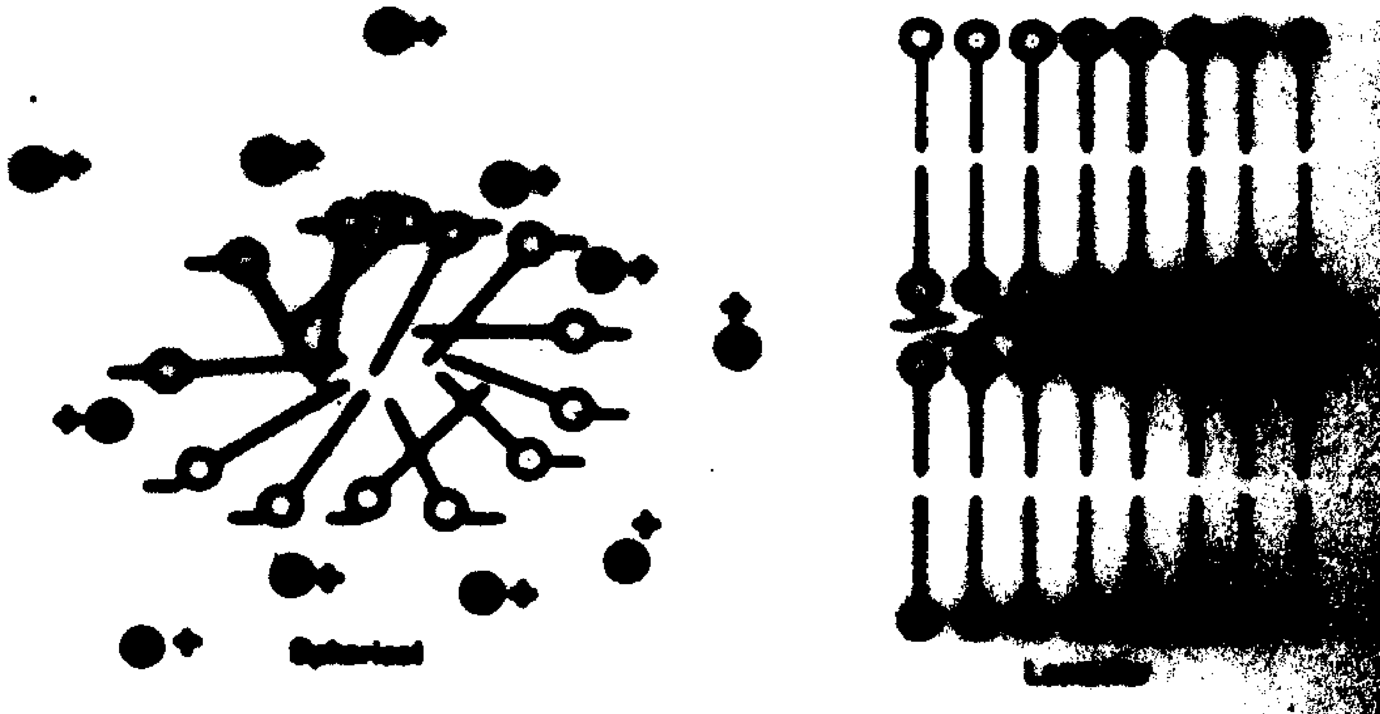


Figure 2

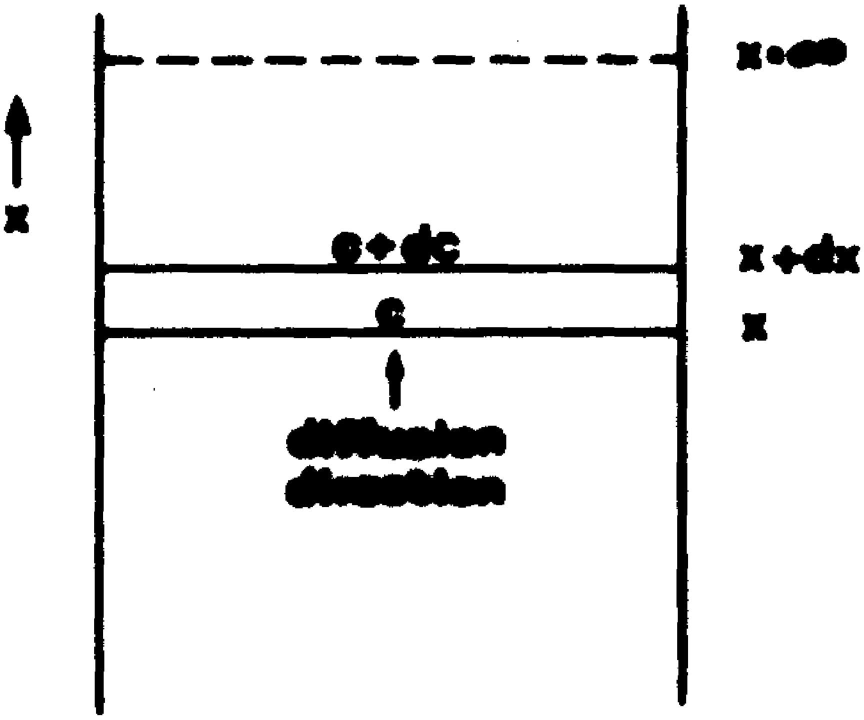


Figure 3

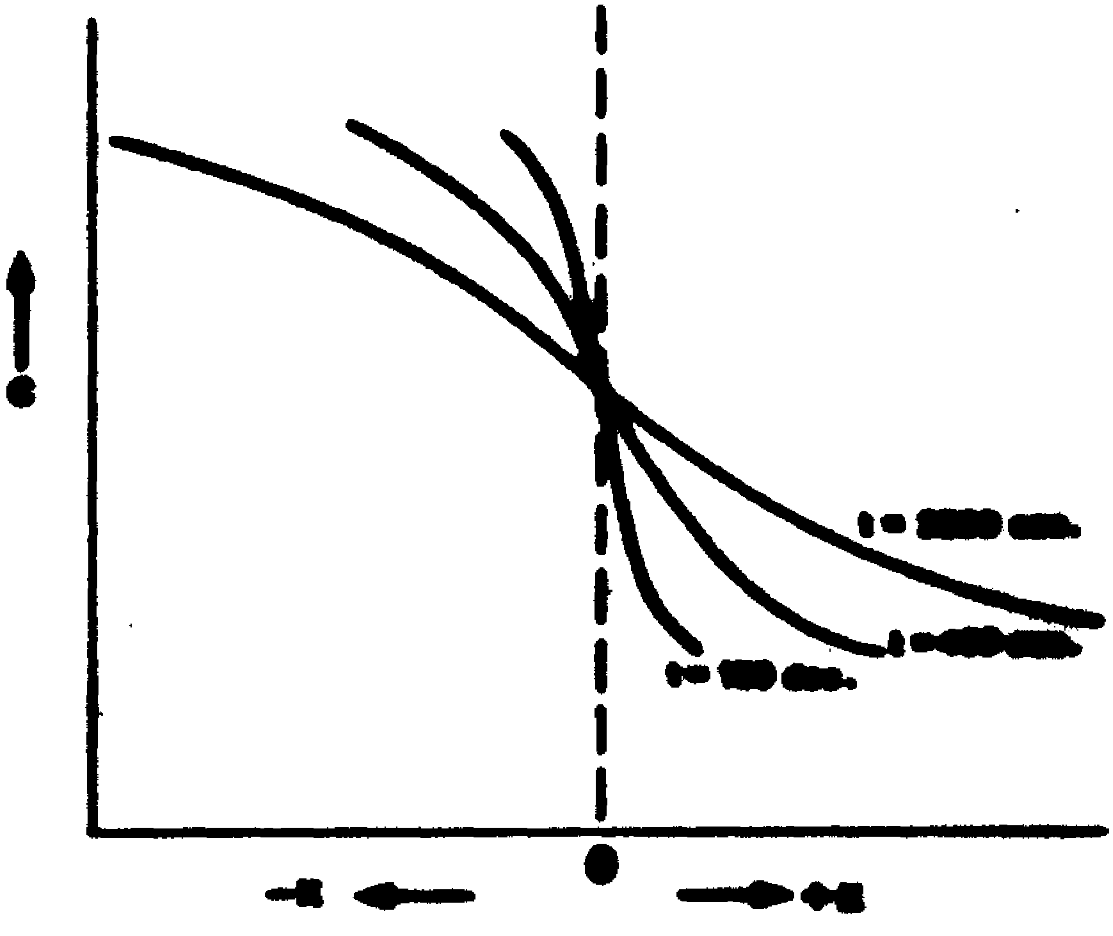


Figure 4

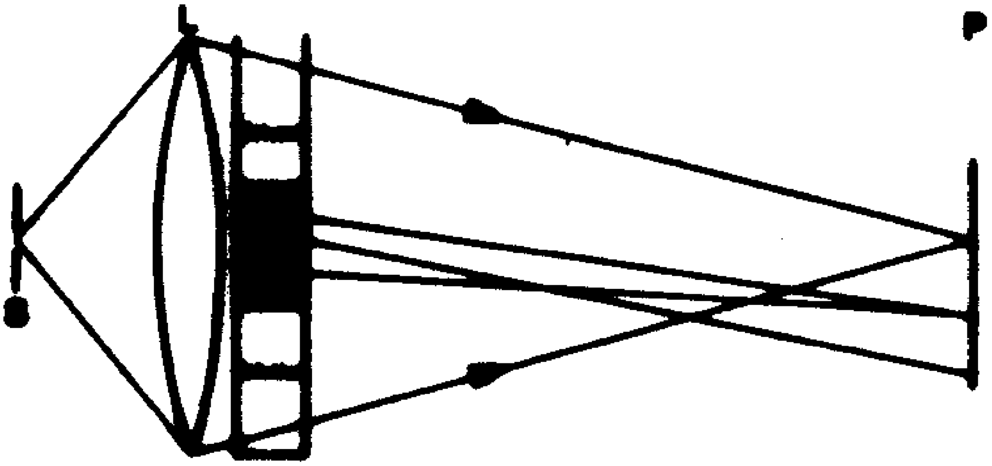


Figure 5

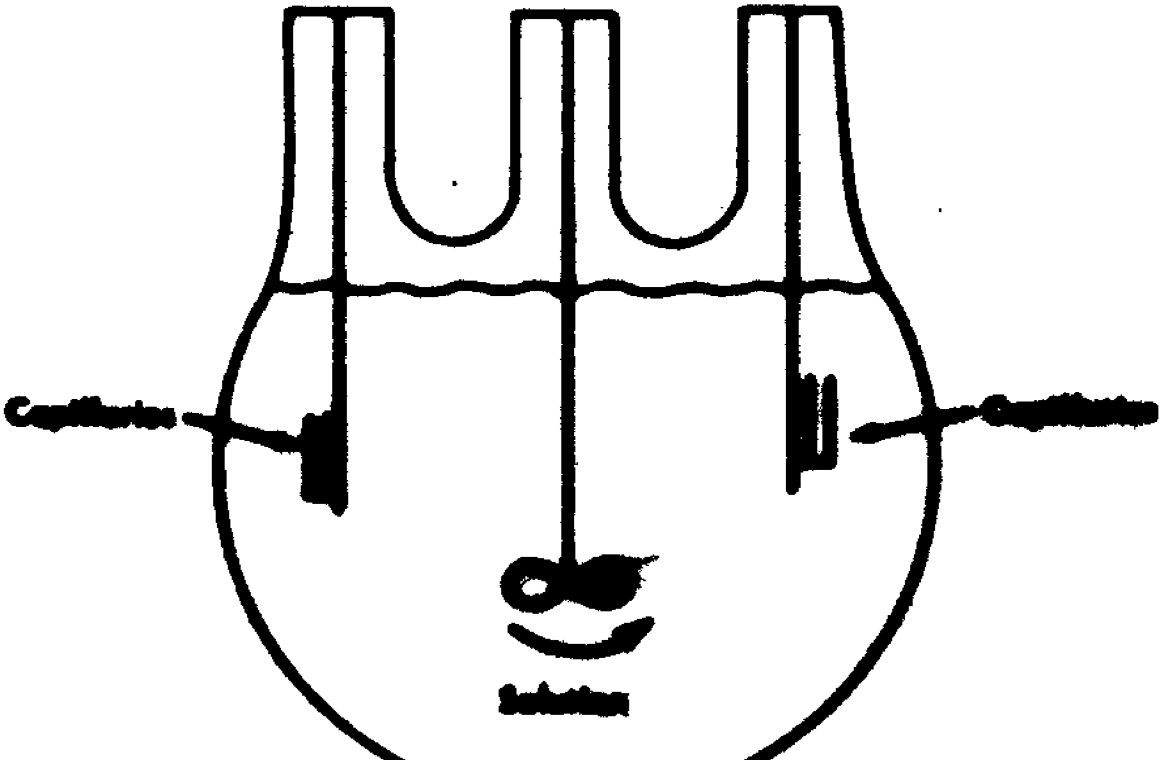


Figure 6

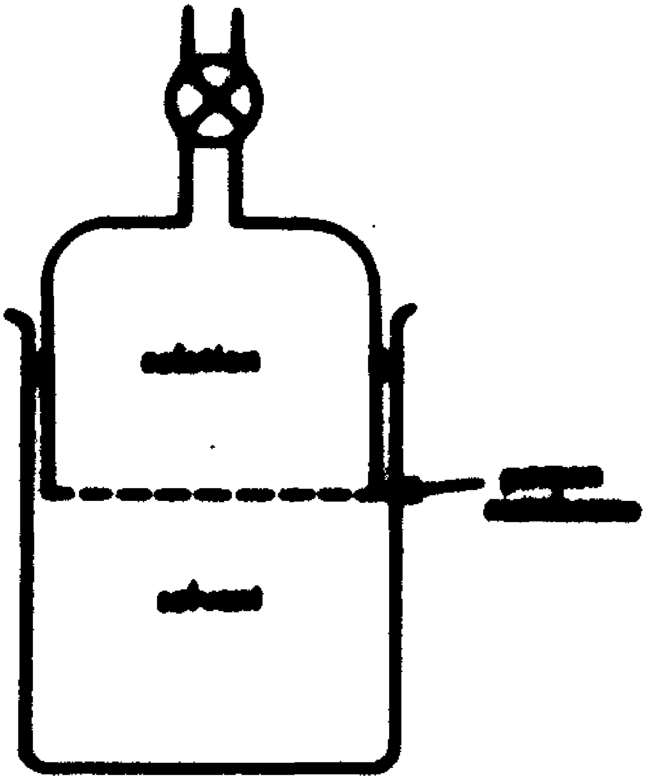


Figure 7

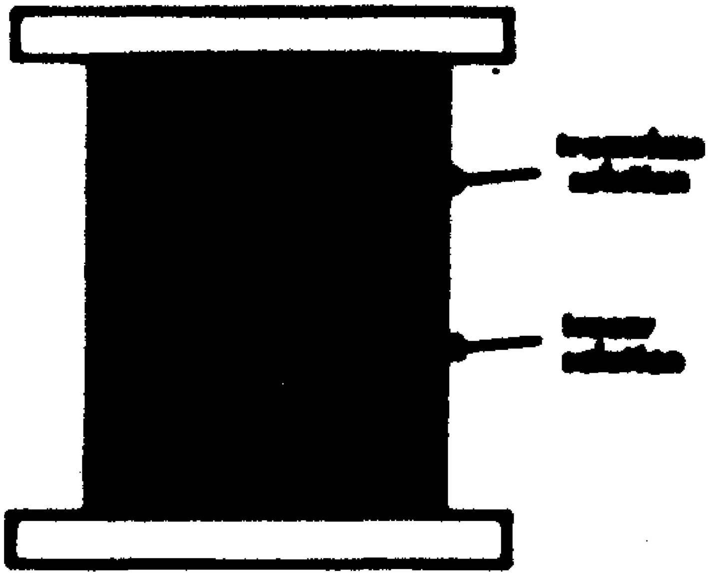


Figure 8

CHAPTER II:

Polarography

A) Theory and Conventional Experiment

The polarographic method of analysis invented by Heyrovsky (61) is based on the characteristics of the current voltage curves obtained when solutions of electroactive materials are electrolyzed at a dropping mercury electrode (DME). The rate of discharge of ions, which is measured as a current, is controlled by the diffusion of the electroactive species to the electrode. The polarograph invented by Heyrovsky and Shikata (62) is an instrument which automatically records the current-voltage curves obtained with the DME.

When a micro-electrode (platinum or some other metal) is placed into a solution of an electroactive species and an EMF is imposed on the electrode so as to equal or to exceed the decomposition potential of the electroactive species, a current will begin to flow due to the deposition of the species. As the electrolysis proceeds and the solution is left unstirred, the area immediately surrounding the electrode will become depleted in this electroactive species and its concentration will approach zero. As equilibrium is established, the current flow will reach a constant value since the rate of discharge of electroactive species at the electrode is totally controlled by its rate of diffusion into the electrode area. By using Fick's law for linear diffusion the diffusion current becomes equal to (63):

$$i = \frac{DnF(c - c_o)}{\delta} \qquad (32)$$

where D is the diffusion coefficient, n is the number of electrons transferred, F is the Faraday, δ is the hypothetical thickness of the diffusion layer and c is the bulk concentration with c_o being the concentration at the electrode surface.

When dealing with reversible electrode reactions, the current versus voltage curves obtained with the metal micro-electrodes hardly ever correspond to the theoretical ones because of polarization phenomena (64). Also the overvoltage for hydrogen is relatively small for many of the metal electrodes; hence they are limited in their electroreduction range. The surface of the electrode is usually easily contaminated and while electro-deposition is taking place the area as well as the electrode characteristics will change.

When the DME is used, the current-voltage curves follow more closely the theoretical ones (64), the hydrogen over-voltage is very high and the surface of the mercury is constantly being renewed.

When using a DME, the equation for the diffusion current must take into account the rate of change of the size of the mercury drop. Ilkovic (65) was the first to derive an expression for the resulting current. The following equation is the theoretical equation for the current at any instant t, in seconds, during the life of a mercury drop (64):

$$i_t = 0.732nFD^{\frac{1}{2}}cm^{2/3}t^{1/6} \qquad (33)$$

where m is the weight of mercury flowing from the capillary per second, (gm/sec), c is the bulk concentration of electro-active species, (mole/cm^3), D is the diffusion coefficient, (cm^2/sec), n is the number of electrons transferred, F is the Faraday (coulombs), and the 0.732 is a combination of numerical constants.

By converting i_t into microamperes, c into millimoles/l and m into mg/sec and substituting 96,500 coulombs for F, the following is obtained:

$$i_t = 706nD^{\frac{1}{2}}cm^{2/3}t^{1/6} \qquad (34)$$

Experimentally, it is easier to measure the average current since most instrument recorders are damped somewhat and the true value of i_t will not be recorded. Thus the average current is the hypothetical constant current which, flowing for a length of time equal to the drop time, would produce the same quantity of electricity as the quantity actually associated with each drop (66). The average current is defined by (64):

$$\bar{i} = \frac{1}{t_{max}} \int_{o}^{t_{max}} i_t dt \qquad (37)$$

where t_{max} is the drop time. Substituting equation 34 for i_t and integrating, the more familiar form of the Ilkovic equation for the average current is derived:

$$i_d = 607nD^{\frac{1}{2}}cm^{2/3}t^{1/6} \qquad (36)$$

Lingane et al (64) pointed out that although Ilkovic begins with the proposition of symetrical spherical diffusion, during his mathematical operations he introduced certain simplifications which were the equivalent of neglecting the curvature of the electrode surface. Rederiving the Ilkovic equation the following was arrived at:

$$i_d = 607nD^{\frac{1}{2}}cm^{2/3}t^{1/6}(1 + 39D^{\frac{1}{2}}t^{1/6}/m^{1/3}) \qquad (35)$$

where $(1 + 39D^{\frac{1}{2}}t^{1/6}/m^{1/3})$ is the correction factor for the curvature of the mercury drop. This factor is of the order of 1.1 for regular ions and about 1.03 for macromolecules. Other authors (67) have derived identical equations differing only in the numerical constant. The correction factors cannot be disregarded since one is of the order of 10%. The actual calculation of a correction factor will be given in Appendix 1 and will be applied to the final calculated value of the micellar diffusion coefficient.

In the standard polarographic experiment the solution to be run is placed in a cell with a reference electrode and a DME. The solution itself must contain an excess of inert electrolyte (discussed later) and any dissolved oxygen must be removed (discussed later) by bubbling an inert gas through the solution. A potential is then applied to the mercury drop (see figure 9 - schematic of a polarographic assembly) and the potential vs current curve is recorded (a polarogram). Measurements of the diffusion current, i_d, and the half-wave potential, $E_{\frac{1}{2}}$, are made by using standard measuring techniques (63).

In the polarographic determination of micellar diffusion coefficients a Leeds and Northrup Dropping Mercury Assembly was used in conjunction with a Leeds and Northrup Electrochemograph for all determinations. The temperature was kept at 25.0 ± 0.1°C by circulating water from a Forma-Temp Jr. constant temperature bath through the outer jacket of the cell. All potential measurements were made against a saturated calomel electrode. Any dissolved oxygen was purged from the system with prepurified nitrogen (discussed later).

In order to determine the diffusion current of a micellar solution, an electroreducible substance must be associated only with the micelle (more detailed discussion will follow). If a certain concentration, c_m, of this reducible species, where each atom of this species is associated with one micelle, is run on the polarograph, the resulting current will be the micellar diffusion current, i_{dm}. This is related to the micellar diffusion coefficient, D_m, by the Ilkovic equation:

$$i_{dm} = 607nD_m^{\frac{1}{2}}c_m m^{2/3}t^{1/6} \qquad (38)$$

Now if the same concentration, c_m, of the electroreducible species is run on the polarograph, in the absence of surfactant, the resulting current, i_d, will be related to the diffusion coefficient, D, of the species, also by the Ilkovic equation:

$$i_d = 607nD^{\frac{1}{2}}c_m m^{2/3}t^{1/6} \qquad (39)$$

By dividing the micellar diffusion current by the diffusion current of the reducible species alone, an equation is obtained relating the two diffusion currents:

$$i_{dm}/i_d = (D_m/D)^{\frac{1}{2}}(m_m/m)^{2/3}(t_m/t)^{1/6} \qquad (40)$$

If one assumes that the mass flow and the drop time of the DME remains constant in both solutions, then by measuring the diffusion currents of the reducible species, with and without surfactant, micellar diffusion coefficients are easily calculated:

$$(i_{dm}/i_d)^2 D = D_m \qquad (41)$$

In the actual experimental determinations of a $3\text{x}10^{-4}$M Cd^{++} solution, both with and without sodium dodecyl sulfate (a $4\text{x}10^{-2}$M $NaDDSO_4$ solution was used), a mass flow of 1.695 mg/sec was obtained for both and a drop time of 4.3 sec/drop and 3.8 sec/drop was obtained without and with $NaDDSO_4$, respectively. When these values are placed into equation 40 and rearranged into the form of equation 41 the following results:

$$(i_{dm}/i_d)^2 D \times 1.04 = D_m \qquad (42)$$

Since the difference in drop times yields a factor of 1.04, this will also be included in the calculation of a correction factor in Appendix 1 and applied to the final calculation of the micellar diffusion coefficients.

The final corrected equation as derived in Appendix A is:

$$(i_{dm}/i_d)^2 D \times 1.14 = D_m \qquad (42a)$$

In the determination of the micellar diffusion coefficients of the sodium alkyl sulfates, the tagging cation used was cadmium (see following sections). The diffusion coefficient for the cadmium ion is given by Macero and Ruffs (68) and is equal to 0.69×10^{-5} cm^2/sec. Substituting this value into equation 42a with the proper experimental diffusion currents allows for the calculation of the diffusion coefficient of the tagged micelle.

Polarographic analysis has been a standard analytical technique for many years. The standardization of this technique, including instrumentation, allows for the relative ease involved in this type of analysis. This ease of analysis and the Ilkovic equation makes the calculation of diffusion coefficients a relatively simple matter. In the application of this technique to the determination of micellar diffusion coefficients, the simplicity of the polarographic method remains. Equation 42a allows for the calculation of the micellar diffusion coefficient by applying a simple algebraic solution, somewhat less involved that the usual differential equations. The time involved in the actual analysis is something under twenty minutes per determination which is a considerable saving in time over the standard methods for determining diffusion coefficients (see Chapter 1).

It is thus obvious that the polarographic method for determining diffusion coefficients of micelles is much less tedious in both technique and calculation than the usual methods. In the following, the actual tagging and degassing techniques that were developed and various assumptions that were made will be discussed.

B) Experimental Modifications

1) Deoxygenation

In the polarographic analysis of most ions it is imperative that there be complete removal of any oxygen within the solution since dissolved oxygen, being easily reduced at the DME, and having polarographic waves at -0.05 and -0.9 volts vs SCE, might interfere with the desired waves.

Removal of dissolved oxygen from aqueous solutions of inorganic salts is a procedure which is well documented. The most widely used method is to bubble an oxygen free inert gas (He, H_2, N_2, Ar) through the solution for a length of time to displace the dissolved oxygen (63,64,69). A second method is to add a substance which will chemically react with the oxygen. As originally suggested by Hohn (70), the addition of sulfite ion to a neutral or alkaline solution will rapidly reduce the dissolved oxygen; hence removing it. The catalytic removal of oxygen with an enzyme was used by Benesch (71) with success.

When surface active materials, in any significant concentrations, are involved in a polarographic analysis, removal of oxygen by the usual degassing techniques results in extensive foaming. Furthermore, the addition of any foreign material may result in changes in the structure of the micelle and so render interpretation of the results difficult and inconclusive.

In previous works, the removal of dissolved oxygen from solutions containing surface active materials was accomplished by evacuating the cold solution until all dissolved oxygen is removed as was done by Saroff et al (72), or by being extremely careful and starting with oxygen free solutions from the beginning (72) or by first flushing the surface of the solution with an inert gas (H_2 (73) or N_2 (74)) and then breaking the surface by either rocking (73) by means of an elaborate device or by shaking (74) in a flask.

In our initial work (74) the air in the flask containing the tagged surfactant solution was displaced with prepurified nitrogen. The flask was then stoppered and the solution was shaken for about thirty seconds. The solution, now with a great deal of foam, was left standing for several minutes so that some of this foam could break. Nitrogen was reintroduced into the flask and the above procedure was repeated for five to ten times to remove all the oxygen prior to polarographic analysis.

The rocking and shaking procedures, although adequate, involved either a mechanical device or were rather time consuming.

A new simple method for speedier degassing of a solution containing surface active materials was developed by designing a device which simultaneously degasses the surfactant solution and breaks any foam that is generated. The degassing disc was fabricated out of Lucite plastic (figure 10) and designed to fit the Leeds and Northrup Dropping Mercury Electrode Assembly (figure 11).

The basic principle behind the operation of the disc is that, as the foam is generated by bubbling the N_2 through the solution, a downward flow of N_2 breaks the foam. The flow of N_2 for deoxygenation of the sample is controlled by valve A (figure 11) while valve B (figure 11) controls the flow of gas for breakage of the foam. The rate of flow of gas in each line is dependent on the volume of the liquid to be deoxygenated, the rate of production of foam, and the height of the disc above the level of solution.

Excellent results were obtained using this device as is seen in figure 12, in which the polarograms of a 4 x 10^{-4}M Cd ion in a 4 x 10^{-2}M $NaDDSO_4$ solution prior to and after degassing with prepurified N_2, saturated with water vapor, for 10-15 minutes, are superimposed on one another. In this work the flow rate of the N_2 used to break the foam was greater than that used to deoxygenate the sample. After deoxygenation is completed, valve A is closed and the flow of N_2 through valve B is diminished so that there is a gentle flow of gas over the solution's surface. The complete removal of oxygen is indicated by the absence of a peak in the region of -0.4 to -0.5 volts vs. SCE.

2) Tagging of Micelles by Solubilization

In order to determine micellar diffusion coefficients, one must be able to polarographically reduce some entity that is specifically associated with the micelle. There are two methods by which this can be accomplished; Solubilization of some water insoluble material in the micelle or adsorption of some species onto the surface of the micelle.

Solubilization of a water insoluble material into the micelle is well recorded (9). Dean et al (59) and Hoyer et al (30) used water insoluble dyes that were solubilized by the micelle to determine micellar properties. The solubilization of a water insoluble metal soap was used in the initial stage of the work as a method to tag the micelle so that a micellar diffusion current can be measured.

Since most ionic micelles have a large surface charge (29,31,75), it should be possible to specifically adsorb some multivalent ion onto the surface of the micelle and have it travel as part of the micelle, thus giving a micellar diffusion current when this ion is reduced at the DME. These two methods, solubilization and surface adsorption will be discussed separately in what follows.

a) Determination of a tagging cation:

When using the polarographic method for the determination of micellar diffusion coefficients, the wave that is recorded for the tagging agent must be chosen so that it does not lie in a region where there are any interfering waves.

A polarogram of a deoxygenated surfactant solution (figure 13) is obtained. The potentials where the current values are relatively constant are considered for the tagging agent. Multivalent cations which are reduced at these potentials are then considered. When one is chosen a test run is tried (figure 14).

In the case of the sodium alkyl sulfate detergents, the polarograms shown are that of a 0.165M $NaDSO_4$ solution without (figure 13) and with (figure 14) a tagging agent. With the sodium alkyl sulfates, the polarograms are identical as the carbon chain length is changed. In this case the tagging cation is cadmium since its reduction half-wave potential is in an area (-0.60 volts vs SCE) where the $NaDSO_4$ solution shows no significant waves. Thus the only wave recorded in this area is that of the tagging agent that is associated with the micelle (figure 15).

b) Solubilization of divalent metal soaps.

Preparation of Metallic soaps: The general procedure for the preparation of cadmium salts of fatty acids is as follows: A weighted amount of the highest purity obtainable fatty acid is reacted with an equivalent amount of 0.5M NaOH solution. A 1 M solution of $Cd(NO_3)_2$ is added to the solution to precipitate the water insoluble cadmium soap. The precipitate is filtered and washed a number of times to remove all ionic residues, and is then dried at 80°C.

A weighted amount of the solid is placed in a flask with 100 milliliters of distilled water and shaken for several days. The solid is then removed by filtering the solution through a high density filter paper (S & S - No. 507) and the remaining solution is run on the polarograph. Figure 14 shows the diffusion currents for the cadmium salts of various fatty acids with the chain length varying from twelve to eighteen carbons. As would be expected, the solubility decreased as the chain length is increased. The diffusion current due to the dissolved cadmium soap is low enough to allow their use as tagging agents since these currents are within the experimental error of the procedure.

In order to give correct values of the micellar diffusion coefficient, no more than one tagging species can be transported by a micelle. No difficulties arise if the average number of solubilized labels is less than unity. Thus, a molar quantity of the solid cadmium fatty acid salt (in most cases cadmium laurate was used) equal to a hypothetical molar concentration of micelles was used. The amount of cadmium salt needed was calculated by assuming that the surfactant solution consisted entirely of micelles, each composed of one hundred monomers.

The tagged surfactant solutions (sodium decyl sulfate - $NaDSO_4$, sodium dodecyl sulfate - $NaDDSO_4$, and sodium tetradecyl sulfate - $NaTDSO_4$, were used and were purchased from Mann Research Labs, New York; purity cited as greater than 99%) were prepared by adding an excess of solid cadmium laurate (CdL) to solutions of the desired surfactant concentration and placed on a Burrel "Wrist Action" Shaker for several days (the usual shaking time was three days). The unsolubilized cadmium laurate (usually more than half of that used) was removed by filtering the solution twice through a dense filter paper (S & S - No. 507) and then centrifuging the solution at 1500 rpm for thirty minutes. The solution is then run on the polarograph.

A solubilization time study was performed in order to establish two points: firstly, to establish a minimum shaking time and secondly, to determine whether or not there is one or more tagging molecules per micelle.

It would be expected that if more than one tagging molecule is solubilized per micelle the diffusion current measured versus time of shaking would continually increase until either the cadmium laurate supply is exhausted or some saturation level is reached. If each micelle picks up only one molecule of tagging agent then the diffusion current versus shaking time curve should level off rather quickly. Values of the diffusion coefficient calculated from the leveling off current should be close to the value expected for the detergent.

Figure 16 shows the diffusion current obtained for a tagged 4 x 10^{-2}M $NaDDSO_4$ solution at various shaking times. The curve levels off after about one day and the calculated value of the diffusion coefficient of the micelle is 0.97 x 10^{-6} cm^2/sec. As is shown later, this is close to published values.

Thus, in the shaking time used, it is concluded that an average of one or less tagging molecules per micelle is present.

c) Determination of divalent cation concentration:

Wet Ashing: In the destruction of organic material, in order to determine amounts of trace metallic elements, a large number of ashing procedures have been described. The method used in this work was a wet oxidation or wet ashing procedure which is described by Smith (76). A slight modification of this method was used.

A ten milliliter aliquot of detergent solution is slowly evaporated. Any foaming during the evaporation was eliminated by using one drop of a 10% aqueous solution of Dow C antifoaming agent. When most of the water was driven off, ten milliliters of concentrated nitric acid are added. This is heated gently until it is almost dry. Another ten milliliters of concentrated nitric acid are added with ten milliliters of 72% perchloric acid. The mixture is heated until it is boiling gently. The heating is continued until it is almost dry.

The mixture is cooled and rinsed out with several portions of distilled water. The rinsings are poured into a ten milliliter volumetric flask and it is then brought up to volume.

A special long necked oxidation flask was built. It was similar to that described by Hamlin (77) except that the elongated neck was covered with asbestos to minimize heat losses (figure 17).

Since the volumes of the unoxidized and oxidized solutions are the same, the concentration of cadmium in each will be identical. When a known amount of cadmium (0.1 mg/ml) is added to a 4×10^{-2}M $NaDDSO_4$ solution and an aliquot of this solution is taken and wet ashed, the error of the wet ashing method was determined. The percent error ranged from a low of 0.2% to a high of almost 25% with a large majority falling between 5-10%.

Flame spectrophotometry: Trace concentrations of metals can be determined by the amount of light that they absorb in a beam of light whose wavelength corresponds to one that the metal emits. Atomic absorption is one method that is applicable to the determination of trace amounts of cadmium in sufractant solutions.

Using a Jarrell-Ash Atomic Absorption Spectrophotometer (Jarrell-Ash Co., Waltham, Mass.) with a cadmium hollow cathode lamp, an attempt was made to determine the cadmium concentration in the tagged surfactant solutions. A great deal of trouble was encountered with obtaining a uniform rate of feed of solution into the flame. Also due to the relatively high salt concentrations, the flame nozzle would frequently clog. An attempt to use a syringe drive also failed since the motor used was not a constant speed motor and the feed rates were not totally reproducible.

d) Results:

The results obtained from the solubilization tagging method are seen in Table 1. The calculated diffusion coefficients for the micelles of $NaDSO_4$, $NaDDSO_4$, and $NaTDSO_4$ are tabulated in Table 2. The value of D for $NaDDSO_4$ agrees within experimental error with that value published by Mysels (25).

The micellar diffusion coefficient decreases with increasing chain length. This would be expected since the chain length increase would cause the micelle to increase which would cause the radius to increase, causing D to decrease.

e) Salt effects on metal soaps:

When the metal salts of the fatty acids are used as tagging agents one must be aware of the effects of the other ions on these materials. If there is any significant ion exchange with the metal soaps (cadmium laurate in this case), doubts may be cast on the solubilization method.

Four different cadmium soaps were prepared for this purpose: cadmium laurate (CdL), myristate (CdM), stearate (CdSt), and palmitate (CdP). The method of preparation is as previously described. All salts used in the experiment were of Baker Analyzed Reagent Grade.

Since sodium alkyl sulfate detergents were used, the effect of the sodium ion on the four cadmium soaps were examined. The solid cadmium soaps were shaken for two or three days with varying amounts of $NaNO_3$ (figure 18). Also CdL was shaken with varying amounts of $NaNO_3$ for both two and three days (figure 19). The removal of the unreacted cadmium soaps is identical with that described previously.

From the results it is clear that the sodium ion does exchange with the cadmium in the cadmium soap. There seems to be a sharp jump initially in the cadmium concentration, as measured by its diffusion current, over that due to the solubility of the cadmium soap in distilled water. It is also clear (from figure 19) that the time of shaking affects the amount of cadmium exchanged.

When the anion is changed from nitrate to sulfate the general trend seems to be the same (figure 20). There is initially a sharp increase in the cadmium concentration. There seems to be no effect due to the changing of the anion since the sulfate curve is almost identical to the nitrate curve for the cadmium laurate.

When the cation is changed to potassium, there is a marked change in the amount of cadmium exchanged. The diffusion current rises to a much higher value prior to its leveling off at higher salt concentrations (figure 21). When ammonium ions are used, the results are similar to that of the sodium; there is a sharp increase in cadmium concentration with it leveling off at higher salt concentrations.

When the pH is changed there is a sharp increase in the amount of cadmium present in solution (figure 22). When the pH's before and after shaking are compared, there is a noticeable increase in the later values. This indicates that hydrogen ions are going into the formation of the free acid, thus liberating cadmium ions. When CdL is shaken with NaOH solutions there is no discernable plateau observed.

f) Overall conclusions:

From the results of the salt effect study, an increase in the amount of cadmium in solution is observed. This seems to indicate that part of the diffusion current observed is due to cadmium that has been exchanged for sodium ions from the solution.

The free sodium ion concentration for the $NaDDSO_4$ concentration used is about 0.02 M (31). At this concentration of sodium ion, there is approximately a 50% increase in the amount of cadmium in solution over that amount which is present when CdL is shaken with water.

Since the presence of sodium ions affects the amount of cadmium that will be present in the solution, one must cast some doubt on the credibility of the solubilization method for the polarographic determination of micellar diffusion coefficients. The micellar diffusion current will be a combination of that amount of current due to the CdL that is solubilized and that amount of current due to the cadmium exchanged by the sodium. This will also show up as a larger current for the ionic cadmium. Thus errors are introduced in both currents and thus some doubt must be placed on the feasibility of the solubilization procedure as a method for the determination of micellar diffusion coefficient.

3) Tagging of Micelles with a Divalent Cation

It is well known from electrophoresis (29,78) and transport numbers (31) that micelles carry a large surface charge. The charge is not as large as the aggregate number since counterions adsorb or associate on the micelle (31,75,79,80). The degree of ionization of the micelle is approximately 25–30% (29,31) with an effective charge of 15 electrons/-micelle (22,24). When a polyvalent cation is added to an anionic micellar solution, the cation will, because of the large electrostatic attraction between the two ions, be found primarily on the surface of the micelle. Two possibilities must be considered: first, the cation is electrostatically adsorbed on the surface of the micelle which is not significantly altered; second, an in situ salt is formed which may or may not produce a structural change in the micelle.

Since the cation is strongly associated with the surface of the micelle, it will act as though it is part of the micelle. Thus, the addition of a small but known amount of divalent cation allows for the polarographic determination of the micellar diffusion coefficient. A method somewhat similar to this was used to determine the diffusion coefficients of high molecular weight substances (81).

Procedure: $NaDSO_4$, $NaDDSO_4$, and $NaTDSO_4$ were the same as previously used. A stock cadmium solution was prepared by dissolving Baker Analyzed Cadmium Rod in HCl, evaporating to almost dryness and diluting to 500 milliliters. All reagents were of ACS grade and distilled water was used in all cases.

The desired surfactant concentrations were prepared by dilution of previously prepared stock solutions. Prior to final dilution, the required amount of cadmium stock solution was added to give the desired cadmium concentration. This cadmium concentration was either equal to or less than the micelle concentration using the same assumptions as previously described. Since volumetric equipment was used in all cases the cadmium ion concentration was within 0.1% of the desired concentration.

The solution is then deoxygenated and run on the polarograph. Standard cadmium solutions with supporting electrolyte were also run polygraphically to obtain a standard diffusion current.

Results: Cadmium ions were used as the tagging cation because the well defined cadmium polarographic wave is unaffected by any wave due to the sodium alkyl sulfates.

Figure 23 displays the results of a series of runs with three anionic surfactants previously mentioned, where the diffusion current, i_d, due to the cadmium versus the cadmium concentration. Except for slight deviations for the $NaTDSO_4$ solutions, all points fall on a straight line passing through the origin. Table 3 tabulates the slopes of the lines and the corresponding diffusion coefficients.

Figure 24 and figure 25 show the results of the variation of $NaDSO_4$ and $NaDDSO_4$ concentrations, respectively. In each case, a sharp break in the curve is indicated very close to the critical micelle concentration.

The Ilkovic equation relates the diffusion current to the concentration and to the diffusion coefficient:

$$i_d = 607nD^{\frac{1}{2}}cm^{2/3}t^{1/6} \qquad (36)$$

If the diffusion current is plotted against concentration, a straight line is expected. The i_d vs c curves in figure 23 shows these expected results. From the Ilkovic equation the slope is:

$$i_d/c = M = 607nD^{\frac{1}{2}}m^{2/3}t^{1/6} \qquad (43)$$

From the ratio of the slope for the detergent, M', to that for ionic cadmium, M, the following relationship results:

$$M'/M = (D'/D)^{\frac{1}{2}} \qquad (44)$$

where D' is the micellar diffusion coefficient and D is the one for the cadmium ions as given previously (68).

In figures 24 and 25, after the cmc (3.1×10^{-2}M for $NaDSO_4$ (62) and 8.2×10^{-3}M for $NaDDSO_4$ (82)) the micellar diffusion coefficients tend to level off. The micellar diffusion coefficient which is calculated from this data give a value of 1.62×10^{-6} cm^2/sec for the $NaDSO_4$ at 0.08M and 0.95×10^{-6} cm^2/sec for $NaDDSO_4$ at 0.04M. These values are in good agreement with those in Table 3.

In order to substantiate the initial premise, that the cadmium ion is associated with the micelle surface, a study of the interaction of the ion with an alkyl sulfate surface was undertaken. This was achieved by doing monolayer and electromotive force studies. The monolayer suggests some sort of interaction while the EMF work shows a drastic reduction in cadmium ion activity above the cmc. This is reported in the next chapter.

C) Supporting Electrolyte

In polarographic analysis it is necessary to eliminate all currents except those due to the diffusion of the reducible species to the electrode. The migration current, which is due to the coulombic attraction or repulsion of the reducible species to or from the DME, respectively, is eliminated by adding an excess of an inert salt to carry the major portion of this current. According to Kolthoff (64) the concentration of the supporting electrolyte need be only 25 times larger than the concentration of the reducible ion in order to eliminate the migration current completely.

Since the micelle consists of a number of monomer units and appears only above a certain concentration (cmc), its concentration is significantly less than the initial surfactant concentration. Since equilibrium exists between the micelle and monomers, the non-aggregated species will be at a concentration that is close to the cmc (31) (Law of Mass Action). Thus the concentration of the micelle will be somewhat less than the monomer concentration. At a $NaDDSO_4$ concentration of $4 \times 10^{-2}M$ the monomer concentration (assuming the cmc is $8.2 \times 10^{-3}M$) is approximately 20 times the micelle concentration. Since the micelle is about 25% ionized (22,24), then the sodium ion concentration is about 45 times greater than the micelle concentration. Also since the micelle is much larger than the monomer and the sodium ions, its rate of migration will be much slower when compared to the migration of the ions. Thus, it is felt that the excess monomer and sodium ion concentration will be sufficient to act as supporting electrolyte.

To test this, varying amounts of inert electrolyte were added to a tagged $4 \times 10^{-2}M$ $NaDDSO_4$ solution. Since the alkyl sulfate micelle has a large negative charge (22,24) associated with it, it would migrate away from the negatively polarized DME. Thus, addition of supporting electrolyte will cause the diffusion current to increase.

Figure 26 displays the effect of inert electrolyte on the current due to the tagged 4 x 10^{-2}M $NaDDSO_4$ solution. The electrolyte was increased until it is approximately 25 times the micelle concentration. As is seen, the current does increase but only slightly. In the case of the sodium ion it increases only 2%. With the NH_4NO_3, the current increase is about 4% while with the KNO_3 shows increase of about 5%.

The sharper rise in current with the potassium ion can be explained by using the information obtained in the salt effect experiment. It was the potassium ion that had the largest effect and it is believed to be manifesting itself in this case.

Thus, since there is no large increase in current when additional inert supporting electrolyte is added, the assumption that no additional supporting electrolyte is necessary is valid.

TABLE 1

HALF WAVE POTENTIALS AND DIFFUSION CURRENTS FOR CADMIUM LAURATE TAGGED SURFACTANT SOLUTIONS

Solutions	Surfactant Concentration (molar)	Half Wave Potential (vs SCE, -volts)	Diffusion Current (microamps)
Sodium decyl sulfate	0.165	0.532±0.003	1.38±0.03
HNO_3-$HClO_4$ oxidized	—	0.587±0.002	3.40±0.11
Sodium dodecyl sulfate (A)	$4x10^{-2}$	0.630±0.02	0.75±0.05
HNO_3-$HClO_4$ oxidized (A)	—	0.608±0.001	2.10±0.05
Sodium dodecyl sulfate (B)	$4x10^{-2}$	0.646±0.008	0.68±0.02
HNO_3-$HClO_4$ oxidized (B)	—	0.628±0.004	1.98±0.18
Sodium tetradecyl sulfate (A)	$1x10^{-2}$	0.656±0.004	0.47±0.01
HNO_3-$HClO_4$ oxidized (A)	—	0.574±0.002	1.40±0.02
Sodium tetradecyl sulfate (B)	$1x10^{-2}$	0.659±0.004	0.37±0.01
HNO_3-$HClO_4$ oxidized (B)	—	0.581±0.010	1.14±0.03

TABLE 2

MICELLAR DIFFUSION COEFFICIENTS AT 25°C USING SOLUBILIZATION AS TAGGING PROCEDURE

Solutions	Diffusion Coefficient (cm^2/sec)		
	This work	Literature	
$1x10^{-2}$M Sodium tetradecyl sulfate	$0.87 \pm 0.04x10^{-6}$	—	
$4x10^{-2}$M Sodium dodecyl sulfate	$0.98 \pm 0.18x10^{-6}$	$0.83x10^{-6}$	(25)
0.165M Sodium decyl sulfate	$1.30 \pm 0.16x10^{-6}$	—	

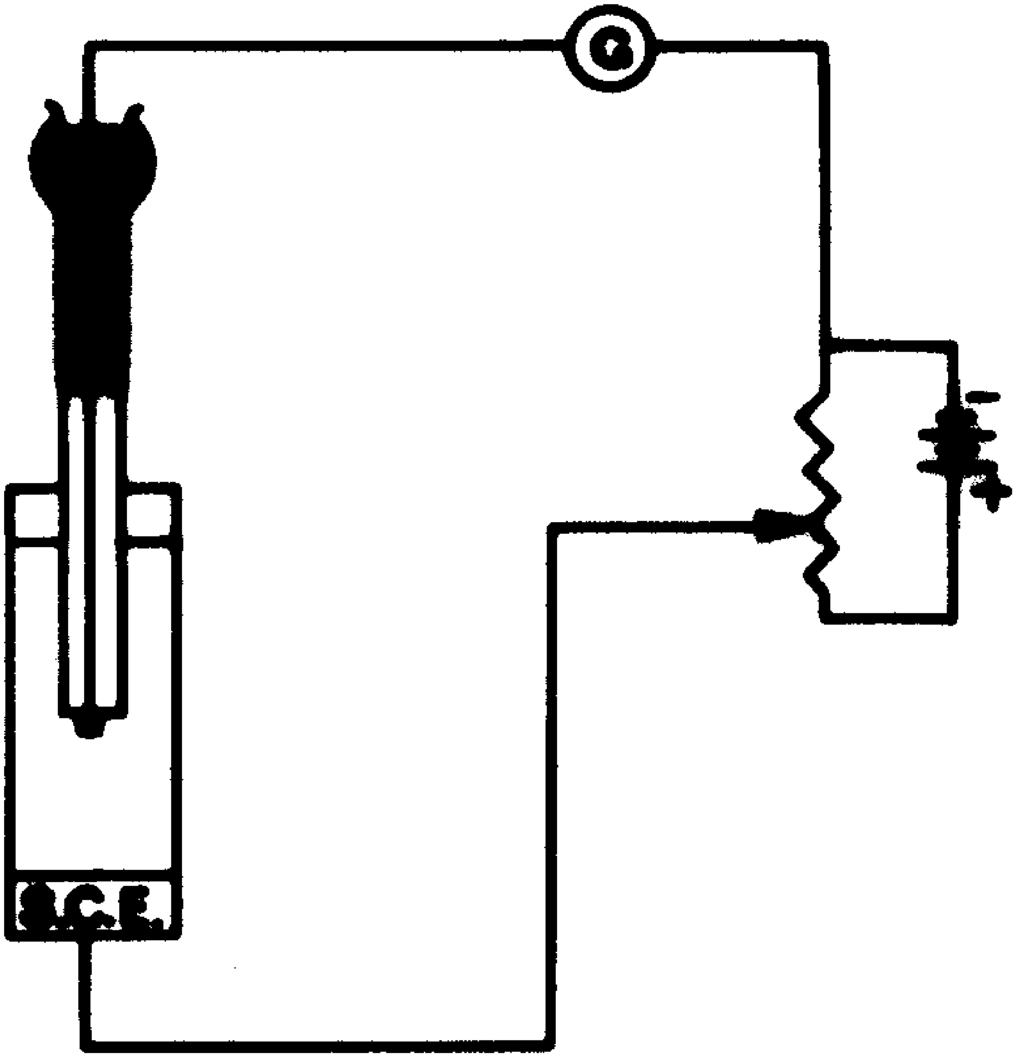
TABLE 3

MICELLAR DIFFUSION COEFFICIENTS AT 25°C USING DIVALENT CATION TAGGING PROCEDURE

Solution	Slope (A/mole)	D_{CALC} (cm^2/sec)	D_{LIT} (cm^2/sec)
Cd^{++} in H_2O alone	6280		6.9×10^{-6} (68)
Cd^{++} in 0.165M $NaDSO_4$	2890	1.66×10^{-6}	1.14×10^{-6} (74)
4.0×10^{-2}M $NaDDSO_4$	2083	0.87×10^{-6}	0.83×10^{-6} (25)
			$.86 \times 10^{-6}$ (74)
1×10^{-2}M $NaTDSO_4$	1890 (a)	0.71×10^{-6} (a)	$.76 \times 10^{-6}$ (74)
	1955 (b)	0.46×10^{-6} (b)	

(a) Best straight line through origin

(b) Best straight line



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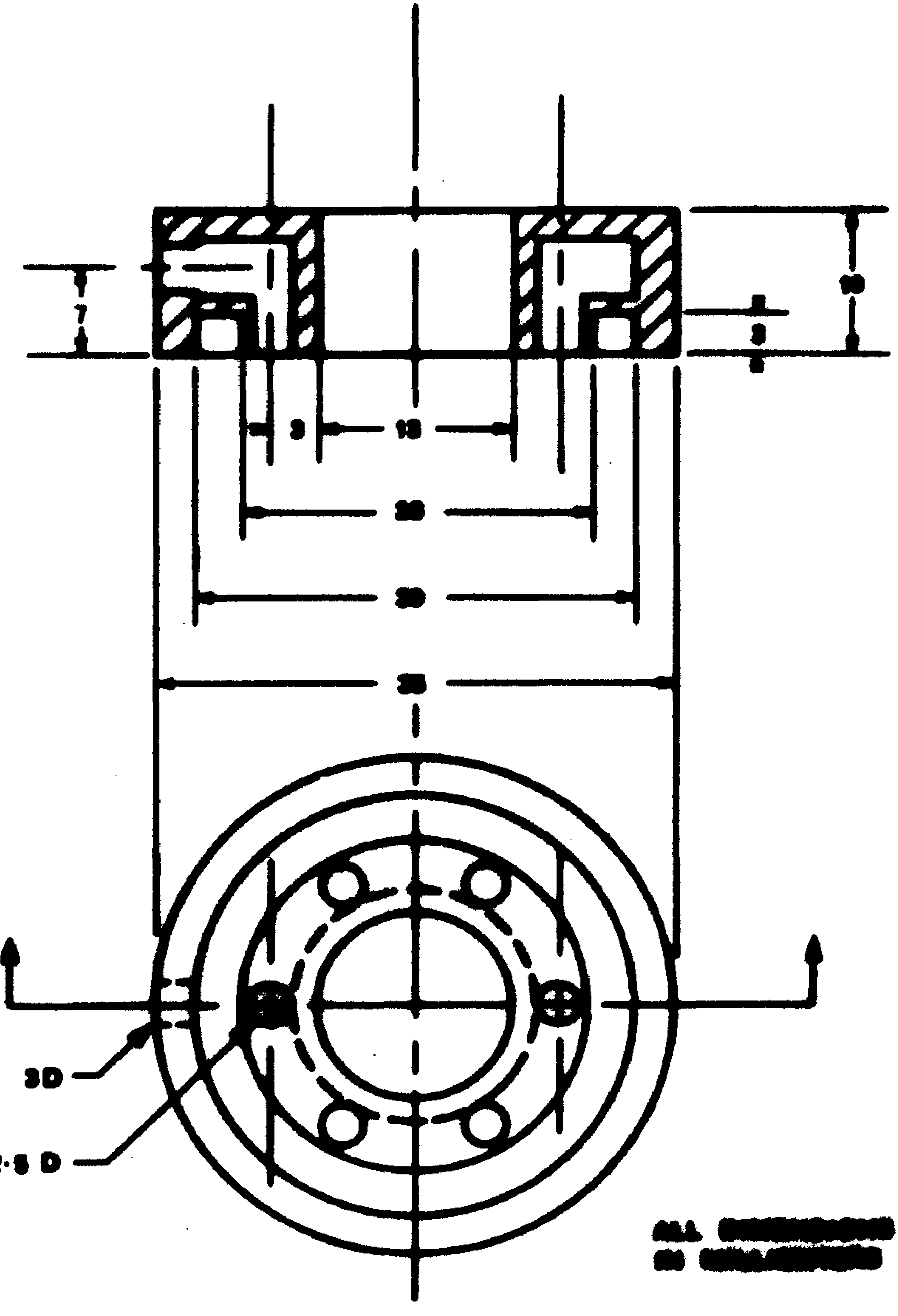

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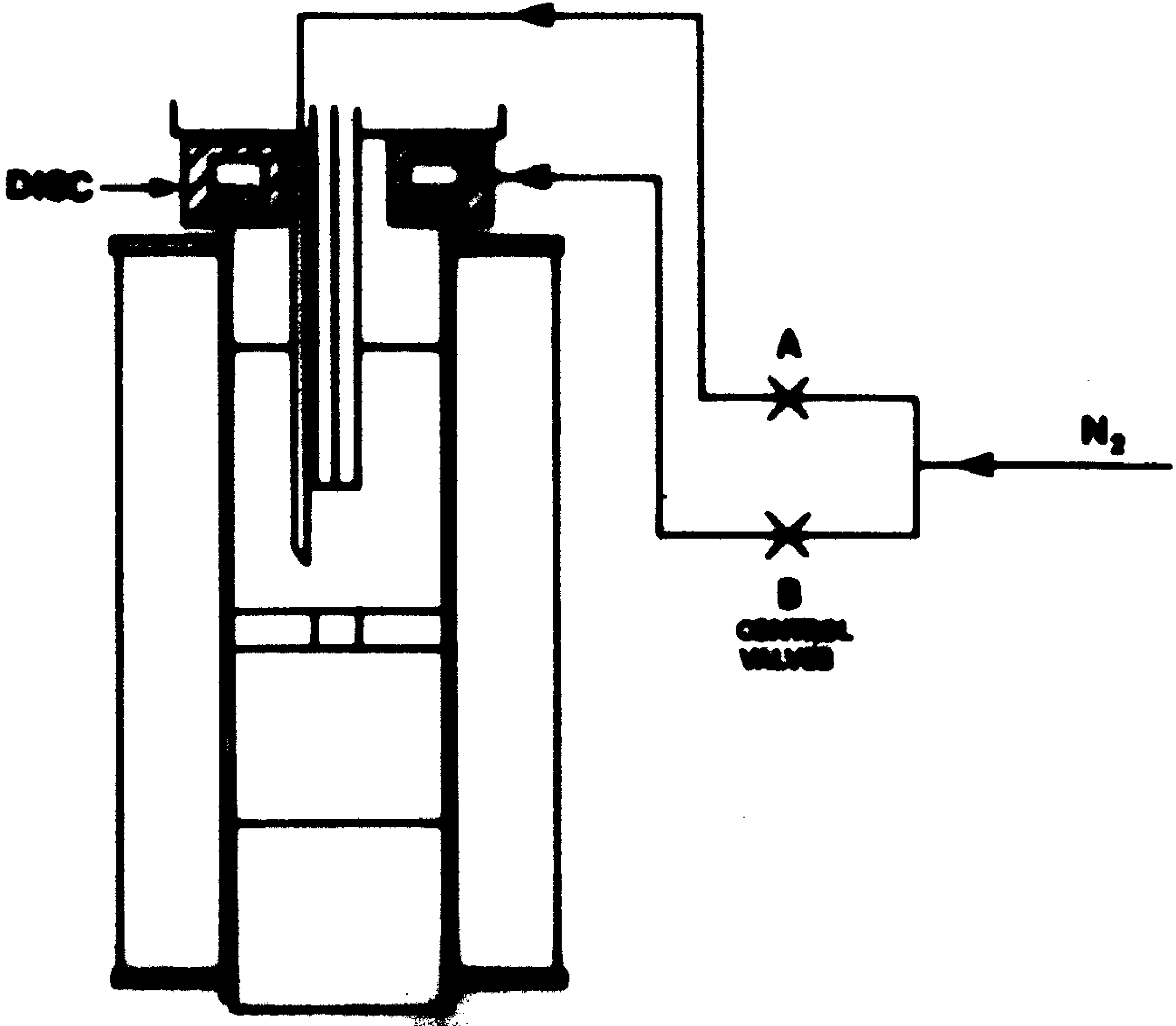
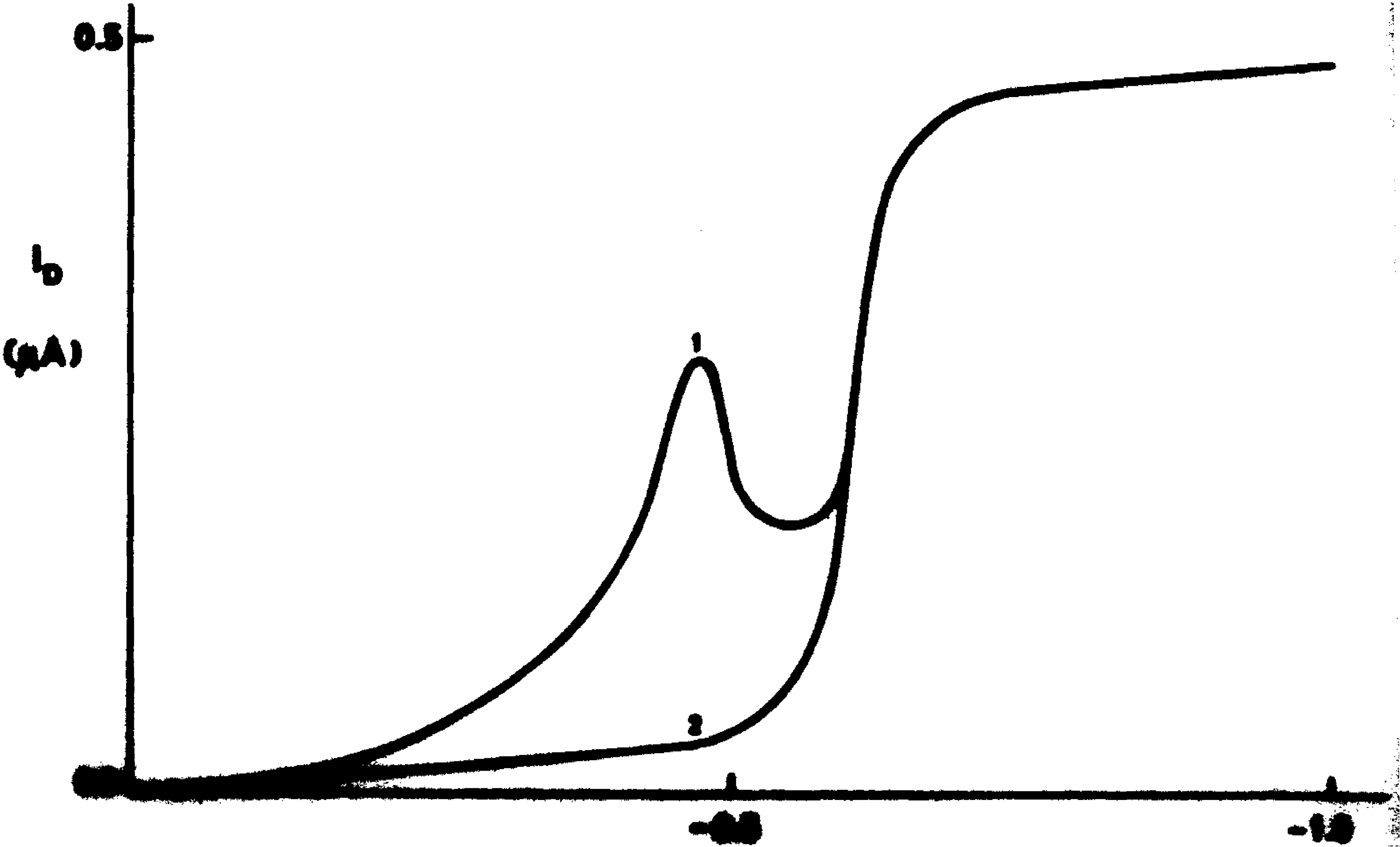
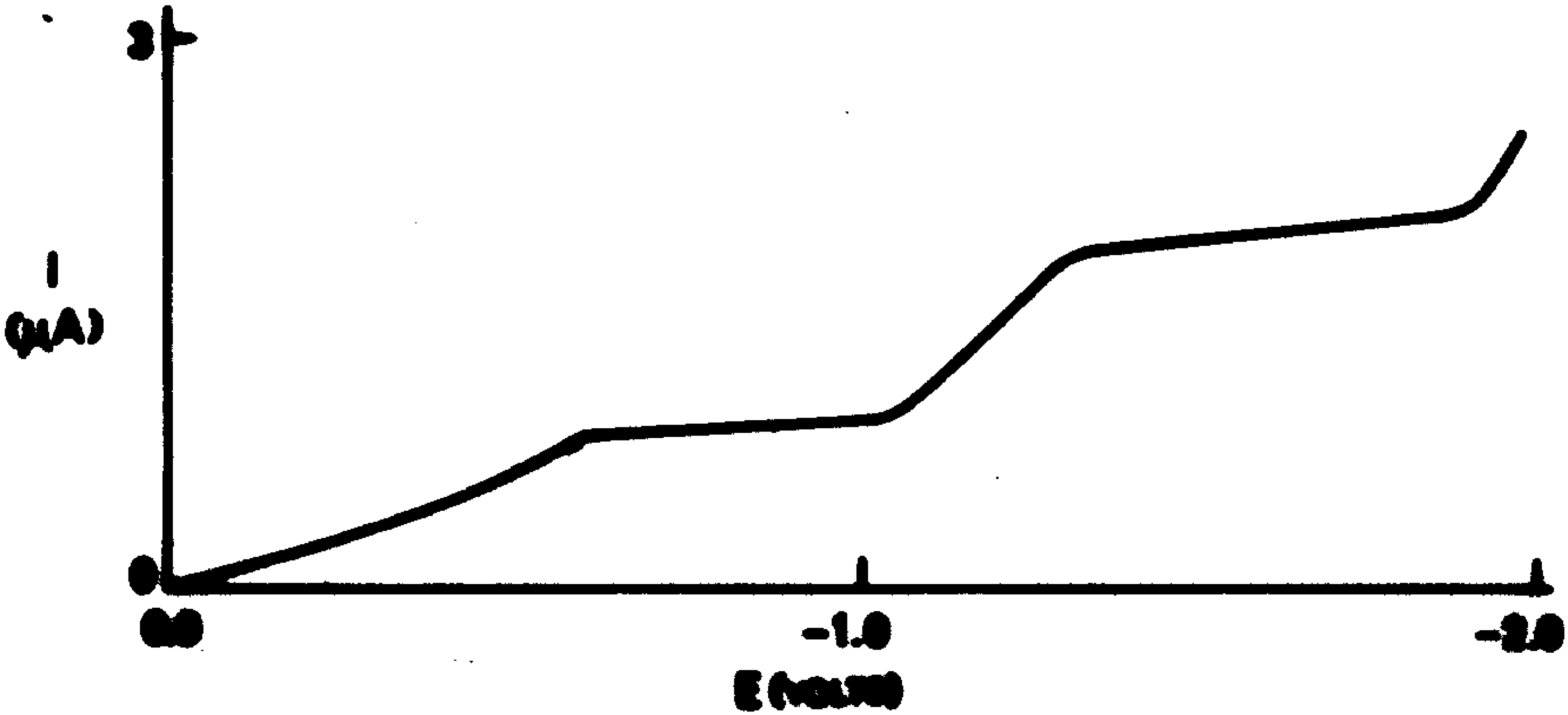

DISC
A
N$_2$
B
CONTROL VALVES

Figure 12





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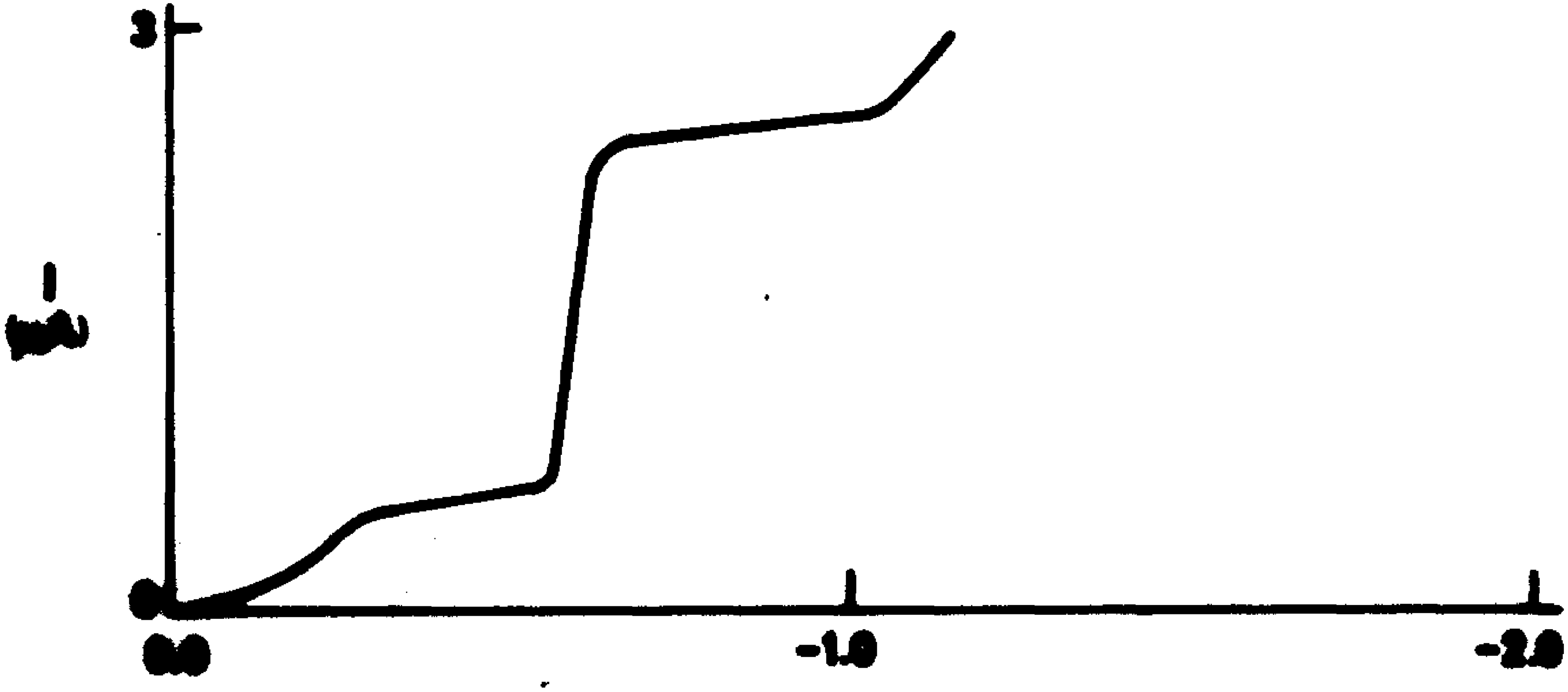

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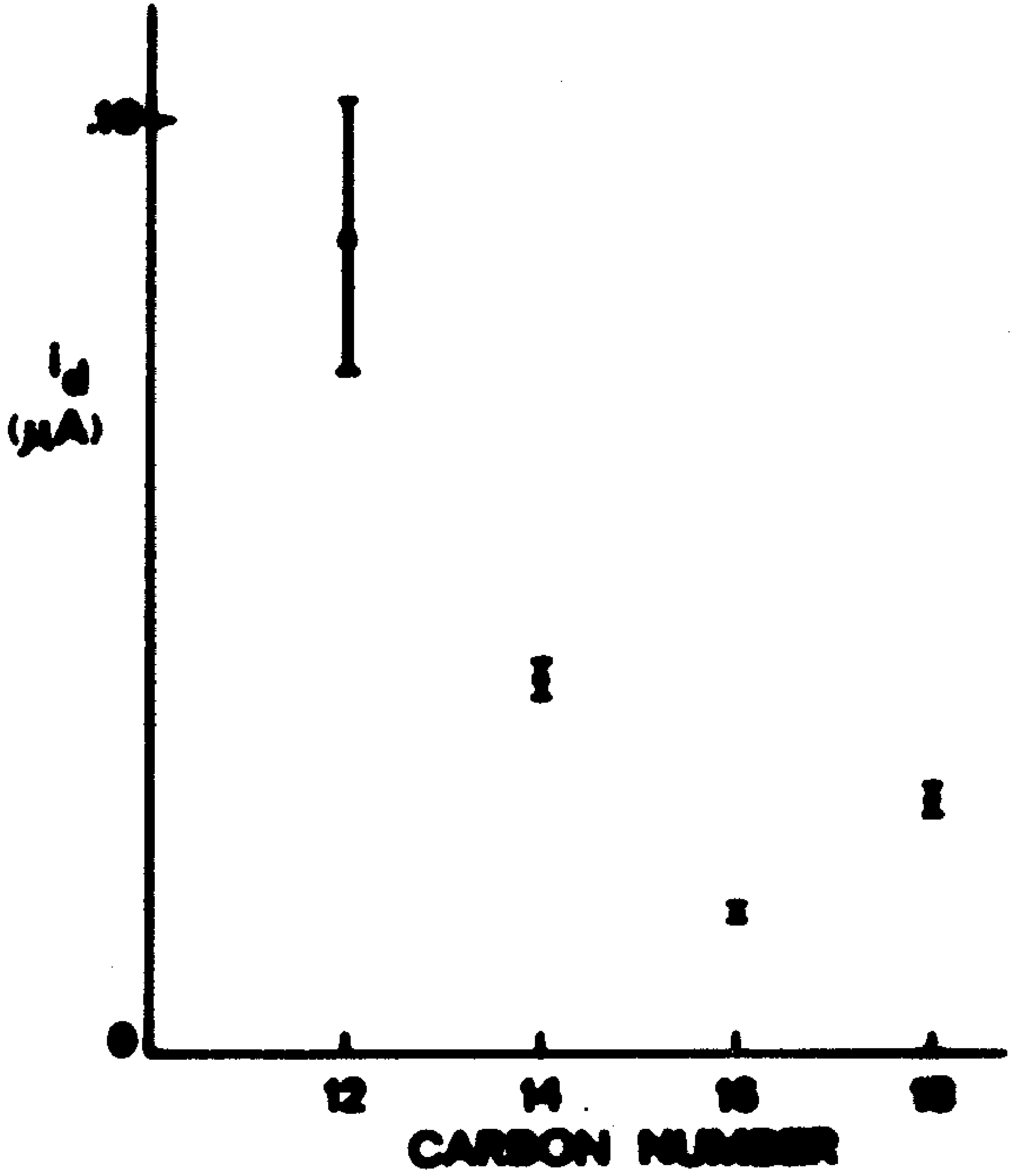
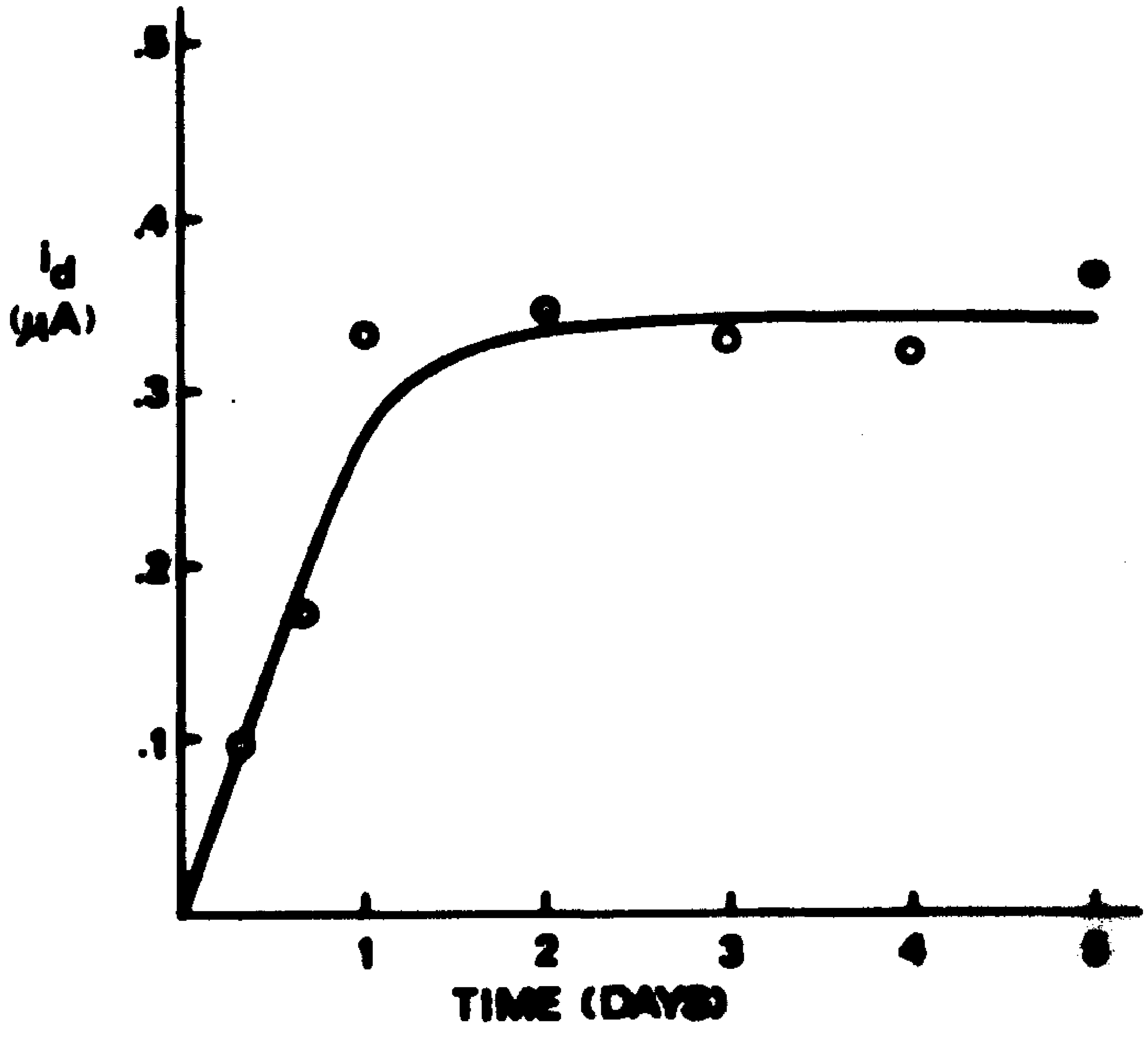


Figure 16



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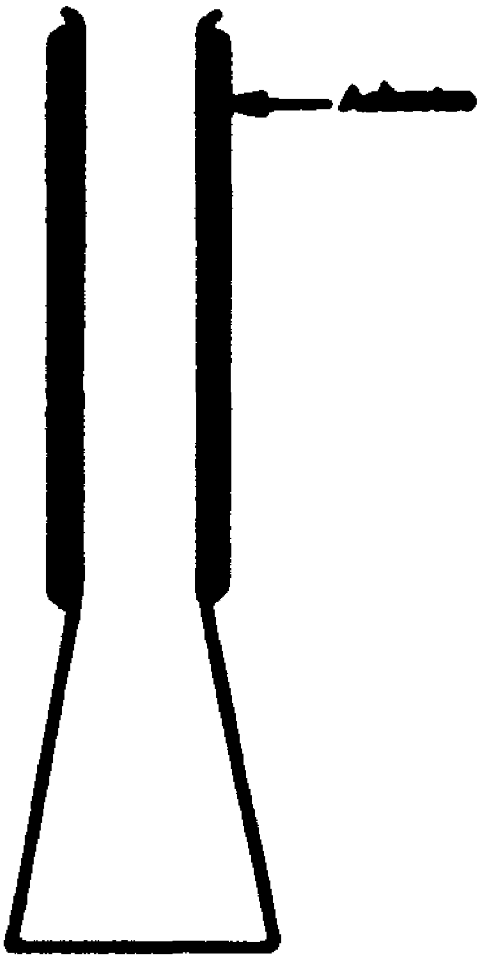


Figure 17

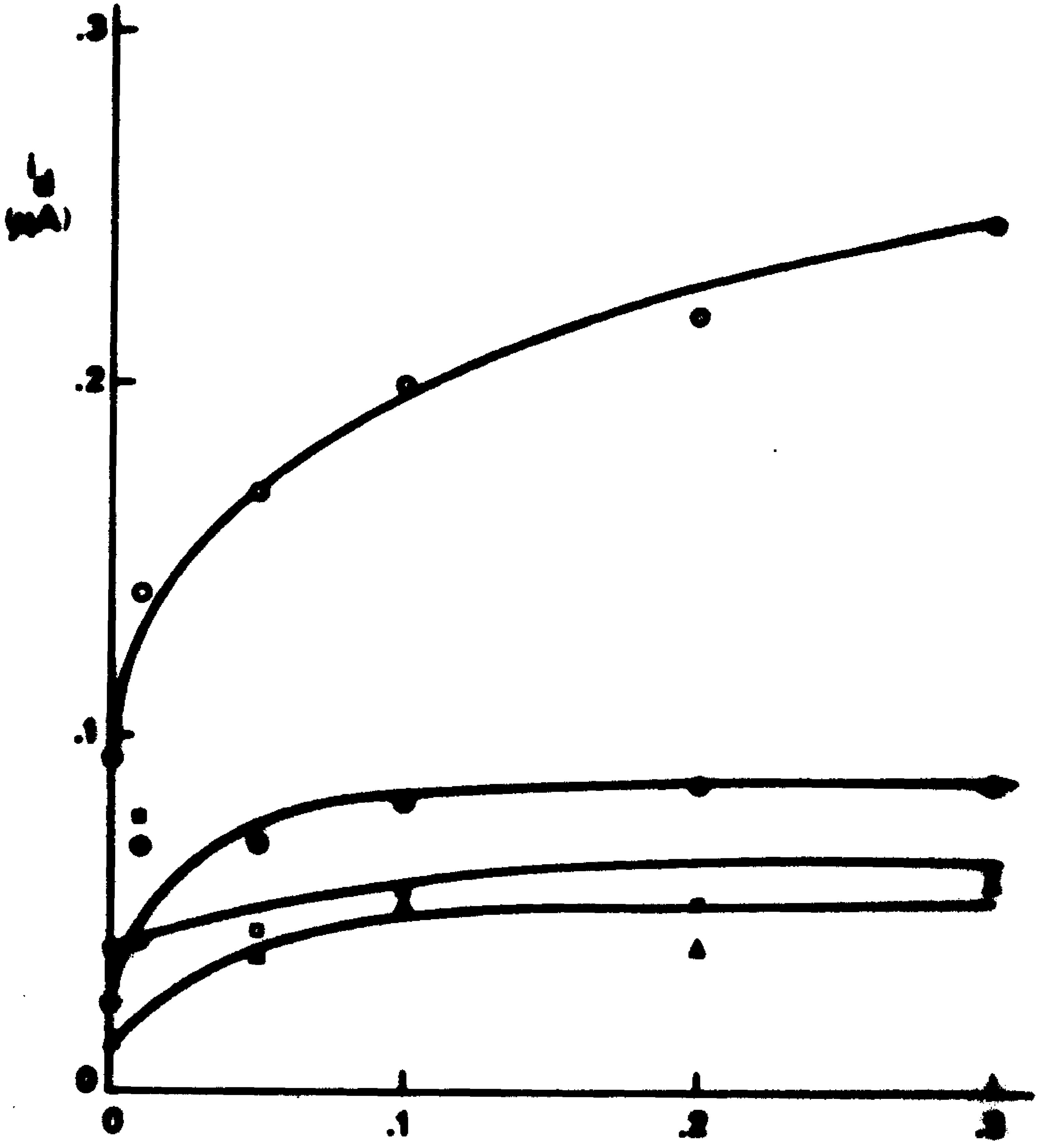


Figure 13

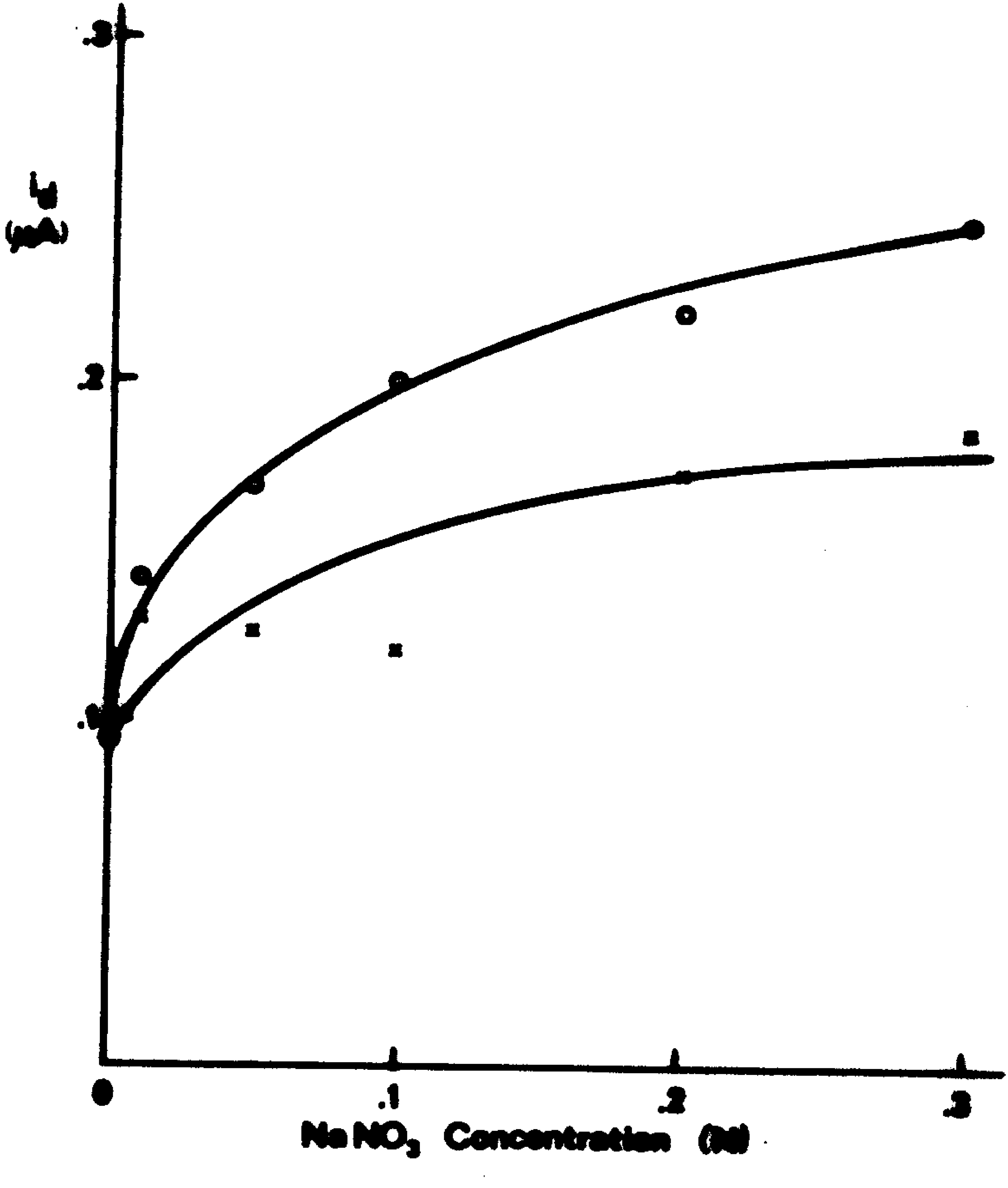


Figure 19

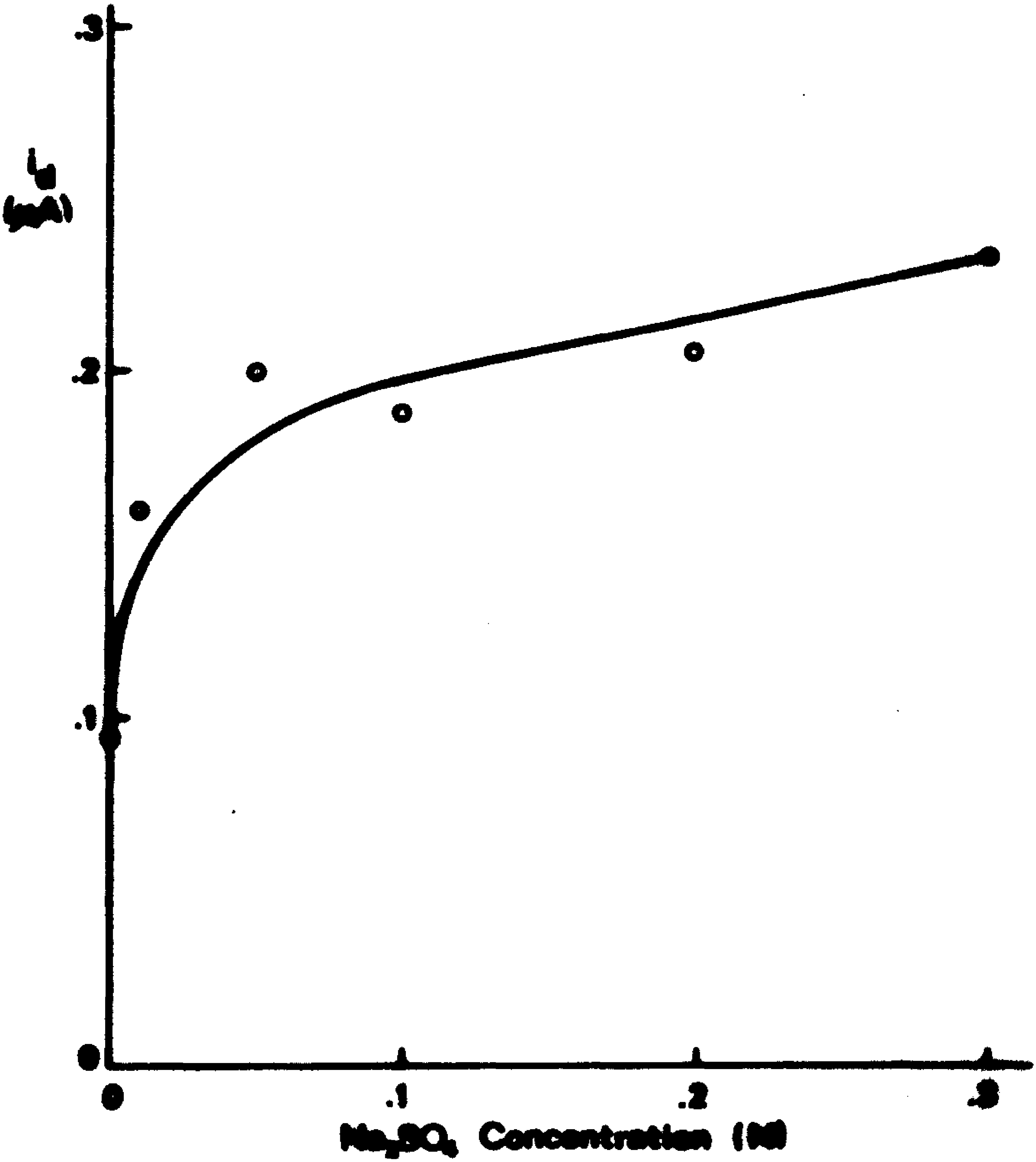


Figure 20

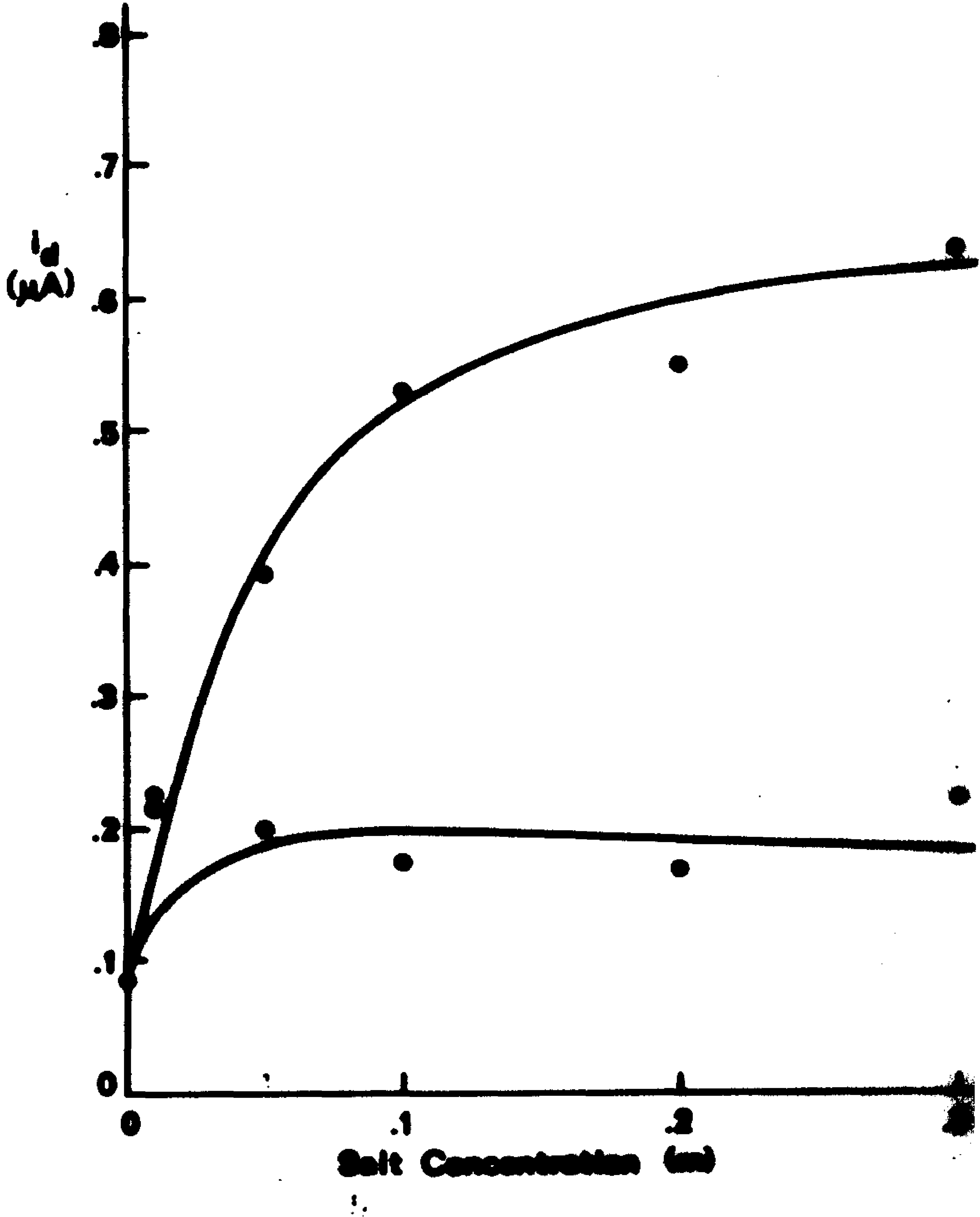
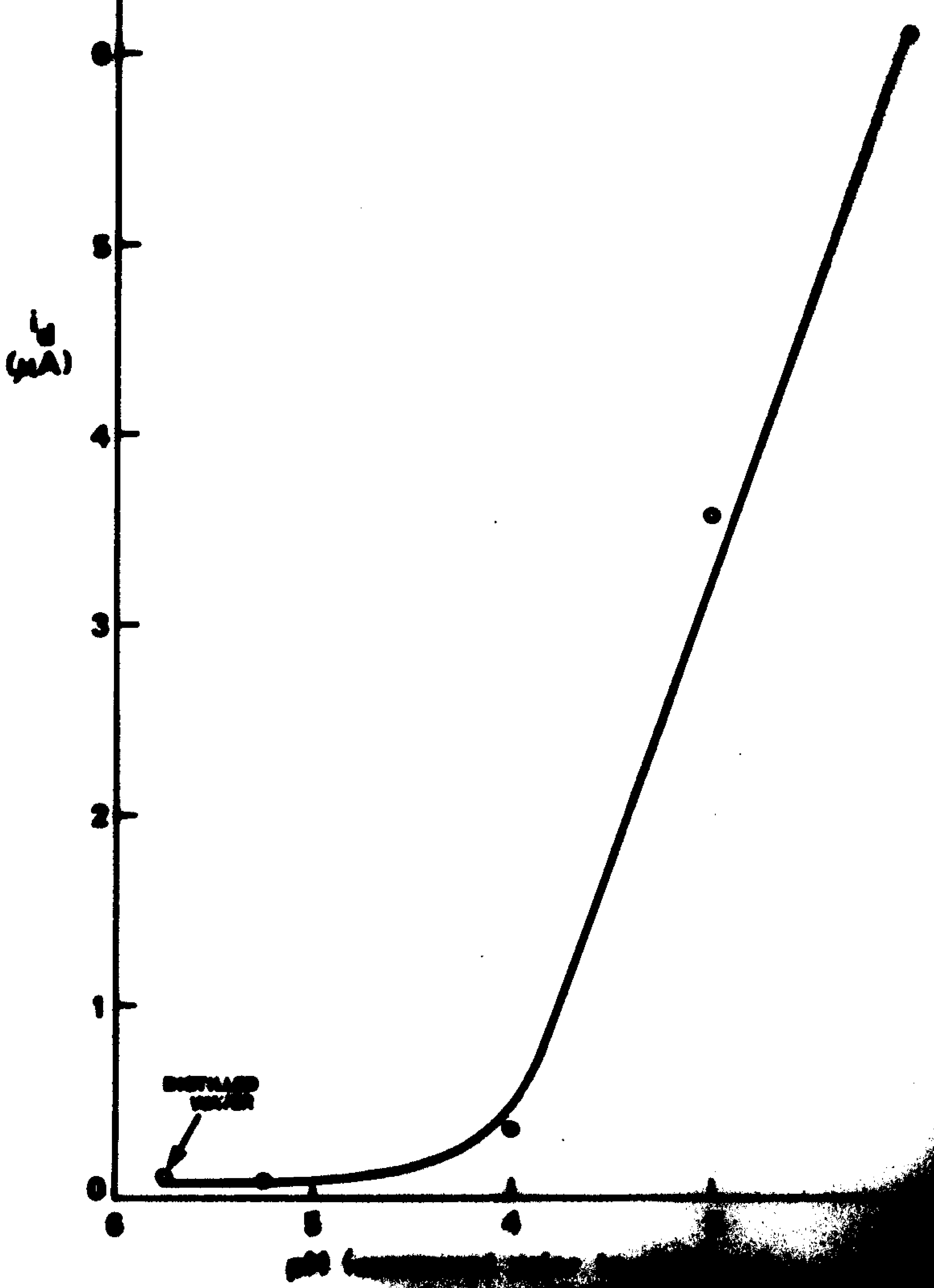


Figure 21



i_d
(μA)
0
1
2
3
4
5
6
DISTILLED WATER
6
5
4
pH

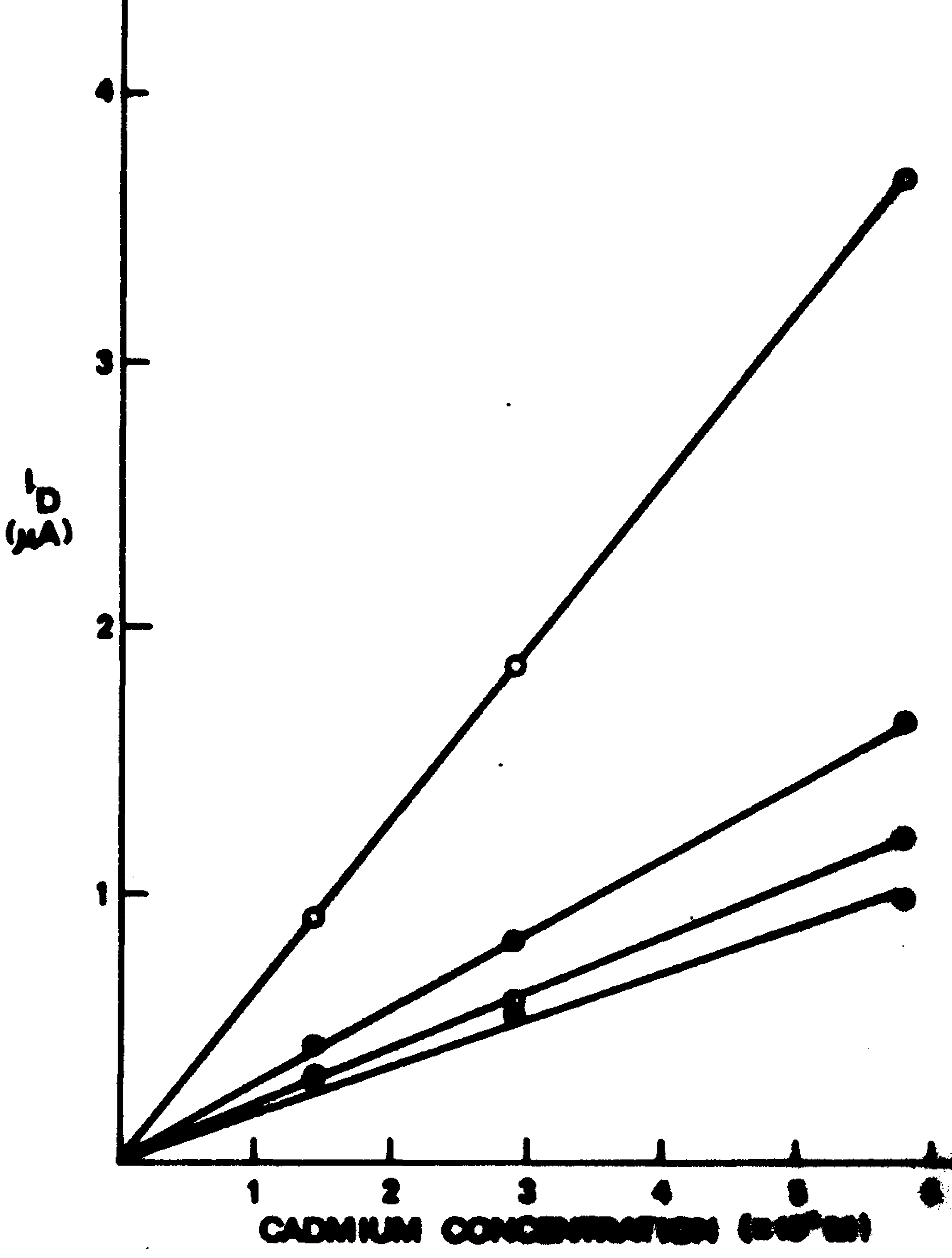
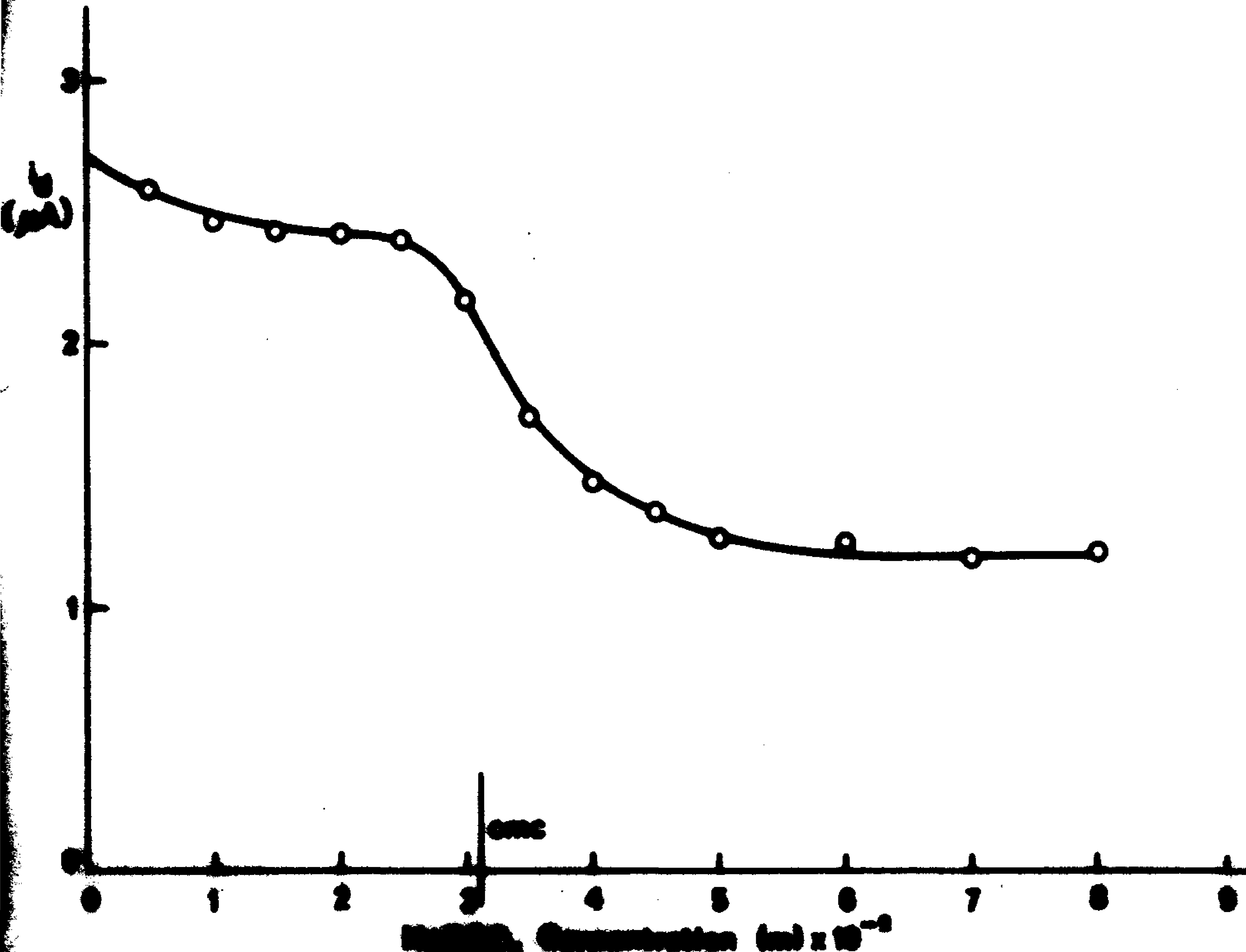
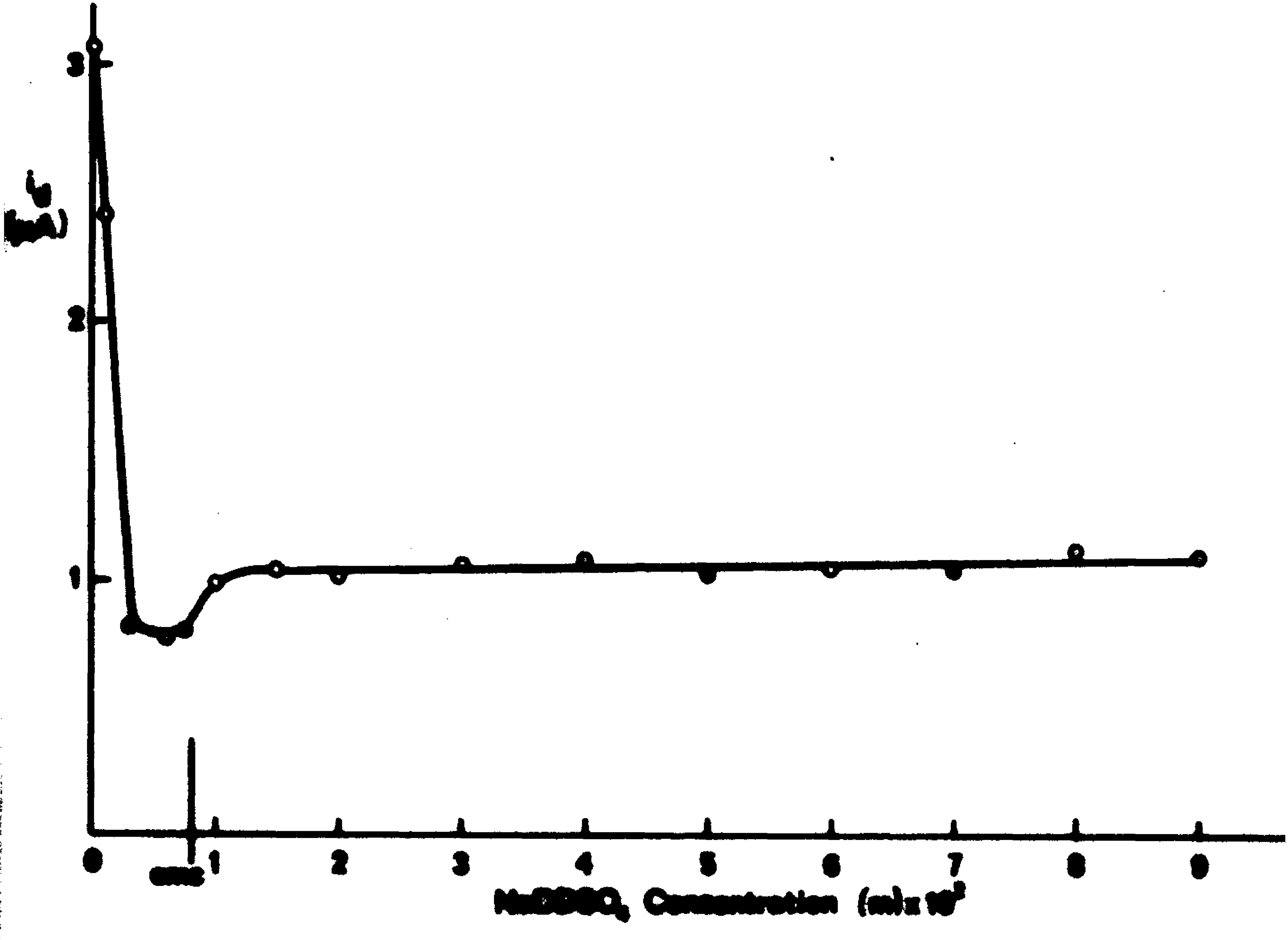


Figure [illegible]


i_d
(μA)
3
2
1
0
cmc
0
1
2
3
4
5
6
7
8
9
[illegible], Concentration (m) x 10⁻³


i_d
(µA)
3
2
1
0
cmc
1
2
3
4
5
6
7
8
9
NaDDSO$_4$ Concentration (m) x 10^2

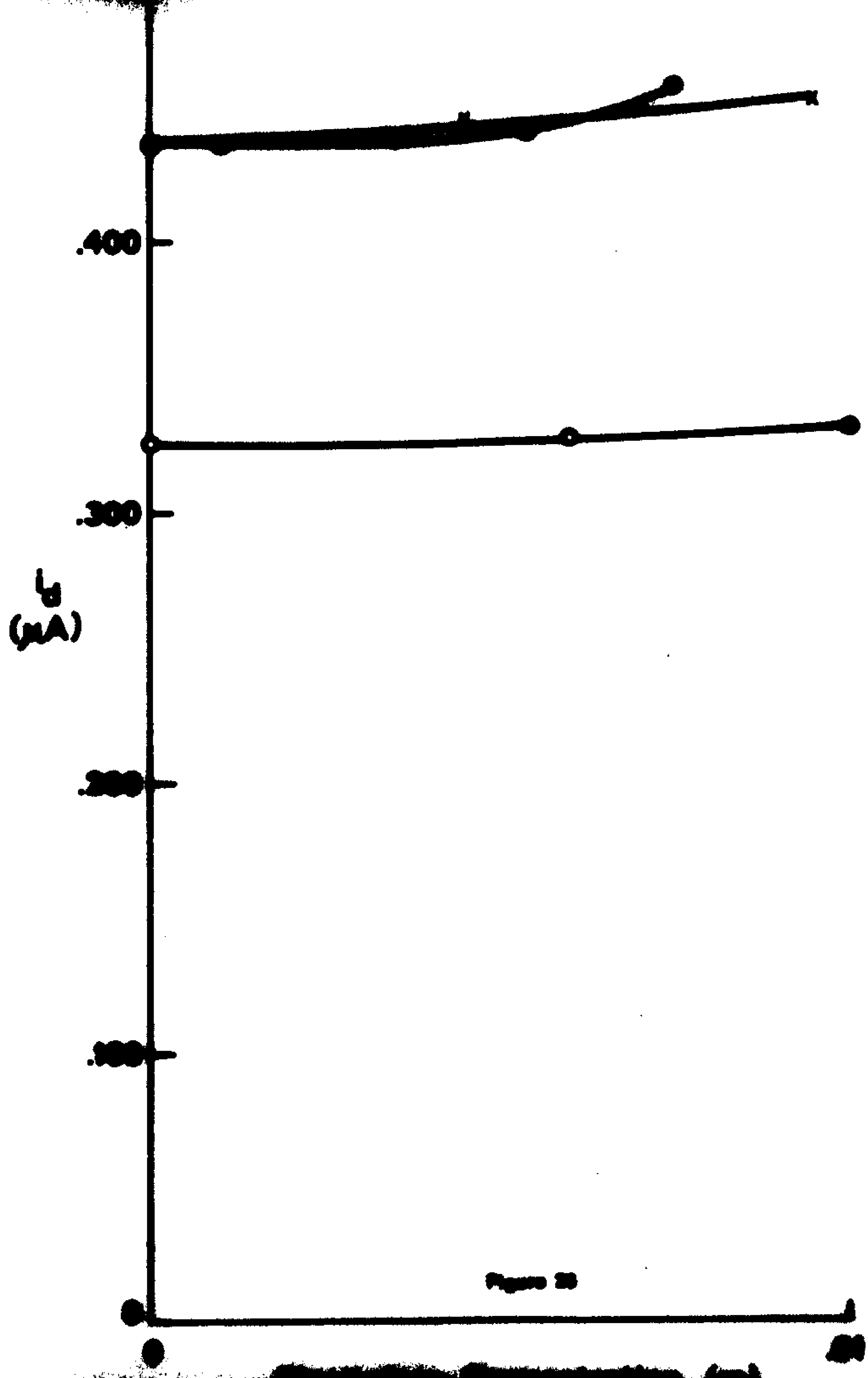


Figure [illegible]

CHAPTER III:

Proof that Divalent Cation Is On Or Near the Micelle Surface

In order to investigate the interaction of divalent cations with the micelle two different studies were undertaken: the first study involved using a monolayer model of the micelle surface in which changes in surface pressure and surface potential were followed as the concentration of divalent cation was changed. The second study involved following changes in divalent ion activity as the concentration of surfactant was changed.

A) Monolayer Study:

Although the study of the effect of monovalent cations on insoluble monolayers is well documented (83,84,85,86), little has been done on the effect of divalent cations (87,88,89). The effects of calcium and magnesium ions on a fatty acid soap is well illustrated by the precipitation of divalent acid soaps in hard water. Linear alkyl sulfate and sulfonates, being soluble in excessive hard water, do not show such a drastic effect with divalent metals.

In order to study a macromodel of a micelle, a monolayer of a linear alkyl sulfate is spread on a substrate containing 8.5×10^{-3}M NaCl solution in which the divalent metal concentration is varied. The NaCl is added to the substrate in order to present the monolayer with an environment that is as close to the actual environment seen by the micelle. By following changes in the surface pressure versus area and surface potential versus area isotherms, conclusions on the interactions of the divalent ion with the monolayer can be drawn.

The solution of sodium eicosyl sulfate ($NaC_{20}SO_4$) (Dr. Theodor Schuchardt GmbH and Co., Munich, Germany - purity 98-100%) was prepared by placing 9.37 milligrams in a 25 milliliter volumetric flask with six drops of distilled water and 17 milliliters of spectro-grade n-Hexane, and bringing it up to volume with reagent grade 2-propanol. The solution remained clear and stable throughout the experiment.

The substrate was prepared by dissolving 99.9% NaCl in water distilled from a Stokes' still. The 8.5×10^{-3}M NaCl solution was foamed in a 600 milliliter medium porosity sintered glass funnel; the foam was removed several times by sweeping the surface. The substrate gave adequately stable base line readings for both surface pressure and surface potential readings. A stock cadmium ion solution was prepared by dissolving 99.6% $CdCl_2$ (Baker Analyzed Reagent, Phillipsburg, N.J.) in distilled water. To prepare the necessary cadmium ion solutions, the stock solution was diluted with the sodium chloride solution. The acid and basic substrates were prepared by dissolving 96% NaOH (Baker Analyzed Reagent, Phillipsburg, N.J.) in distilled water. Both solutions were foamed as previously described.

A diagram of the experimental apparatus (84) for measuring surface pressure and surface potential is shown in figure 27. In the series of runs (figures 28 and 29) the cadmium concentration was varied by adding the necessary amounts of concentrated stock solution to the substrate. Several minutes were allowed for the complete mixing of stock solution with the substrates. The temperature was maintained at $25 \pm 1^{\circ}C$ with water circulated through a glass cooling coil immersed in the trough. All experiments were conducted inside a Faraday box.

The long chain sodium sulfate ($NaC_{20}SO_4$) solution was deposited onto the substrate surface by means of an Alga Micrometer Syringe (Burroughs Wellcome and Company, Tuckahoe, N.Y.). The substrate and film were retained in a fused silica trough (31.2 cm x 14.0 cm x 2.5 cm). A substrated volume of 1100 ± 50 milliliters was maintained in the trough. A Teflon movable barrier was used for the compression of the film.

The substrate surface was cleaned by dusting calcinated talcum powder onto it and cleaning it with the aid of a hollow glass tip connected to an aspirator as the surface was compressed.

Surface pressures were determined from surface tension measurements, which were made by suspending a sandblasted platinum blade (2.5 cm x 1.0 cm) from a transducer-amplifier (Model 311 A – Sanford Company, Waltham, Mass.). The transducer output was recorded continuously on a recorder.

Surface potentials were measured with an air ionizing electrode (a radium 226 source – U.S. Radium Corp., Morristown, N.J.) placed 1-2 millimeters above the liquid substrate surface and connected to a high resistance electrometer (Model 610 B – Keithley Instrument Inc., Cleveland, Ohio), a precision potentiometer and a saturated calomel reference electrode dipped into the bulk of the substrate. The radioactive electrode was connected to the input terminal of the electrometer with an Amphenol low noise graphitized shielded cable and connectors. The potential measurements were recorded continuously.

Results:

Figures 28 and 29 show the surface pressure (π) and surface potential (ΔV) versus area isotherms for the $NaC_{20}SO_4$ monolayer with varying cadmium ion concentration in a substrate of 8.5×10^{-3}M NaCl. A phase change in the monolayer is indicated in all curves at an area of 55 A^2/molecule. The monolayers formed in the absence of cadmium ion and those formed over the extremely dilute cadmium ion solution collapse at an area of about $18A^2$/molecule and a pressure of approximately 50 dynes/cm. With higher cadmium concentrations the monolayer consistently collapses at significantly lower film pressures. The surface pressure and surface potential versus area isotherms are in agreement with the sodium alkyl sulfate systems used by Stenhagen (90), Pethica and Few (91) and Thomas and Schulman (92). The surface pressure isotherm agrees with the one obtained by Goddard et al (85) for a sodium alkyl sulfate system although his surface potential does not enter the positive region at all.

In changing the substrate to an 8.5×10^{-3}M NaOH solution (figure 30), the surface pressure and surface potential versus area isotherms for the $NaC_{20}SO_4$ monolayer shows no significant changes over those obtained on the 8.5×10^{-3}M NaCl substrate. The only minor difference is in the surface potential isotherm in that the one obtained on the NaOH substrate is shifted to a slightly more positive potential at higher areas. When the substrate was changed to an 8.5×10^{-3}M HCl solution (figure 30) there was a marked change in the isotherms. The surface pressure versus area curve indicates a highly expanded film which collapses at 36 A^2/molecule and 21 dynes/cm. The surface pressure versus area curve shows a minimum between 30-40 A^2/molecule and increases sharply at an area of less than 20 A^2/molecule (not shown on figure 30). The potential does not rise above -75mV.

The pH of the substrate solutions which were used in the study of the interaction of cadmium ion with the $NaC_{20}SO_4$ monolayer varied from 5.5 to 5.0. By comparing the isotherms obtained on an acid and base substrate to that obtained on the NaCl substrate, it is concluded that in the above pH range there was no competition from hydrogen ions and that the monolayer is essentially completely ionized. This was the same conclusion reached by Thomas and Schulman (92).

With the cadmium ions added to the substrate, there is no interaction with the $NaC_{20}SO_4$ monolayer until the ionic concentration reached $3x10^{-5}$M (figure 29). A sharp drop in the surface pressure necessary to collapse the monolayer is noted. As the cadmium ion concentration in the substrate is increased, the surface pressure versus area isotherm shows the properties of a more expanded monolayer. The surface potential isotherm shows a trend of increasing potentials at the higher areas and a decrease in potential at the lower area as the cadmium ion concentration increases.

The sharp drop in the collapse pressure of the $NaC_{20}SO_4$ monolayer as the cadmium concentration is increased, indicates that the divalent cation is interacting with the monolayer, neutralizing its charge and allowing the film to collapse more easily. The monolayer becomes more expanded also indicating an interaction between it and the cadmium.

The slight changes in the surface potential isotherms is also indicative of an ion-monolayer interaction.

A number of divalent cation studies were previously performed on alkyl sulfate and sulfonates (90,92,93). The lack of an effect of barium ion on a sodium docosyl sulfate monolayer was noted by Stenhagen (90). Thomas et al (92) found the absence of an effect of polyvalent metal ions on an alkyl sulfate monolayer when compared to their effect on fatty acid monolayers (89,94); although at high concentrations a strong interaction is indicated. In the work of Dreher et al (93) on alkyl sulfonates, the same conclusions were drawn; there was no drastic change in the isotherms of the monolayers when divalent and monovalent cations are compared.

The analogy between the monolayer study and the cation-micelle interaction taking place in solution has its limits, namely, the monolayer can be compressed at will while this is not the case with the micelle. An application of the Gibbs equation to surface tension versus ln of concentration of long chain sodium alkyl sulfate solutions, leads to values in the order of 40-80 A^2/molecule. Using measured micellar dimensions (24,29) the area per molecule for the $NaDDSO_4$ is about 65 A^2/molecule in the micelle. It is clear that in this region, the presence of cadmium ion in the substrate does not markedly affect the surface isotherms of the $NaC_{20}SO_4$ monolayer although a slight change in the shape of the surface pressure isotherm and a small increase in surface potential is measured.

Thus, from the monolayer study it is seen that the cadmium ions have a minor effect on the monolayer, hence, presumably, a minor effect on the micelle structure. It is also concluded that since there is a slight interaction, the cadmium ions must be close to the surface of the monolayer; thus by analogy, close to the surface of the micelle. In order to further support this, emf studies were undertaken.

B) Electromotive Force Study:

The determination of the activity of ions with varying surfactant concentration will give some insight into the binding of these ions to the micelle. Botre' et al (95,96) using membrane electrodes of both negative and positive type determined cation activity in various anionic and cationic surfactants. The degree of association between the micelle and the counterions were determined from experimental activity coefficients, indicating that the strong electrostatic field of the charged micelle tends to bind a large fraction of the counterions. Shedlovsky et al (97) and Feinstein et al (98) found that there is a break in the activities of the counterions of sodium alkyl sulfates after the cmc, and that the activity levels off somewhat (97). Pearson et al (99) found that the activity of the sodium ion increased as the concentration of calcium ion increased and atrributed this to the binding of the divalent ion to the micelle displacing two sodium ions for each ion bound.

It would be expected that if the cadmium ions adsorb on or interact with the surface of the micelle, the activity of the cadmium ions will drop and become relatively constant above the cmc. The activity of cadmium ions was studied in a series of solutions containing different cadmium nitrate concentrations and varying surfactant concentrations. A cadmium ion specific electrode (Orion Research Inc., Cambridge, Mass.) was used in conjunction with a silver-silver chloride reference electrode; potentials were measured in a stirred solution at 25±0.1°C with a Leeds and Northrup Type K potentiometer. E^o values for the electrode system, in effect a calibration of the solid state and reference electrodes, were determined with standardized cadmium nitrate solutions in distilled water and from published values of the activity coefficient (100). The EMF values which were obtained for the surfactant solutions were then used to calculate the activities of the cadmium ion in solution by using the Nernst equation.

Figures 31 and 32 are plots of the Cd ion activity vs $NaDDSO_4$. In these solutions the concentration of cadmium ion was held constant (at 1×10^{-4}M in figure 31) while the $NaDDSO_4$ concentration was varied. In the 1×10^{-4}M Cd in experiment there is a sharp fall off in activity to a substantially constant value at concentrations slightly above the cmc. The activity drops from 1×10^{-4} to 2.7×10^{-7} as the $NaDDSO_4$ cmc goes from 1×10^{-3}M to 8×10^{-2}M. The same effect is noted when cupric ion was used (figure 33). The cupric ion concentration was held constant at 2×10^{-4}M while the $NaDDSO_4$ concentration was varied. The cupric activity, calculated using the same method as was the cadmium activity (100), drops from 2.2×10^{-4} to about 9.5×10^{-7}. In the cadmium determinations no precipitation was noted in the solutions even when a cadmium ion concentration of 1×10^{-2}M is mixed with an 8×10^{-2}M $NaDDSO_4$ solution and was left standing for several days. The same results were observed with the cupric ion determination although only one cupric concentration was used. Pearson (99) indicated that a 5 x 10^{-3}M calcium ion concentration will cause precipitation of the calcium salt of dodecylsulfate when mixed with a 7 x 10^{-2}M NaDDSO_4 solution.

From the above it can be concluded that the divalent metal ion (either cadmium or copper) is associated with the micelle surface and is not available as the free ion in solution as indicated by the large drop in activity. It can also be seen that the cadmium ion does not interact strongly with the alkyl sulfate since no precipitation is noted when high concentrations of cadmium and NaDDSO_4 are mixed.

From the results obtained in these two studies, the basic premise that the divalent cation is on the surface of the micelle and that it does not change the structure of the micelle, is substantiated. Thus the polarographic method is valid as a technique for the determination of micellar diffusion coefficients.

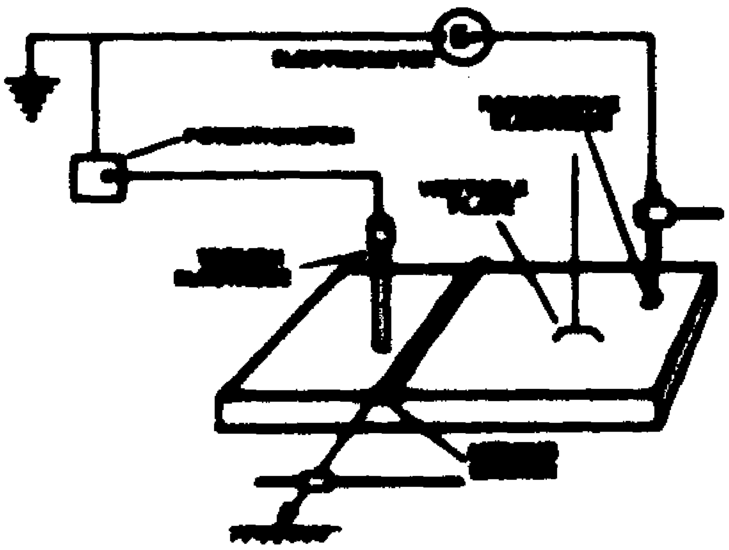
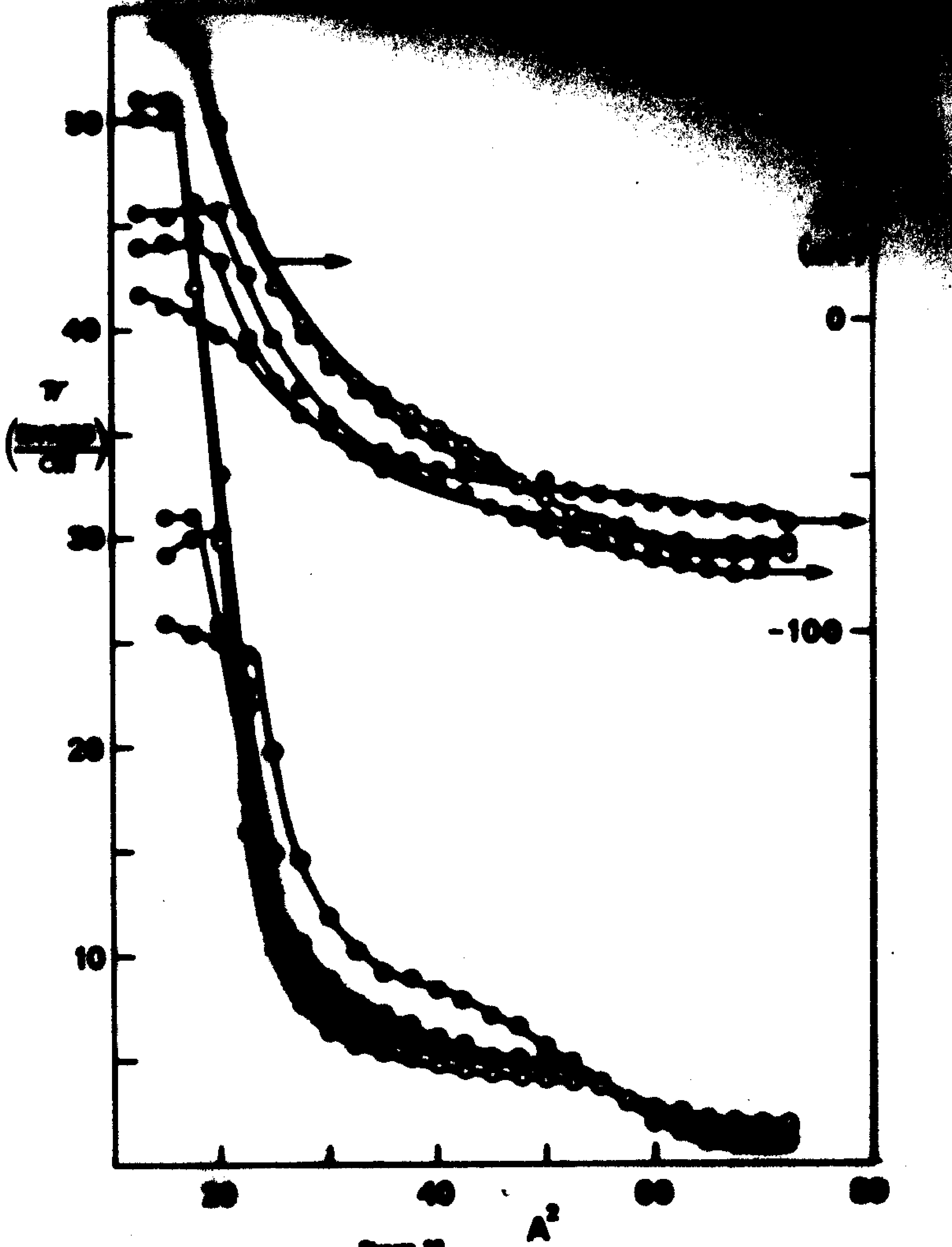


Figure 27



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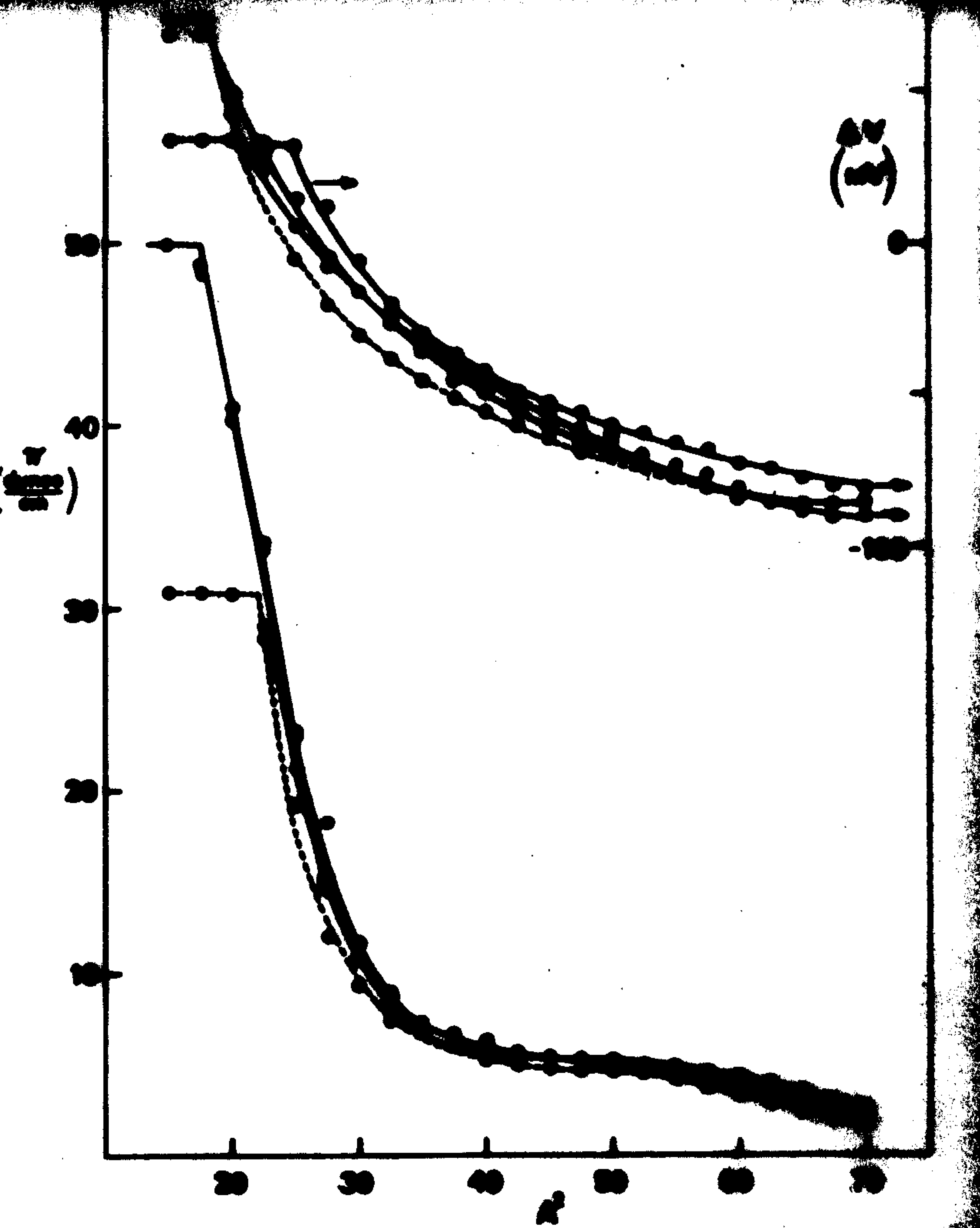


γ (dyne/cm)
50
40
30
20
10
20
30
40
50
60
70
Å²
ΔV (mV)
-100

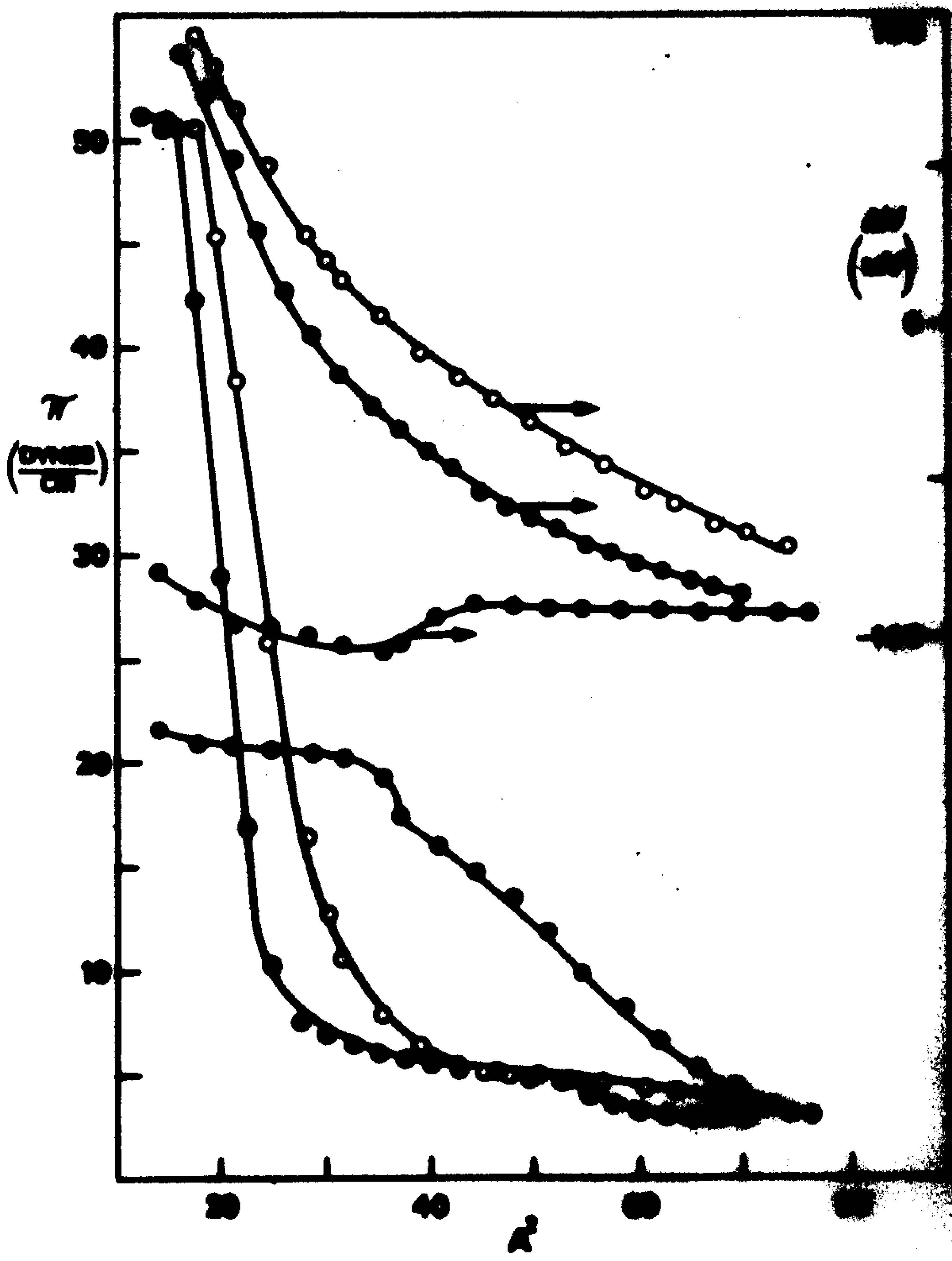
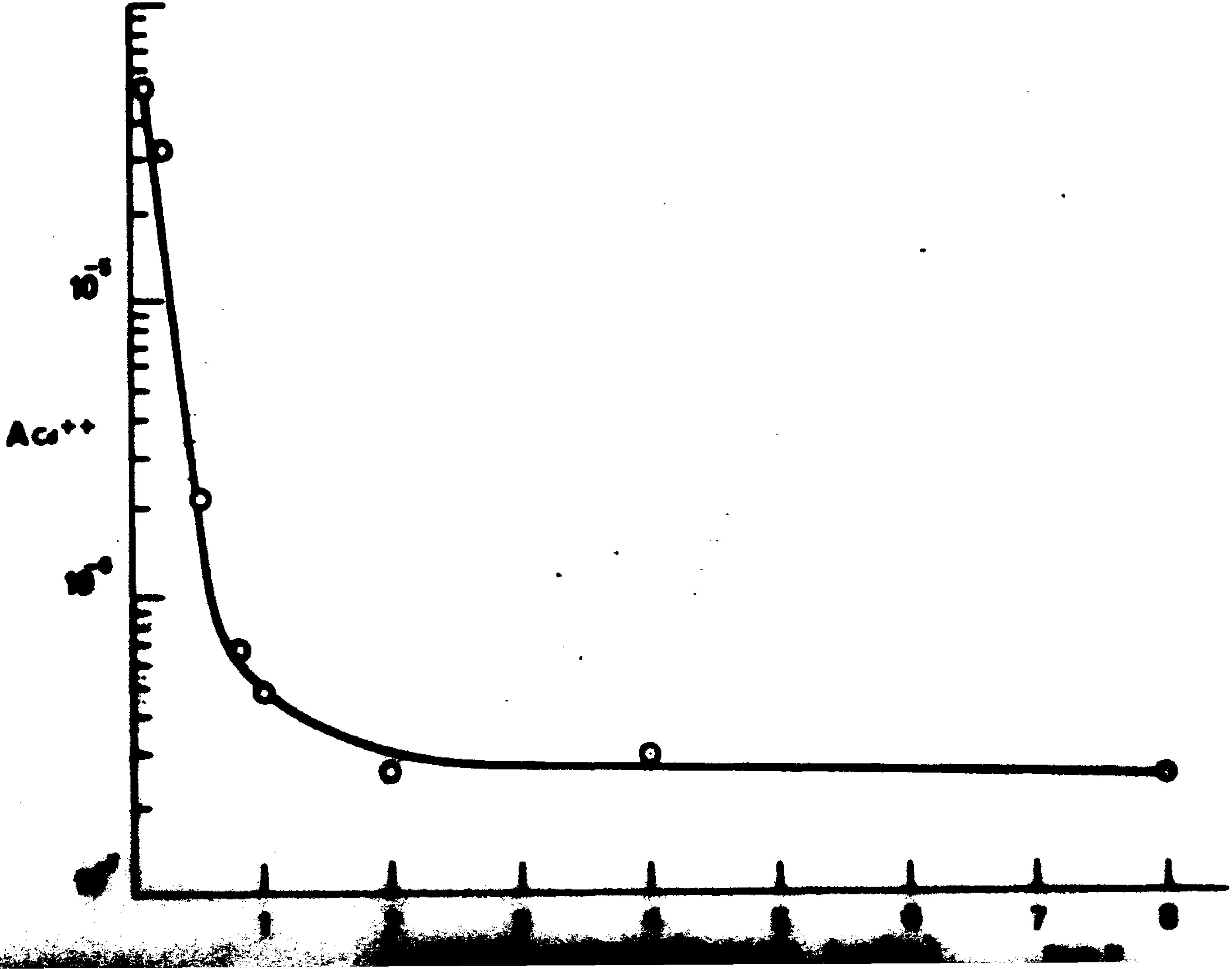
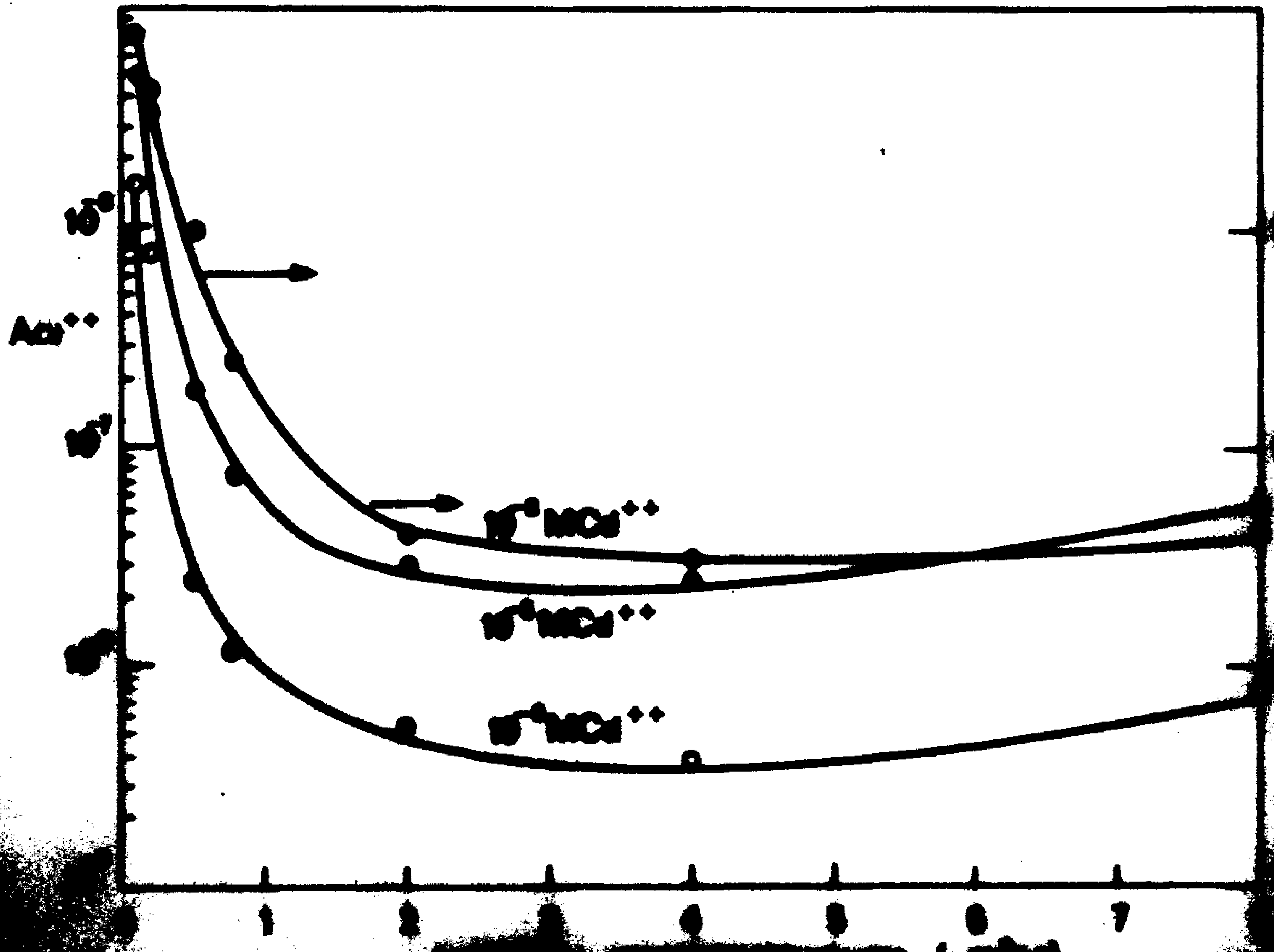
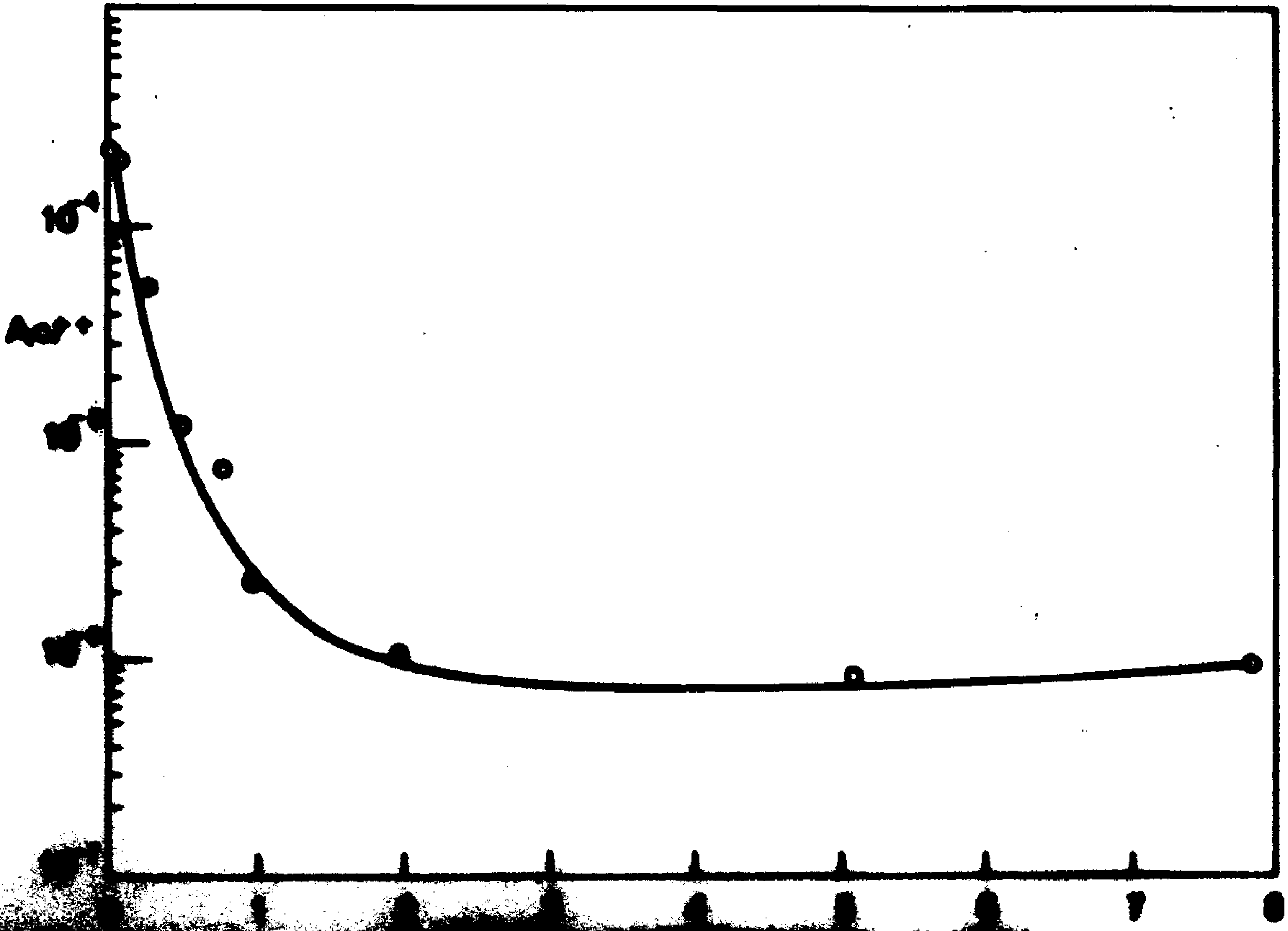


Figure 20


10^{-5}
Ag^{++}
10^{-6}
1
7
8

Acu++
10^{-6}
10^{-7}
M Cu++
M Cu++
M Cu++
0
1
2
3
4
5
6
7


10⁻⁴
Acr+
10⁻⁵
10⁻⁶
1
2
3
4
5
6
7
8

CHAPTER IV:

Summary and Conclusions

A survey of the chemical literature reveals many techniques for the determination of diffusion coefficients. Some of these methods involve: the following of a spreading boundary optically, allowing a radioactive species to diffuse from an open ended capillary tube into a non-radioactive bulk solution, and following of the diffusion of a species across a permeable membrane. These methods are usually experimentally tedious and involve rather complex mathematics to eventually determine the diffusion coefficients. When applied to surfactant solutions the overall difficulties tended to increase.

The polarographic method is a standard analytical technique using readily available, reliable instrumentation allowing for measurements of a diffusion current of a reducible species. The measured diffusion current is related to the diffusion coefficient of the species by the Ilkovic equation. In the application of polarography to the determination of micellar diffusion coefficients, a reducible species must be associated with the micelle, either adsorbed on the micelle surface or solubilized within the micelle. When the species is reduced, a diffusion current which is related to the micellar diffusion coefficient is obtained.

An equation which relates the micellar diffusion current, i_{dm}, and the current obtained from an equal concentration of ionic species, i_d, to their respective diffusion coefficients was derived with a correction factor which takes into account the spherical nature of the drop and the differences in the drop times:

$$(i_{dm}/i_d)^2 D \times 1.14 = D_m$$

Determination of the proper tagging cation was accomplished by first running a polarogram of the untagged sodium alkyl sulfate and then finding an area where the current is relatively constant over several tenths of volts. A divalent cation which is reduced in this area is chosen; the cadmium ion fit this criteria in this work. A polarogram of the surfactant was run and a clear unobstructed plateau for cadmium was obtained.

The dissolved oxygen, which proved to be an initial problem, was removed using a specially designed degassing disc which simultaneously broke the foam that was produced when prepurified nitrogen was bubbled through the test solution. No excess supporting electrolyte was necessary as it was proven that the unassociated ions left in solution were sufficient to significantly reduce any migration current.

Of the two methods of tagging the micelle, only one proved totally acceptable. The solubilization of the cadmium salt of a fatty acid into the micelle, although theoretically sound, had one major drawback. The excess sodium ions from the sodium alkyl sulfate caused some of the cadmium to exchange with the sodium ions. Thus some doubt is cast on the solubilization method as a way of tagging the micelle.

The second method makes use of the large electrostatic field on the micelle. If a divalent cation is placed in an anionic micellar solution, the cadmium ion is adsorbed on the micelle surface due to coulombic attraction. Thus, by adding a known amount of cadmium ion to solutions of $NaDSO_4$, $NaDDSO_4$ and $NaTDSO_4$, their micellar diffusion coefficients were easily calculated from the measured diffusion currents.

By using monolayer and electromotive force studies, it was proven that the cadmium ion is found on the surface of the micelle and does not significantly alter the micelle's structure. The lack of a drastic change in the surface pressure and surface potential isotherms of a $NaC_{20}SO_4$ monolayer (used as a macromodel of the micelle surface) which was spread over a substrate of 8.5×10^{-3}M NaCl in which the cadmium ion concentration was varied shows that there is no major interaction between the monolayer and the cadmium ions; although it was concluded that, from minor changes in the surface pressure and surface potential isotherms, the cadmium ion is close to the surface of the monolayer. A large decrease in the activity and the eventual leveling off of the activity after the cmc of the cadmium ion as the $NaDDSO_4$ concentration was increased shows that the cadmium ion is being adsorbed on the surface of the micelle. A lack of precipitation when the cadmium and $NaDDSO_4$ concentrations were both large shows a lack of any strong interaction which will disrupt the micellar structure.

It can then be concluded that the polarographic method for the determination of micellar diffusion coefficients is a valid method provided the proper tagging agent is used. It is also concluded that for the sodium alkyl sulfate systems, the cadmium ion is an excellent tagging agent in that it will be preferentially found on the micelle surface without changing the micelle structure. The system developed in this thesis is valid for solutions of anionic surfactants which are neutral or slightly acidic. In basic solutions the cadmium ion is removed by the formation of cadmium hydroxide. Thus, although the method developed is a general method, it is limited by the chemistry of the ions involved.

APPENDIX 1

CALCULATION OF CORRECTION FACTOR FOR DIFFUSION COEFFICIENT CALCULATION

The corrected Ilkovic Equation is:

$$i_d = 607nD^{\frac{1}{2}}m^{2/3}t^{1/6}(1 + AD^{\frac{1}{2}}t^{1/6}/m^{1/3})$$

where A has a numerical value between 17 (67) and 36 (66). An average value of 28 will be used in the following calculation. The diffusion coefficient used for the micelle will be $9 \times 10^{-7}\text{cm}^2/\text{sec}$ and for the cadmium ion a value of $7 \times 10^{-6}\text{cm}^2/\text{sec}$ will be used. The two correction terms become:

for the micelle: $$1 + \frac{28(9\text{x}10^{-7})^{\frac{1}{2}}(3.8)^{1/6}}{(1.7)^{1/3}} = 1.028$$

for the cadmium ion: $$1 + \frac{28(7\text{x}10^{-6})^{\frac{1}{2}}(4.3)^{1/6}}{(1.7)^{1/3}} = 1.078$$

Thus, $$\frac{i_{dm}}{i_d} = \left(\frac{D_m}{D}\right)^{\frac{1}{2}}\left(\frac{t_m}{t}\right)^{1/6}\left(\frac{1.028}{1.078}\right)$$

Solving for the micellar diffusion coefficient and substituting the proper values of the drop times:

$$D_m = \left(\frac{i_{dm}}{i_d}\right)^2 \text{x}D\text{x}\left(\frac{4.3}{3.8}\right)^{2/6}\left(\frac{1.078}{1.028}\right)^2 = \frac{i_{dm}}{i_d}^2 D\text{x}(1.04)(1.048)^2$$

Thus the diffusion coefficients must be multiplied by a factor of 1.14. The corrected equation for the calculation of the micellar diffusion coefficients is listed as 42a.

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