UNITED STATES
DEPARTMENT OF THE INTERIOR

EFFECTS OF IMPRESSED ELECTROSTATIC FIELDS ON THE SALT WATER/AIR INTERFACE

BY

TRACOR, INCORPORATED
AUSTIN, TEXAS

MARCH 3, 1849

OFFICE OF SALINE WATER

RESEARCH AND DEVELOPMENT PROGRESS REPORT NO. 67

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FOR

OFFICE OF SALINE WATER

CHARLES F. MACGOWAN, DIRECTOR

W. SHERMAN GILLAM, CHIEF, DIVISION OF RESEARCH

GEORGE F. MANGAN, JR., CHIEF, BRANCH OF
ORGANIC AND BIOLOGICAL CHEMISTRY

SEPTEMBER 1962

FOREWORD

This is the sixty-seventh of a series of reports designed to present accounts of progress in saline water conversion with the expectation that the exchange of such data will contribute to the long-range development of economical processes applicable to large-scale, low-cost demineralization of sea or other saline water.

Except for minor editing, the data herein are as contained in the reports submitted by Tracor, Incorporated under Contract No. 14-01-001-200, covering research carried out through June 30, 1962. The data and conclusions given in this report are essentially those of the Contractor and are not necessarily endorsed by the Department of the Interior.

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I. INTRODUCTION

This report covers all work completed under Contract No. 14-01-001-200 during the period 5 April 1960 to 30 June 1962.

The object of this contract was to study the influence of impressed electrostatic fields on the surface excess (or deficiency) of NaCl solutions up to sea water concentrations (3.5%). The surface concentration was investigated using surface tension measurements obtained with a surface energy balance in fields up to ±6700 v/cm. An attempt was made to measure directly the surface concentration change by using a skimming apparatus. It was concluded that surface concentration changes of NaCl solutions due to applied electrostatic fields, although qualitatively detectable, are too small to be measured quantitatively and are therefore unsuitable for practical desalination processes. Some methods other than the ones mentioned above were tried and led to the same conclusion.

A paper arising from work with the surface energy balance was published in Science 135, 791 (1962), a more thorough account being scheduled for publication in the September 1962 issue of the Journal of the Electrochemical Society. The successful application of the skimming apparatus to the direct measurement of surface concentration of surface active substances was described and published in Nature, 194, 439 (1962).

II. SURFACE ENERGY BALANCE

A. Background

It has long been known that the concentration of dissolved substances deviates from the bulk concentration in the surface region, increasing for surface active materials like organic soaps and decreasing for surface inactive materials like ionized electrolytes. This decrease in concentration near the surface of salt solutions has been proposed as a possible method of recovering pure water from saline water. Attempts to do this, by skimming or foaming, have been unsuccessful.

In addition to the changes in concentrations at the surface, there also exists a potential drop across the air/water interface. This potential drop (at least for ionized solutes) must be closely associated with the concentration gradient. The possibility therefore arises that both the potential drop and the concentration gradient at the interface may be changed appreciably by the application of external electrostatic fields. These changes can be studied either directly by skimming experiments or indirectly by surface tension measurements.

The object of the first phase of this research program, of which this is the final report, was to determine the effects of applied electrostatic fields on the surface tension of salt solutions, and to correlate these to surface concentration changes.

For uncharged particles, changes in surface concentration are related to surface tension through the Gibbs adsorption Equation (1). For charged particles, this equation has to be modified to take into account the specific properties connected with their strong electrostatic fields. Attempts have been made in this direction by Lewis (2). A more direct approach has been used by Wagner (3) and was further developed by Onsager and Samaras (4) and by Falkenhagen and Schmutzer (5). No direct measurements of surface concentrations are available to check the validity of these theories.

According to Kamienski (6), the potential drop across the air/water interface leads to a field of the order of 10^7 v/cm. If this is true, then it is very unlikely that it would be possible to change the surface concentration of charged particles by externally applying an electrostatic field of, say, 10^4 v/cm. On the other hand, Barnett (7) and Guastalla (8) were able to show that his is not necessarily so. These experiments, however, still did not allow quantitative treatment.

B. Experimental

Apparatus

The surface energy balance used in this work is essentially that of Allan and Alexander (9), slightly modified so that a potential can be applied across the air/solution interface. A rigid and heavy brass frame, resting on three leveling screws, serves as support for both a 25 x 15 x 4.5 cm Pyrex glass trough and an aluminum balance beam (Figure 1). The electrodes, 0.1 x 9 x11 cm, are made of plate Monel, to resist the corrosive actions of the salt water. A hole is drilled into the bottom of the glass trough and the frame to allow mounting of the "water electrode." A water-tight seal is obtained with a Teflon gasket. The "air electrode" is supported by an insulating Lucite plate directly above the water electrode.

The air gap between the solution surface and air electrode was 1.2 cm. The balance beam is supported 20 cm above water level by two diamond points which pivot on two microscope slides resting on the frame. The slides are replaced frequently to avoid formation of grooves by the cutting action of the diamonds. The beam has two notches to allow calibration of the balance. A rigid wire with a Pt wire prong reaches down into the solution. A small mirror attached to the beam projects a light beam onto a scale, 230 cm away, thus allowing accurate observation of balance deflections.

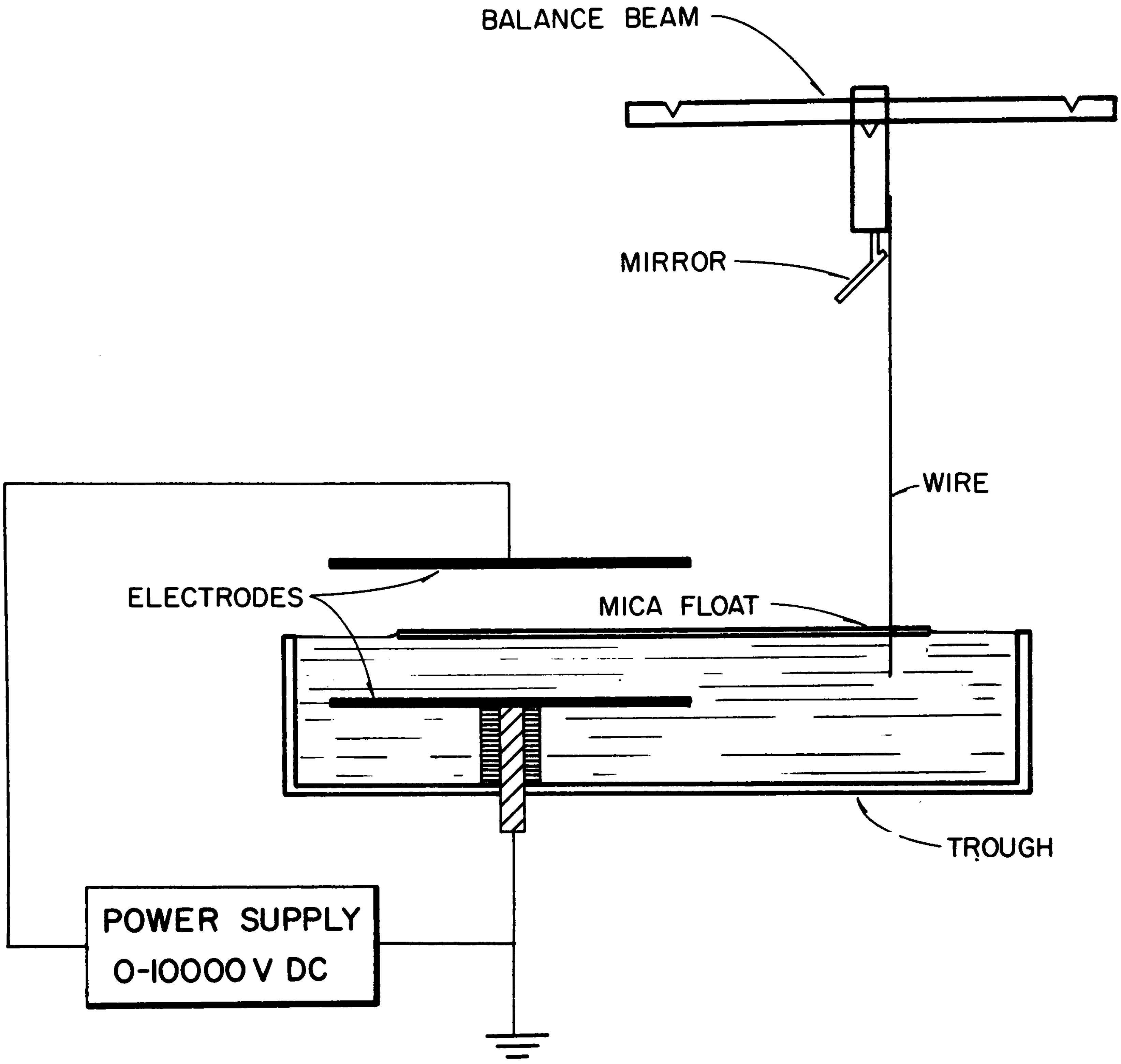

Fig. 1 SCHEMATIC OF SURFACE ENERGY BALANCE

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A thin sheet of mica, generally 7.3 x 12.8 cm, floating on the solution, serves as indicator. It has two holes on one end, large enough for the Pt wire prong of the balance body to move in and out freely. The other end of the mica float projects 4.5 cm into the space between the electrodes. Thus a change in surface tension between the electrodes as compared to the area outside the electrodes results in a force on the mica float which is indicated by a deflection of the balance beam.

The voltage applied across the interface was taken from a 0-10,000 v dc power supply. Water electrode, frame and balance beam were grounded at all times. The balance arrangement had a sensitivity of 0.052 dynes cm^{-1} per cm of deflection, as determined by calibration with small weights (pieces of platinum wire) placed directly on the balance beam.

Application of an electric field leads to an attractive force between the air electrode and balance beam. This force was blocked by separating the two with a mica sheet, perpendicular to the air/solution interface, reaching into the solution to obtain effective grounding, and placed as close to the electrodes as possible without arcing. A slot was cut into the shield so as to allow free movement of the mica float.

In measurements of this kind, contamination of the air/solution interface with dust and other foreign substances must be minimized. This was done by keeping the whole experimental setup covered with a Lucite hood. Float and balance beam were removed frequently and the solution surface cleaned by sweeping with mica barriers several times over the whole surface, including the edges of the trough.

Procedure

At least two forces other than surface tension changes are indicated by the balance and have to be corrected for to obtain the desired effect of the field on surface tension.

First, application of an electric field across the air/solution interface raises the solution underneath the air electrode. The resultant forces on the mica float are represented schematically in Figure 2. The mica float, the edge of which lies between the two plates, becomes tilted. This results in a force, G, on the balance body, in addition to the force due to a change in surface tension. G can be calculated to a first approximation as the force of gravity, mg, projected onto the float, i.e.,

$$G = mg \sin \beta \tag{1}$$

with

$$\sin \beta = h/l \tag{2}$$

where

β = angle of tilt
l = length of float
h = hydrostatic overhead due to the field

The force, G, can be accounted for by keeping h and l constant (constant field strength, constant length of float) and varying m.

Second, it was observed that the balance deflection caused by a mica sheet, floating on a salt solution with an electric field impressed across the air/solution interface, is dependent on the position of the "working edge" of the float in the field. This is due to electrostatic attraction of the mica float, which must be proportional to the area of the part of the float in the field. Again, this area is proportional to the mass of the float in the field.

The experimental procedure used to make both corrections is based on the following: Consider a rectangular float of fixed dimensions (Figure 3) floating on a salt solution with area ABDC inside a perpendicular and constant electric field. There are four forces acting on the float. A surface tension γ' is effective on the "working edge" $\overline{AB}$ and a surface tension γ on the "balance edge" $\overline{GH}$ of the float ($\overline{AB} = \overline{GH}$). The force we are interested in is

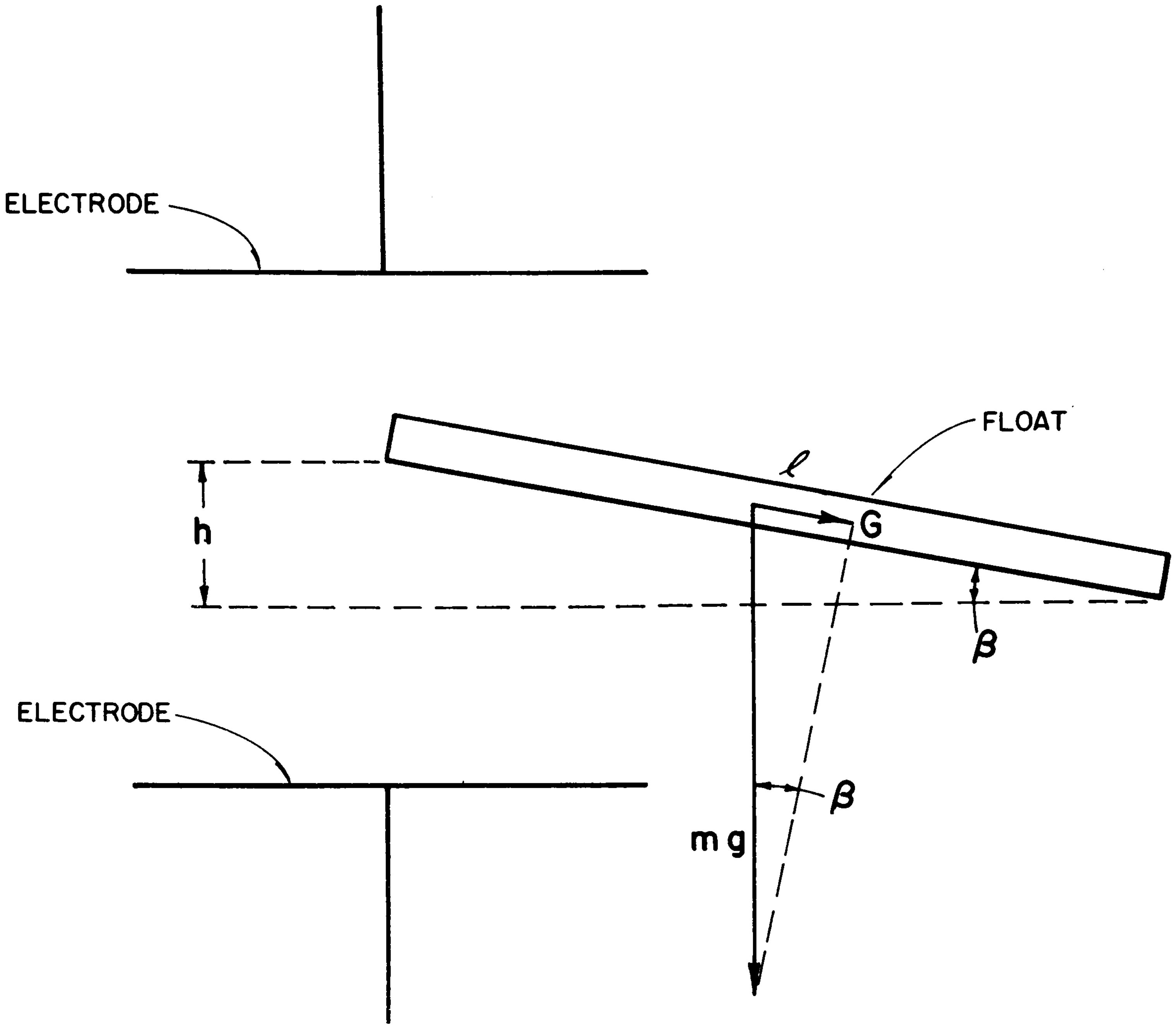

Fig.2 - SCHEMATIC OF HYDROSTATIC FORCE ON FLOAT

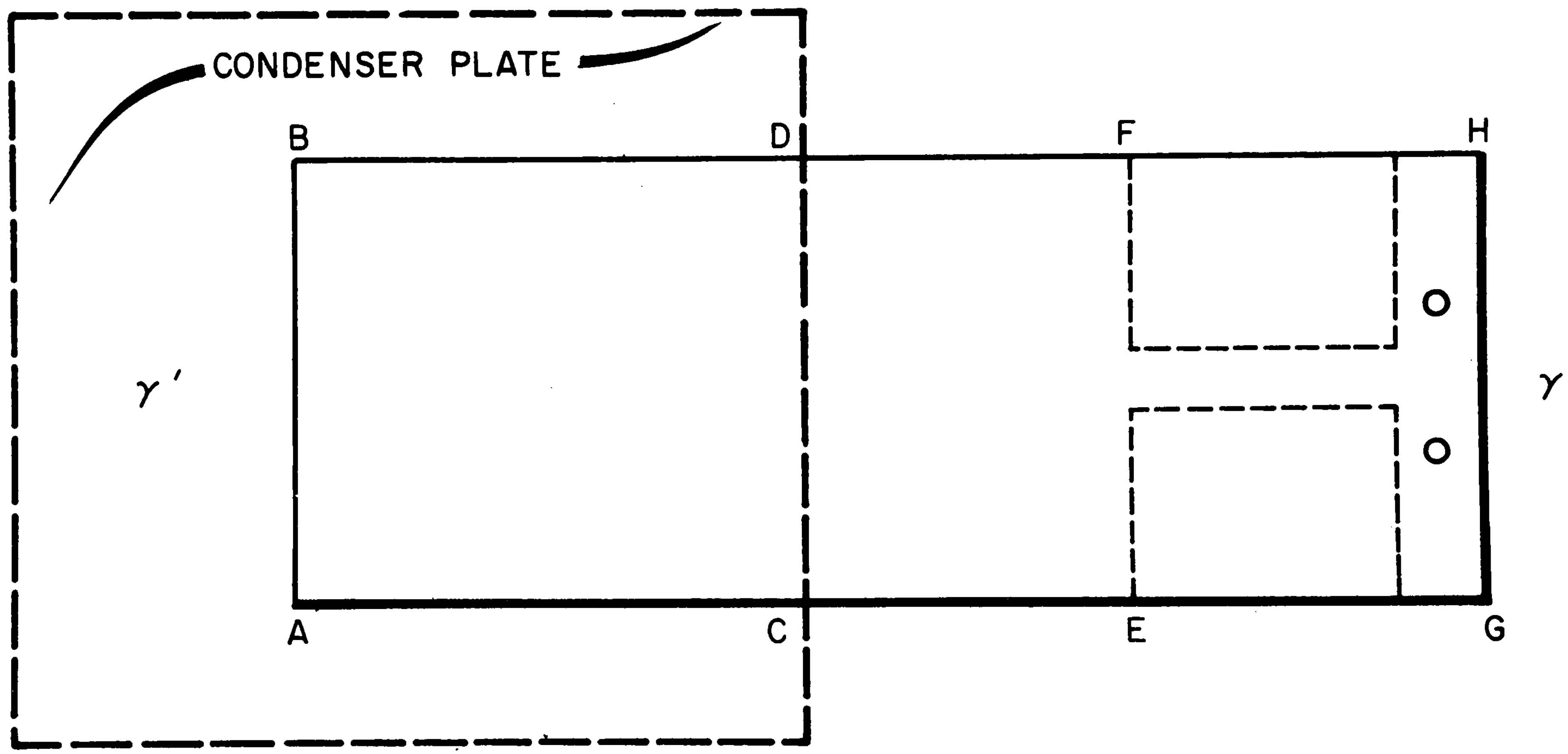

Fig. 3-GEOMETRICAL VIEW OF FLOAT

$\gamma' - \gamma = \Delta\gamma$. Due to the hydrostatic head developed in applying the electric field, there is a force of gravity which is proportional to the mass of the float. On the ABDC portion of the float a charge is induced by the field, resulting in a force which is proportional to the area of the float between the electrodes. Since the float is of constant thickness, this area is proportional to the mass of that part of the float.

We now cut the float as indicated by the dotted line shown in Figure 3, leaving a small bridge between the front part of the float, ABFE, and the rear part at GH. We assume that the width of the bridge is small, as compared to the balance edge $\overline{GH}$. The effects of the surface tension difference, $\Delta\gamma$, and the electrostatic force are not changed by this procedure, provided that area ABDC < ABFE. We do, however, change the mass of the float. Making ABFE successively smaller, keeping ABDC < ABFE, and plotting balance deflection vs mass of float, shows the dependence of the force due to effects of the hydrostatic head on the mass of the float.

As $\overline{AE}$ is made successively smaller by this process, we finally arrive at $\overline{AE} < \overline{AC}$. Provided that the constant electric field is homogeneous up to $\overline{CD}$, and the width of the bridge is negligible compared to $\overline{AB}$, then the net surface tension forces on the float should disappear at $\overline{AE} < \overline{AC}$. Since now the electrostatic attraction of the float is proportional to the area ABFE and thus also to the mass of the float, we still plot deflection vs mass of float for ABFE < ABDC. This plot shows the electrostatic effect plus the gravity effect due to the remaining mass of the float, but without the surface tension effect.

Thus, we will have two plots of balance deflection vs mass of float (Figure 4), one of which, for $\overline{AC} < \overline{AE}$, gives the influence of gravity plus a constant electrostatic attraction and surface tension effect; the other, for $\overline{AC} > \overline{AE}$, gives the influence of electrostatic attraction plus the effect of gravity for the remaining mass of the float with no surface tension effect.

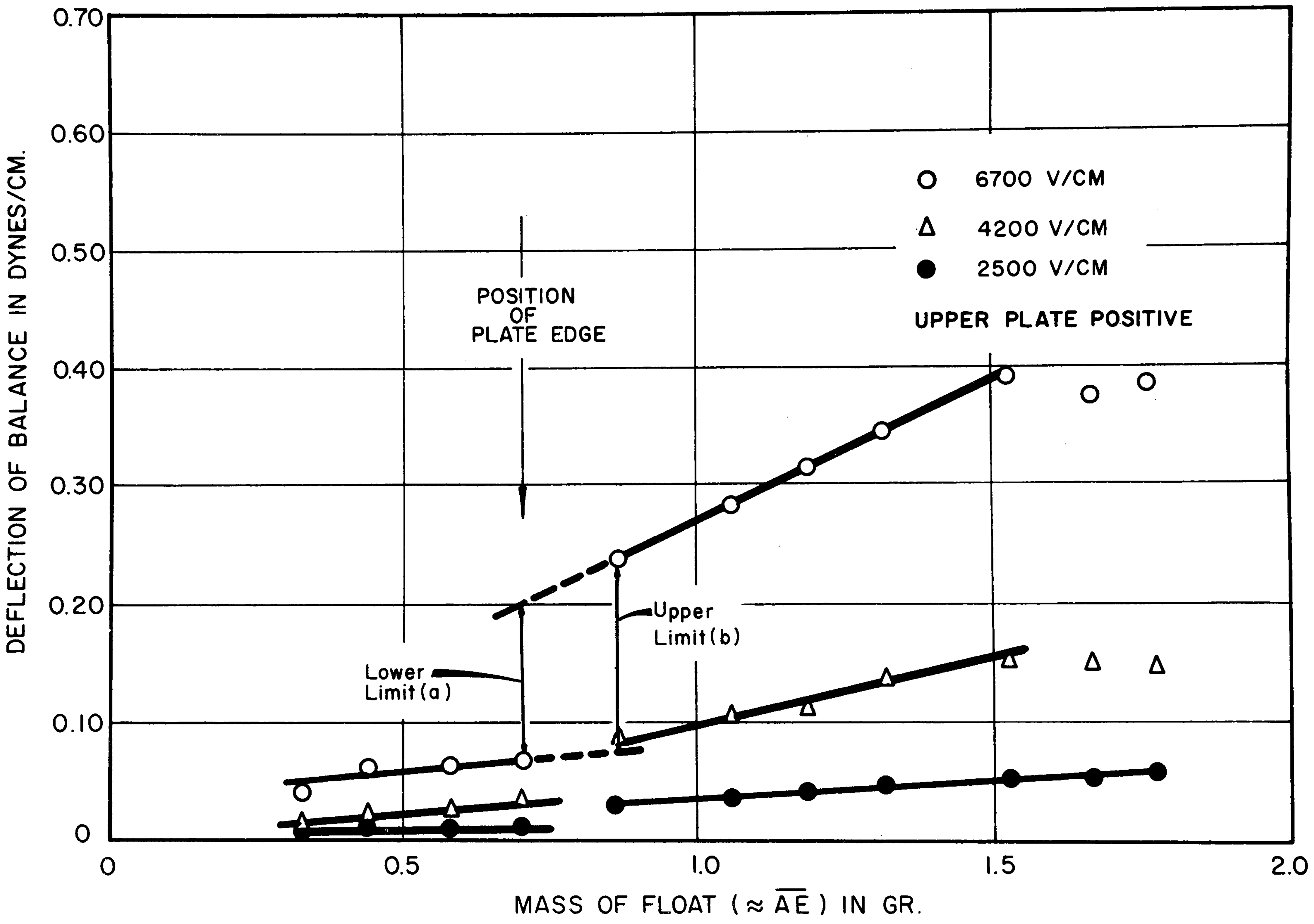

Fig. 4 - BALANCE DEFLECTION vs MASS OF FLOAT FOR 3.5% NaCl SOLUTIONS

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Extrapolation of the two plots toward each other to a point to the left of which the surface tension effect is zero and to the right of which the surface tension effect has a definite value gives a difference in ordinate which corresponds to the surface tension effect only.

It is seen from Figure 4 that the slopes of the upper part of the curves become larger with increasing field strength, which is expected for increasing hydrostatic head. The deflection exhibited a slight maximum at the greatest masses, which may be due to forces involved in "lifting" water outside the field by surface tension effects on the rigid float. It is believed that these forces are not important in the linear portions of the curves.

Extrapolation of the lower parts of the curves to $m = 0$ should intercept the origin. The small deviations from zero intercept in Figure 4 are accounted for by the fact that the bridge between front and rear part of the float cannot be made infinitely small, and also because a finite rear part is necessary to operate the balance.

The point to the left of which the surface tension effect is zero and to the right of which the surface tension effect has a finite value cannot be determined precisely. The point lies, however, between the abscissae of the highest point of the lower curve and the lowest point of the higher curve (between points a and b in Figure 4). Taking the difference in ordinates at these two points gives a lower and upper limit for the surface tension effects.

The method was checked by using floats having different working edges, different masses, and different areas in the field. The results for a 3.5% NaCl solution at positive "air electrode" are shown in Figure 5 and are in satisfactory agreement. Each point in Figure 5 is the mean of a maximum and minimum value obtained from a plot of mass of float vs balance deflection. The

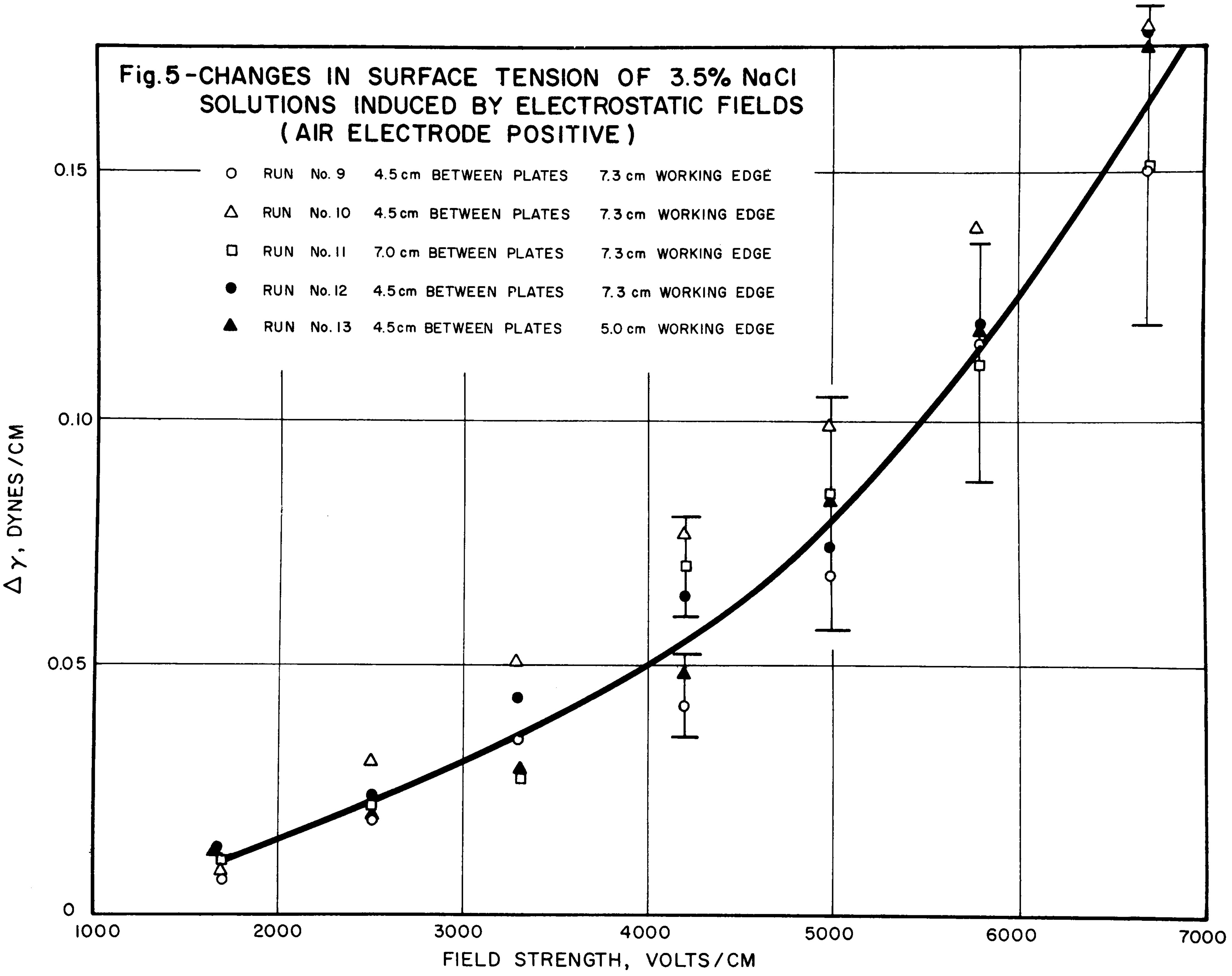

Fig. 5-CHANGES IN SURFACE TENSION OF 3.5% NaCl SOLUTIONS INDUCED BY ELECTROSTATIC FIELDS (AIR ELECTRODE POSITIVE)

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curve is the average of the surface tension change thus obtained. Maximum and minimum values are indicated. Positive values of $\Delta\gamma$ correspond to a lowering of surface tension due to the electric field.

It has been pointed out (10) that the balance deflections observed on application of the field may be caused by Cl^- adsorption at the float/solution boundary, due to the difference in dielectric constants and induced by the applied field. This adsorption should depend strongly on dielectric constant and material of the float. A run was therefore made with a mica float carefully coated with paraffin. The results did not differ from the ones obtained with plain mica floats, proving that Cl^- adsorption at the float/solution boundary is either absent or does not influence the measurements.

Solutions of 0 to 3.5% NaCl content have been used for the experiments described here with the air electrode both positive and negative, using fields up to 7000 v/cm.

C. RESULTS

The $\Delta\gamma$ values measured in the experiments just described were converted into absolute γ's using Handbook data (11). Figures 6 and 7 give a plot of surface tension vs NaCl concentration with field strength as parameter for positive and negative air electrodes respectively. The surface deficiencies, Γ, have been calculated using the Gibbs adsorption equation and are presented in Figures 8 and 9.

It is seen from Figures 6 and 7 that both a positive and a negative air electrode lowers the surface tension of pure water, a negative air electrode more so than a positive one. The surface concentration of NaCl solutions is increased by a negative air electrode (Figure 8), as compared to the surface concentration without a field. A positive air electrode leads, on the contrary, to a lower surface concentration (Figure 9). The field strength necessary to lower the surface concentration by a given amount at a given bulk concentration is, however, considerably larger than

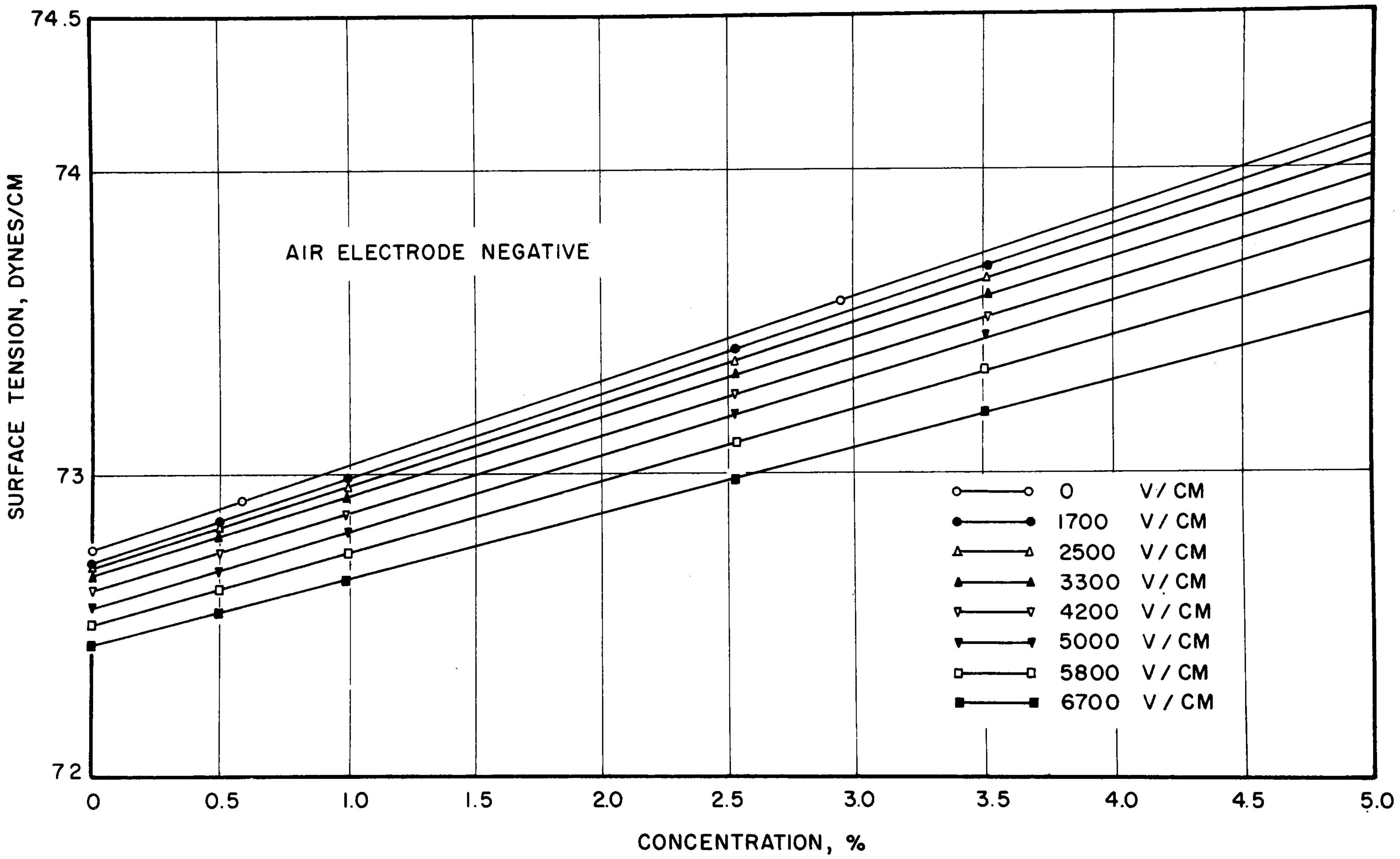

Fig. 6 - SURFACE TENSION OF NaCl SOLUTIONS

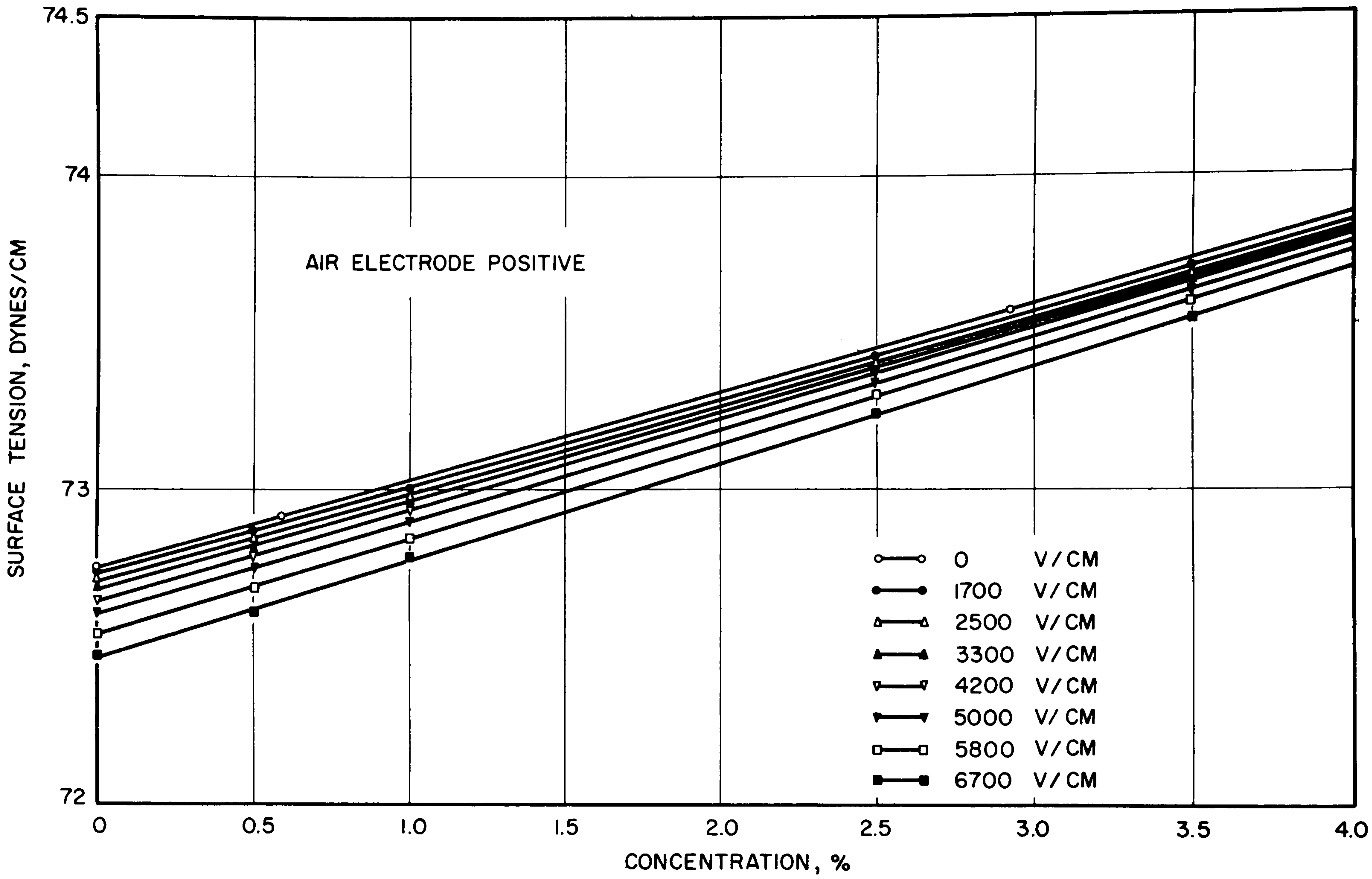

Fig. 7 – SURFACE TENSION OF NaCl SOLUTIONS

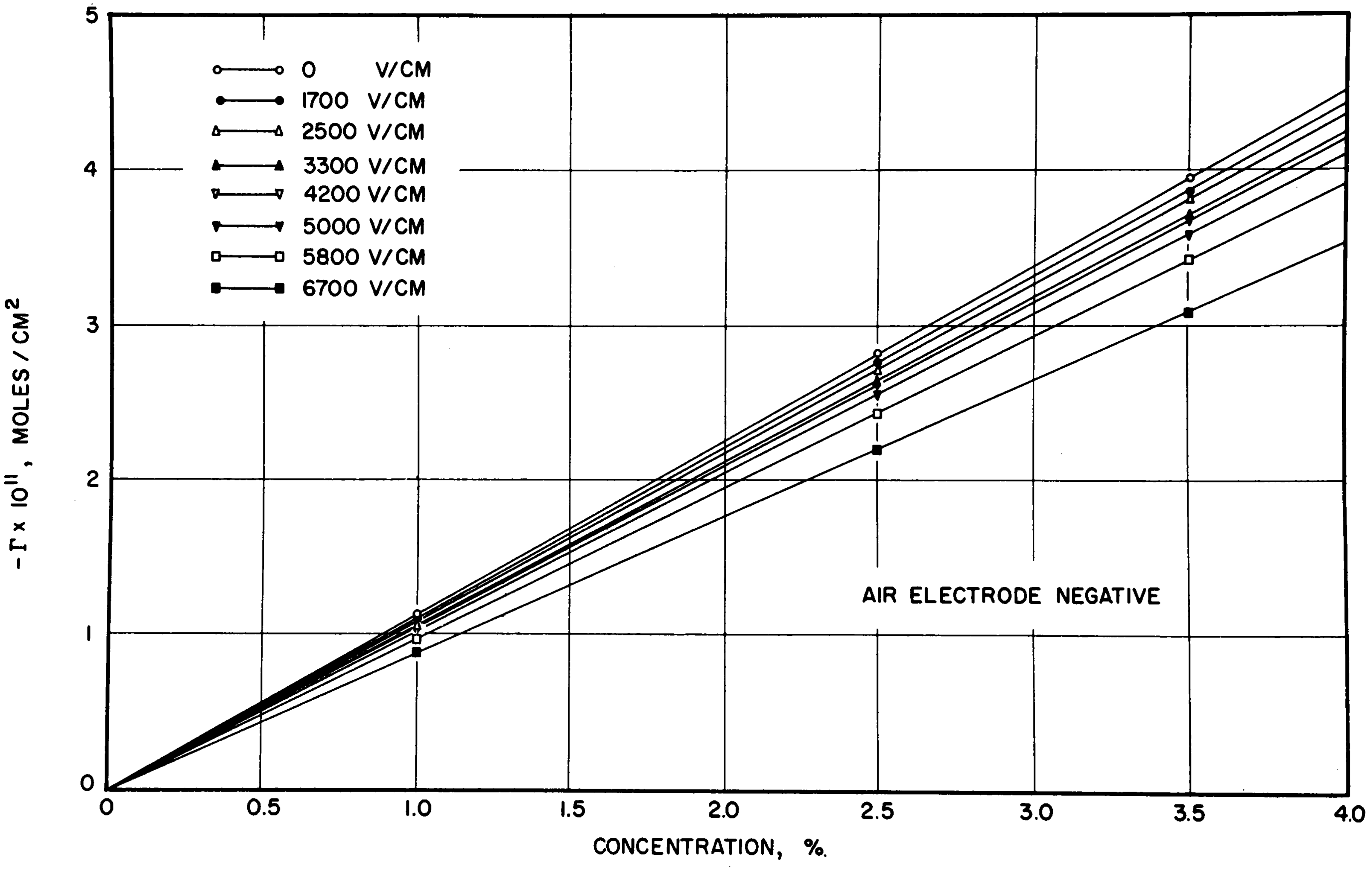

Fig. 8 – SURFACE CONCENTRATION OF NaCl SOLUTIONS

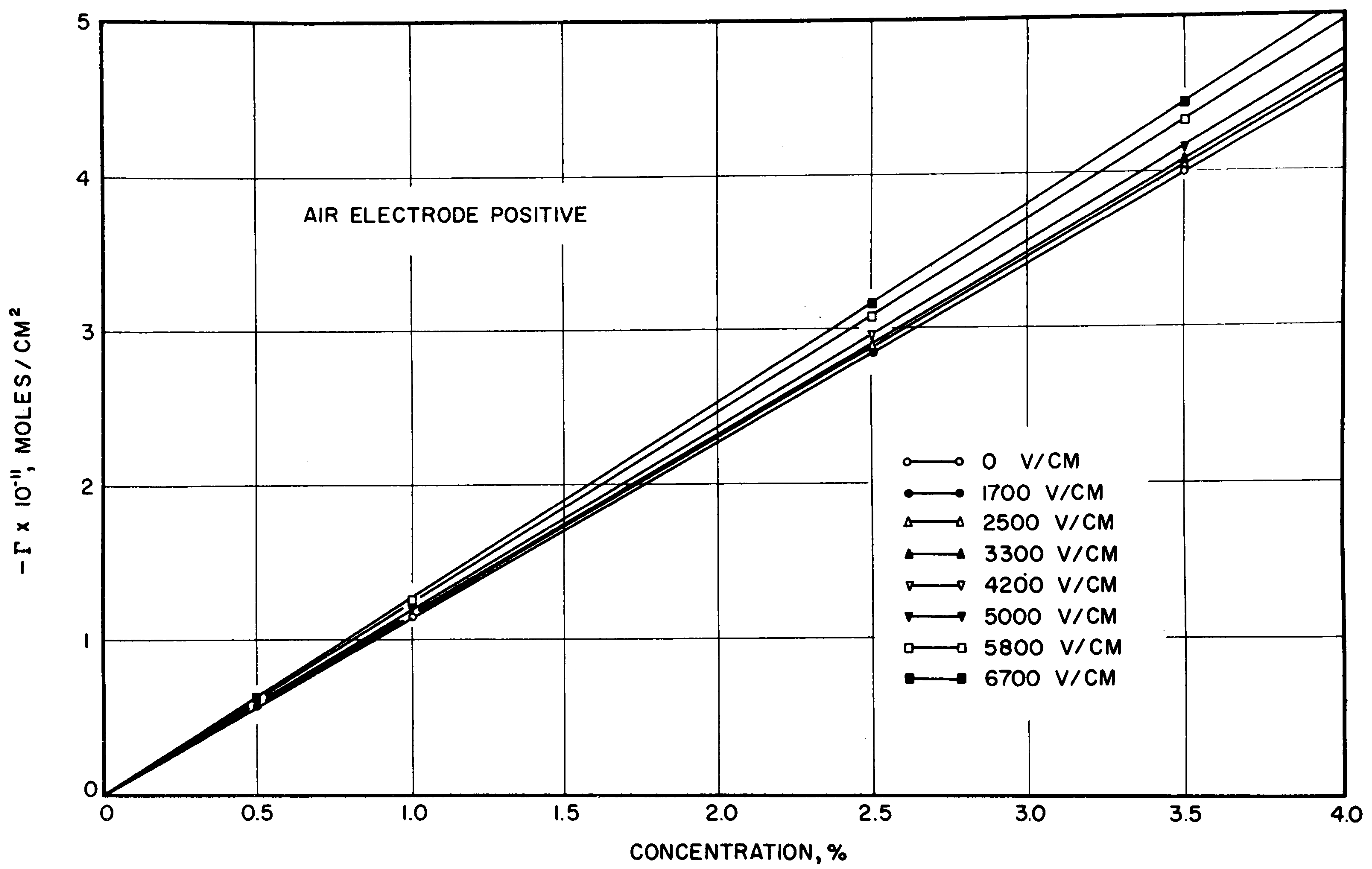

Fig. 9 — SURFACE CONCENTRATIONS OF NaCl SOLUTIONS

the field strength necessary to raise the surface concentration by a like amount.

D. Discussion

Dipole Orientation

The potential drop at an air/water interface is according to Kamienski (6), about 1 v, and according to Frumkin (12), 0.1 v to 0.2 v. Assuming 10 Å for the thickness of the oriented layer of water dipoles at the interface, one obtains a field strength of 10^7 to 10^6 v/cm. It is unlikely that with such a high field strength already present, application of less than 10^4 v/cm would produce a measurable change in surface tension. Since a measureable change is observed, it appears that either the potential drop across the interface is much smaller than previously thought, or that the thickness of the oriented layer of water dipoles is larger by one to two orders of magnitude.

Both a positive and a negative air electrode lowers the surface tension of pure water. It can be reasonably assumed that this lowering is caused by increased orientation of water dipoles. Equally oriented dipoles repel each other, thus leading to a decrease in surface energy. This leads to the conclusion that the orientation is very slight to start with, since both field directions enhance the orientation, i.e., the surface potential is very close to zero. Pronounced orientation of water dipoles in one direction would lead, on application of a field, to a lowering of surface tension with one polarity and a raising of surface tension with the other, which may be followed by a lowering in case the field is strong enough to reverse the dipoles. This has not been observed. The fact that a negative air electrode lowers the surface tension more than a positive electrode leads to the conclusion that a slight orientation is present with the hydrogen atoms pointing towards air.

Surface Concentration of NaCl

From the usual form of the Gibbs adsorption equation

$$\Gamma = -\frac{c}{RT}\frac{d\gamma}{dc} \qquad (3)$$

and available data on the surface tension of salt water solutions without an applied field, a calculation of the concentration of a skimmed layer as a function of the thickness skimmed can be made, using only two assumptions, i.e.,

(1) All of the concentration change occurs within the skimmed layer.

(2) A true value of Γ is obtained from the Gibbs equation, which was derived for nonionized solutes.

As for the validity of the assumptions, the first is certainly valid for any reasonable thickness of a skimmed layer (say > 1000 Å), while the second probably does not affect the true value of Γ sufficiently to influence the discussion of skimming processes as a practical method of purifying salt water.

Results of such a calculation for 3.5% (=0.6M) salt solutions are shown in Figure 10, both without applied field and with what we now believe Γ to be with our maximum positive and negative fields. The fourth curve on Figure 10 is from a calculation using a value of Γ which is thought to be required to make a skimming process a promising method of purification. This value turns out to be about -1.0×10^{-9} moles/cm^2, or more than an order of magnitude greater than -4×10^{-11} moles/cm^2 present without the field. (The dashed portions of these curves are indicative of the uncertainty involved in assumption (1), since with thin enough skimmed layers, the shear plane would intersect the surface concentration gradient.)

It is clear from Figure 10 that, unless the field has a much greater influence on Γ than our surface tension measurements

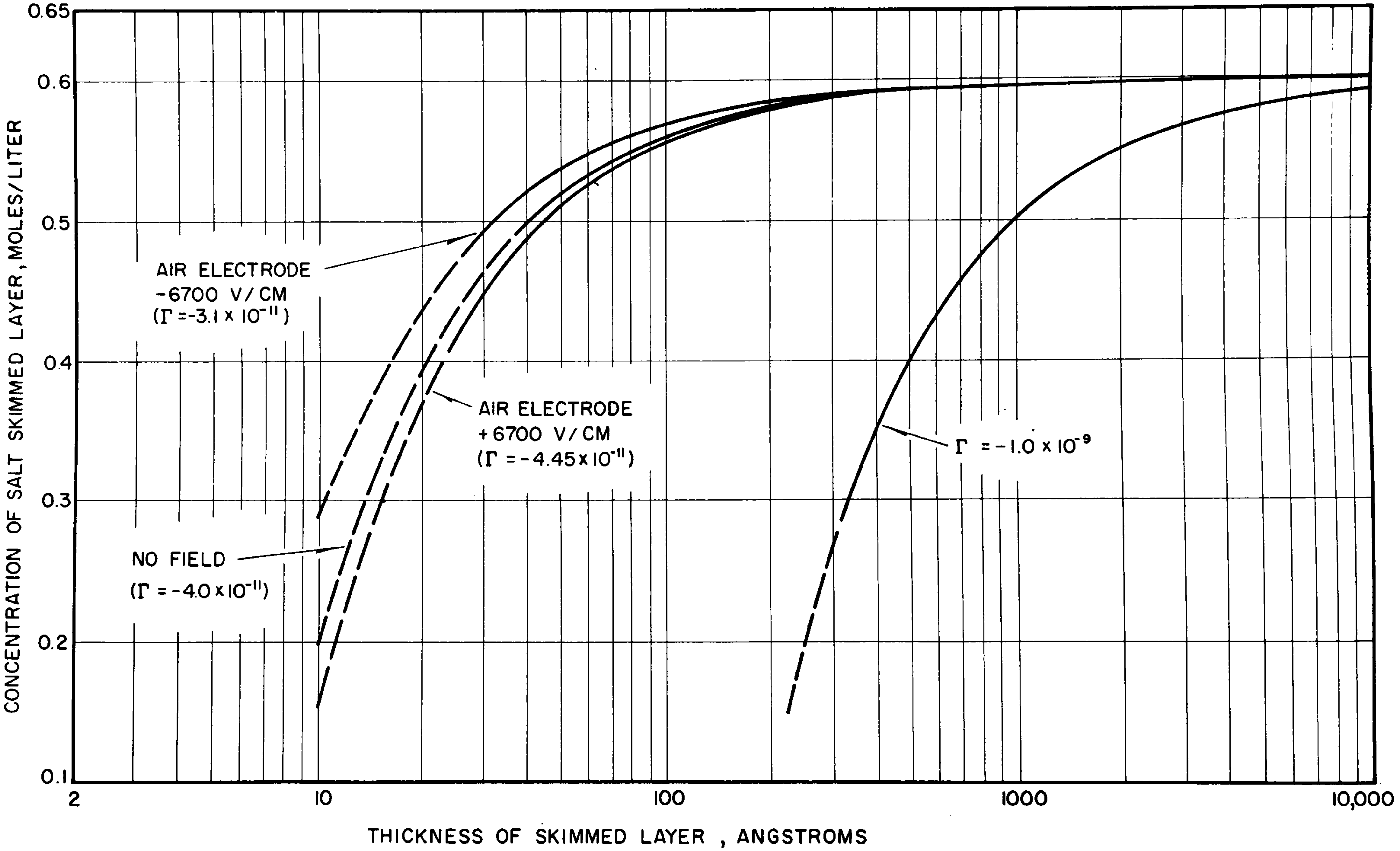

Fig. 10 – CONCENTRATION OF SKIMMED SOLUTIONS

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indicate, skimming processes (and, indeed, any process which depends directly on the surface concentration gradient) offer very little hope of being a practical purification method. This can be proved unequivocally only by actual skimming experiments, carried out with an apparatus which is known to be operating properly. Because of uncertainties involved in using the Gibbs equation on ionized solutes, this can only be established by measurements on nonionized solutes, for which the Gibbs equation was derived. Such an apparatus and the measurements which have been made to demonstrate its applicability to this research, will be described in Section III.

The necessity of doing the skimming experiments lies in the uncertainty of the second assumption above, which in turn introduces a question about using the unmodified Gibbs equation for calculating Γ from our surface tension data. The modified form of the Gibbs equation, and other effects of electrostatic fields on surface concentrations and surface tensions for solutions of ionized species, are discussed in mathematical terms in the following section.

E. Theoretical Interpretation

The surface deficiency of solutions of strong electrolytes has been shown by Wagner (3) to be principally due to image forces. In his treatment, the concentration c(x) is given as a function of the distance from the surface x by the usual Boltzman expression

$$c(x) = c \exp(-W(x)/kT), \qquad (4)$$

where the adsorption potential W(x) is the work required to bring a charged ion from the solution bulk to a point x cm below the surface. For binary electrolytes, Wagner took W(x) as equal for cations and anions, treated them as point charges, and from electrostatic theory obtained

$$W(x) = \frac{D-1}{D+1}\,\frac{e^2}{4Dx}, \qquad (5)$$

where

D = dielectric constant of water

e = charge on the ion.

It is easily seen that integration of Equation (4) with W(x) as expressed by Equation (5) would lead to an infinite amount of adsorbed solute. Ions, however, are not point charges, and in ionic solutions, the screening effect of the ion atmosphere limits the effective range of the electrostatic forces to a distance $1/\kappa$, where k is defined by

$$\kappa^2 = \frac{4}{DkT} \sum_i c_i z_i^2, \tag{6}$$

(13, 14) where c_1, c_2, ... is the concentration (number of ions/cm^3) of ions with charges z_1, z_2, ... Introducing the mean distance of approach, a, from Debye-Hückel theory, and neglecting variation of κ with x, Equation (5) is modified to

$$W(x) = \frac{e^{\kappa a}}{1 + \kappa a} \frac{e^2}{4Dx} e^{-2\kappa x} \tag{7}$$

This expression, when introduced into Equation (4), leads to a reasonable solution of c as a function of x. Onsager and Samaras (4) used this treatment to solve for a theoretical value of the surface excess, Γ, thus:

$$\Gamma = \int_0^\infty c_{bulk}\, dx - \int_0^\infty c(x)\, dx$$

$$= -c_{bulk} \int_0^\infty [\exp(-W(x)/kT) - 1]\, dx \tag{8}$$

Values of Γ obtained from this integration were shown to check satisfactorily with values of Γ obtained from the usual form of the Gibbs equation and surface tension measurements.

Application of an external field across the interface changes the value of the adsorption potential W(x), which from Equation (7) occurs through (or is associated with) a change in κ, which in turn is a function only of the ionic strength (Equation 6). The changes in Γ with applied field, as measured in our experiments, are a direct measure of these changes in ionic strength, and could theoretically be used to calculate back to the change in adsorption potential induced by the field. This would, however, be a rather tedious procedure, and the uncertainties involved in many of the assumptions made by Wagner and by Onsager and Samaras are probably of greater magnitude than the influence of the field on this potential.

One conclusion which seems to be clear from the experiments, however, is that the difference in W(x) between cations and anions must be taken into account in any refined treatment of the theory. No dependence of Γ on the direction of the applied field would be expected from the derivations above, yet it is clear that a negative air electrode increases the surface concentration while a positive electrode decreases it, and that the magnitude of the effects is different, being greater for the negative electrode. From this dependence of Γ on the field direction, it appears that the main influence is centered on the sodium ion, although the reason for this behavior is not immediately clear. The explanation may lie in the difference in the screening effect $1/\kappa$ of the cations and anions as influenced by the electric field, which may be explained by the smaller radius (and resultant higher charge density) of the cation.

An alternative treatment of the concentration gradient at the surface of solutions of strong electrolytes has been given by Lewis (2). This treatment assumes an electrical double layer, made up of the positive and negative ions, at the surface, and leads very simply to a modified form of the Gibbs equation:

$$\Gamma = -\frac{c}{RT}\left(\frac{\partial\gamma}{\partial c}\right) - (\epsilon_1 + \epsilon_2)\frac{\partial\gamma}{\partial\psi} \qquad (9)$$

or, using activities,

$$\Gamma = -\frac{a}{RT}\left(\frac{\partial\gamma}{\partial a}\right) - (\epsilon_1 + \epsilon_2)\frac{\partial\gamma}{\partial\psi} \qquad (10)$$

where ϵ_1, ϵ_2 = electrochemical equivalent of cations and anions respectively, and ψ = potential drop across the double layer.

The dependence of ψ on the externally applied potential, E, is not known. We assume, as a first approximation, a linear dependence of the interface potential on the applied potential, i.e.,

$$\Delta\psi = \beta\Delta E \qquad (11)$$

where β is a dimensionless factor.

The charge, σ, for a diffuse double layer is given by the Gouy-Chapman theory (13, 15) as

$$\sigma = \sqrt{\frac{DRTc}{2\pi}}\left(e^{F\psi/2RT} - e^{-F\psi/2RT}\right), \qquad (12)$$

with c = concentration of the electrolyte. On the other hand, σ is given by

$$\sigma = EC \qquad (13)$$

where C = the capacity of the condenser formed between air-electrode and air-solution interface, per unit area,

$$C = \frac{D'}{4\pi d} \qquad (14)$$

where

D' = dielectric constant of air

d = distance between air-electrode and air-solution interface.

Combination of Equations (12) and (13) gives

$$CE = \frac{DRTc}{2\pi} \left(e^{F\psi/2RT} - e^{-F\psi/2RT}\right), \tag{15}$$

and one obtains, $dE/d\psi$ being a total differential,

$$\frac{d\psi}{dE} = \beta = \frac{2RTC}{F} \sqrt{\frac{2\pi}{DRTc}} \left(e^{F\psi/2RT} + e^{-F\psi/2RT}\right)^{-1}. \tag{16}$$

Using hyperbolic functions one obtains β as a function of E from Equations (15) and (16):

$$\beta = \frac{2RTC}{F} \sqrt{\frac{\pi}{2DRTc + \pi E^2 C^2}} \tag{17}$$

For all practical purposes, $2DRTc >> \pi E^2 C^2$ and one gets

$$\beta = \sqrt{\frac{2\pi RTC^2}{F^2 Dc}}$$

$$= K\sqrt{\frac{1}{c}} \tag{18}$$

with $K = \sqrt{\frac{2\pi RTC^2}{F^2 D}}$ and C as given by Equation (14).

With D, the dielectric constant of the electric double layer, assumed to be about 4, and C = 0.1 e.s.u./cm^2, we obtain $K = 6.5 \times 10^{-11} (\text{mole/cm}^3)^{1/2}$. For c = 0.5 moles/1 and $\Delta\gamma/\Delta E = 10^{-4}$ dynes/volt cm, one calculates (Equations 10, 11, and 18)

$$(\epsilon_1 + \epsilon_2) \frac{1}{K} \sqrt{c \frac{\Delta\gamma}{\Delta E}} \approx 10^{-9} \text{ moles/cm}^2$$

a number which seems unreasonably high.

In the preceding calculations, we have assumed the electrical double layer at the air-solution interface to be of a diffuse nature. This assumption was prompted by the experimental results showing that the effect of the field is mainly on cations, which are usually not thought of as being adsorbed in the inner double layer.

Grahame (16) found that the potential drop ψ_u across the inner double layer is a linear function of the charge, σ, adsorbed. Using Grahame's equation for ψ_u

$$\psi_u = 2\pi\sigma\delta/D \tag{19}$$

where σ is given by Equation (13), δ = radius of the hydrated ions, one obtains from (11), with ψ_u instead of ψ:

$$\Delta\psi_u = \frac{2\pi\delta C}{D} \Delta E \tag{20}$$

$$\beta' = \frac{2\pi\delta C}{D} . \tag{21}$$

Now, with

$\delta = 10^{-7}$ cm
$C = 0.1$ e.s.u./cm^2
$D = 4$ e.s.u./cm

one obtains $\beta \approx 10^{-5}$. This leads to a value of $\approx 10^{-11}$ moles/cm^2 for the correction term in the modified Gibbs equation (10). This is comparable to the order of magnitude given by the standard form of the Gibbs equation and agrees well with the values of Γ obtained in our experiments with the field, so that it is thought to be entirely reasonable. There are too many assumptions involved, however, to warrant systematic calculations of Γ using Equation (10).

III. SKIMMING APPARATUS

In the preceding section the effects of electro-static fields on the salt water-air interface were observed as change in surface tension. These changes can be attributed to orientation of water dipoles as well as variations in the surface concentration of the salt solution. Therefore a means of direct measurement of this surface concentration is desirable.

The classic surface concentration measurement was performed by McBain and co-workers (17). The experiment involved the use of precision ground silver rails on which rode a catapulted microtome blade moving at about 30 mph, automatic trap doors to permit passage of the blade through the controlled atmosphere surrounding the silver trough which contained the solution to be measured and elaborate braking arrangements for the blade. As described by Adam: "The whole apparatus constitutes a triumph of mechanical skill." Other, simpler methods, like the bubble method or radioactive measurements have been developed and give satisfactory results in selected cases (18).

The following describes a simple and inexpensive apparatus using the same principle as McBain's microtome, but in which the solution, rather than the cutting edge, is the moving component. The apparatus permits investigation of the effect of electrostatic fields impressed across the interface.

The skimmer (Figure 11) consists of a small diameter metal tube with one end carefully ground to a sharp edge. It is readily made from a stainless steel hypodermic needle. The hole is hit squarely by a jet of slightly larger diameter, flowing under pressure (∼100 cm of water) out of a rigidly fixed pipette. The hypodermic needle tip is joined to large diameter tubing to allow the liquid coming through the base of the needle to flow off freely. This tubing carries a collar to collect the liquid which flows down the outside of the apparatus. The needle assembly is

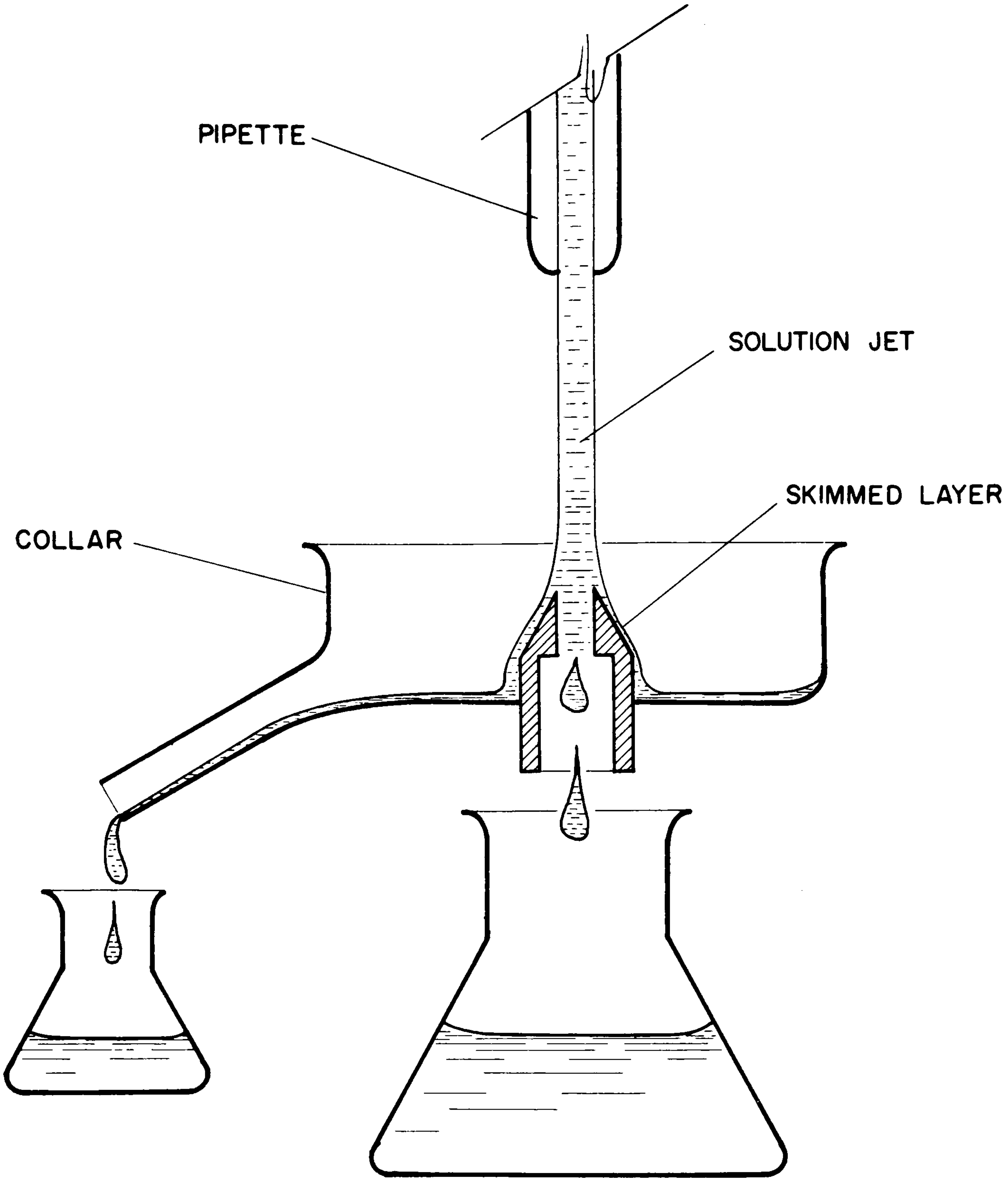

Fig. 11 - SCHEMATIC DIAGRAM OF SKIMMER

mounted on a three-way microscope stage so that its position relative to that of the pipette can be controlled precisely. The skimmer is enclosed in a lucite box in which 100% relative humidity is maintained to prevent evaporation losses.

To test the apparatus for its usefulness in the measurement of surface concentrations of NaCl solutions, the surface concentration of an aqueous surfactant solution was determined experimentally and compared with its surface excess calculated from the Gibbs adsorption equation. The surfactant used was n-decylbenzene sodium sulfonate supplied by Continental Oil Company. This compound was selected because of its large $(\partial\gamma/\partial c)$ coefficient and the existence of a strong adsorption peak at 223 mμ, which permits accurate concentration determination by differential UV spectrophotometer measurements. The surface tension-concentration relationship was obtained for aqueous solutions from 5×10^{-6} to 1×10^{-3} molar using the capillary rise method. Previous experiments with trimethylphenylammonium chloride and sodium benzoate had to be discarded partly because the solutions decomposed slightly and partly because the $(\partial\gamma/\partial c)$ coefficient was too small to obtain reasonable accuracy.

A. Relation Between Concentration of a Skimmed Layer and the Gibbs Surface Excess, Γ

From the thermodynamic treatment employed by Gibbs (1), the surface excess, Γ, expressed in units of moles/cm^2, is a rather difficult concept to grasp. The following simple arithmetical derivation of the relation between the concentration of a skimmed layer of thickness x and the value of Gibbs' Γ, while not essential to the proof of the successful operation of the "skimmer," may be of some help in understanding its operation.

Figure 12 is a schematic drawing of a concentration-distance relation near the surface of a surfactant solution, in which the concentration varies linearly over a distance, d, from bulk concentration, c_B, to some concentration c' immediately at the surface. While it is obvious that such an idealized gradient does

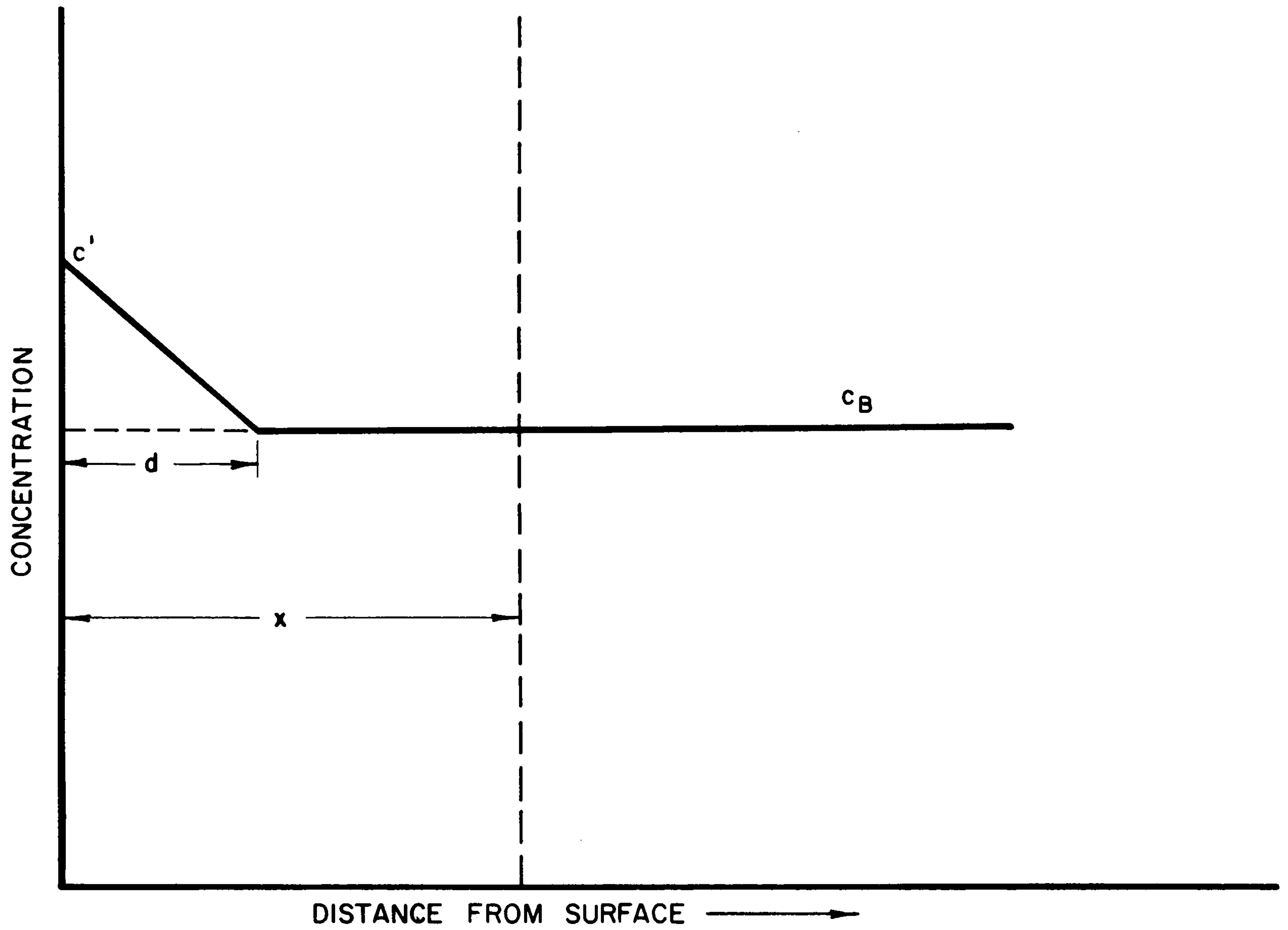

Fig.12- SCHEMATIC OF CONCENTRATION-DISTANCE RELATION AT THE SURFACE

not exist, expression in this manner is entirely analogous to the commonly used diffusion layer treatment, and as will be seen later, is not important in the derived final relationship.

Counting the total number of moles of solute in a layer of thickness x, skimmed from the surface yields, for each square centimeter of surface skimmed.

$$(x - d)c_B + d\,\frac{c_B + c'}{2}\ \text{moles.} \tag{22}$$

Since the total volume of the skimmed layer per square centimeter of surface is simply x, the concentration c_s of solute in this layer is:

$$c_s = \frac{(x - d)c_B + \frac{d(c_B + c')}{2}}{x} \tag{23}$$

which simplifies to:

$$c_s = c_B + \frac{d}{x}\left(\frac{c' - c_B}{2}\right) \tag{24}$$

Examination of Figure 12 reveals that the quantity $d(c' - c_B)/2$ is actuallly the area of the small triangle enclosed by the increasing concentration line over the distance, d, and is the number of moles in the surface region in excess of that which would be present if the bulk concentration were maintained right up to the surface, which is by definition the quantity Γ. Thus, Equation (24) becomes:

$$c_s = c_B + \frac{\Gamma}{x} \tag{25}$$

It can now be seen that the linear concentration gradient assumed in the derivation is of no consequence in the use of

Equation (25), since both the value of d and the nature of the gradient are incorporated into a simple quantity Γ.

B. Experimental

Experimental Γ values of an n-decylbenzene sodium sulfonate in water solution were obtained in the following way: The flow of the solution jet was started and the ratio, R, of solution flowing through the hole to that flowing down the outside of the metal cone and collected by the collar was measured volumetrically. Since the diameter of the jet varies slightly with distance from the pipette tip, various values of this ratio could be obtained by simply varying the distance between the pipette tip and the ground edge of the needle. This distance was approximately 10 cm in these experiments, with variations of less than 1 cm to cover the ratios studied. The upper limit of distance between pipette tip and needle is that at which the jet of solution breaks up into droplets.

The thickness, x, of the skimmed layer, assuming the jet strikes the ground opening concentrically, is given in terms of the ratio, R, and the radius, r, of the opening by

$$x \approx \frac{r}{2R} \qquad (26)$$

which follows from the exact expression

$$\frac{r^2 - (r - x)^2}{(r - x)^2} = \frac{1}{R} \qquad (27)$$

when R is greater than 20 for r = 0.029 cm, as used in these experiments. For ratios of 100, which could be obtained fairly easily, the thickness of the skimmed layer is 1.5×10^{-4} cm.

It is not necessary for the jet to strike the opening concentrically in order to use the method. If it strikes off center, provided only that the edge does not cut across or into the region where the concentration begins to deviate from that in the bulk (probably < 100 Å from the surface), the value of x as obtained from Equation (26), though an average, is here just as valid as if the jet would strike concentrically.

From the definition of surface excess, Γ, we can write

$$\Gamma = (c_s - c_B)\, x \tag{28}$$

where c_s and c_B are the concentrations (in moles/cm^3) of the skimmed layer and of the bulk solution. Equations (26) and (28) give

$$(c_s - c_B) = \Gamma \frac{2R}{r} \tag{29}$$

so that a plot of $(c_s - c_B)$ versus 2R/r yields a straight line with slope Γ.

Values obtained in this manner for one set of experiments are shown in Figure 13. The scatter in the data is believed due to the edge cutting across the surface some fraction of the time during the course of the experiment.

Theoretical surface excess values, Γ, were calculated, using the approximate form of the Gibbs equation. From measurements of surface tension as a function of concentration, using the capillary rise method, $\partial\gamma/\partial c_B$ was found to be -4.2×10^3 dynes liter/cm mole.

Figure 14 gives a comparison between the experimentally determined points according to Equation (29) and the theoretical line, calculated from Equation (3). It is seen that the agreement with theory is within less than 10% over two decades of concentration change. Appreciable deviation occurs from 10^{-3}M solutions. Here the limit of solubility is almost reached, and one suspects micelle formation and/or surface film formation.

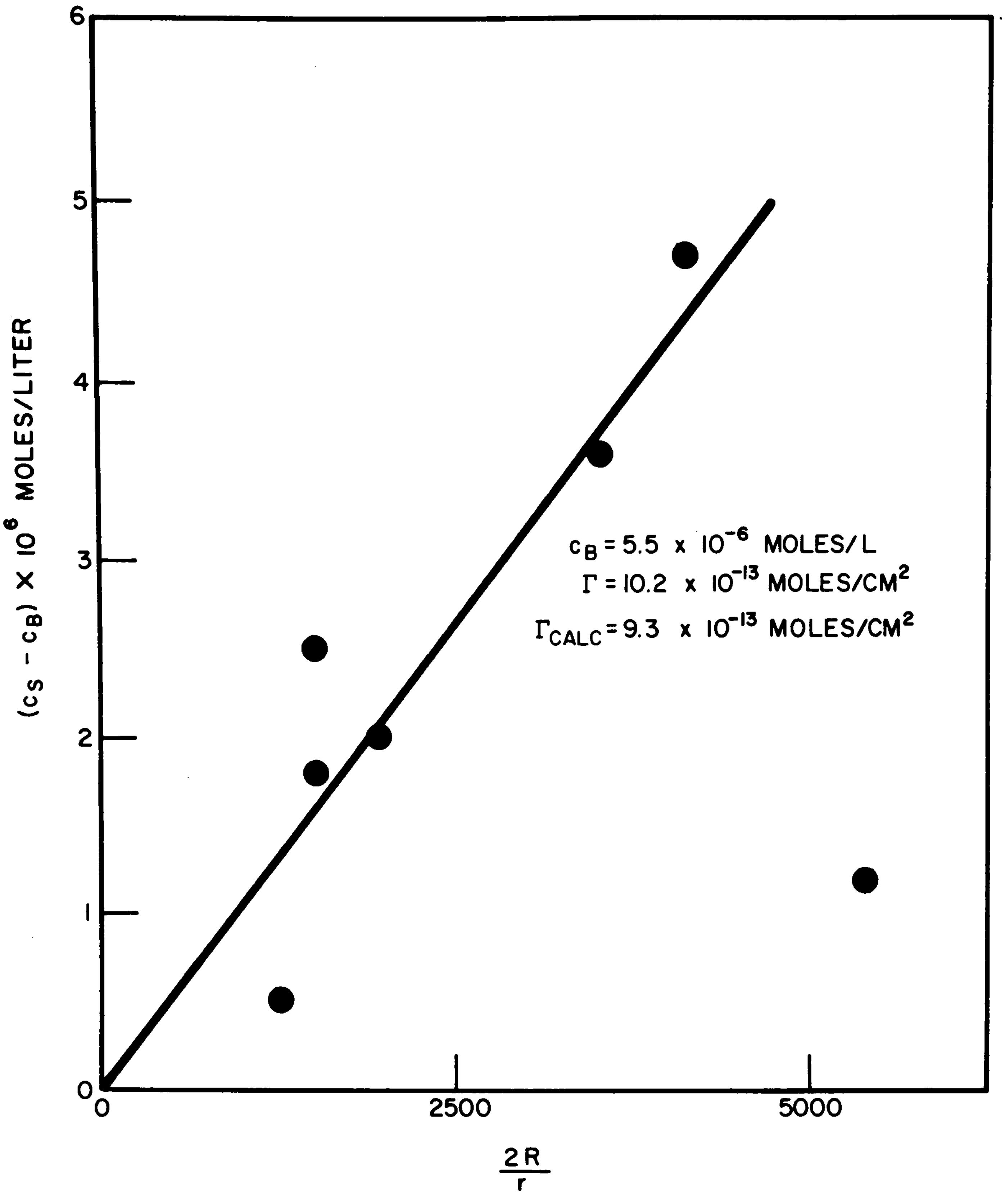

Fig.13 - PLOT OF $(c_S - c_B)$ vs 2R/r FOR N-DECYLBENZENE SODIUM SULFONATE

DWG 4500-28

GMS MM

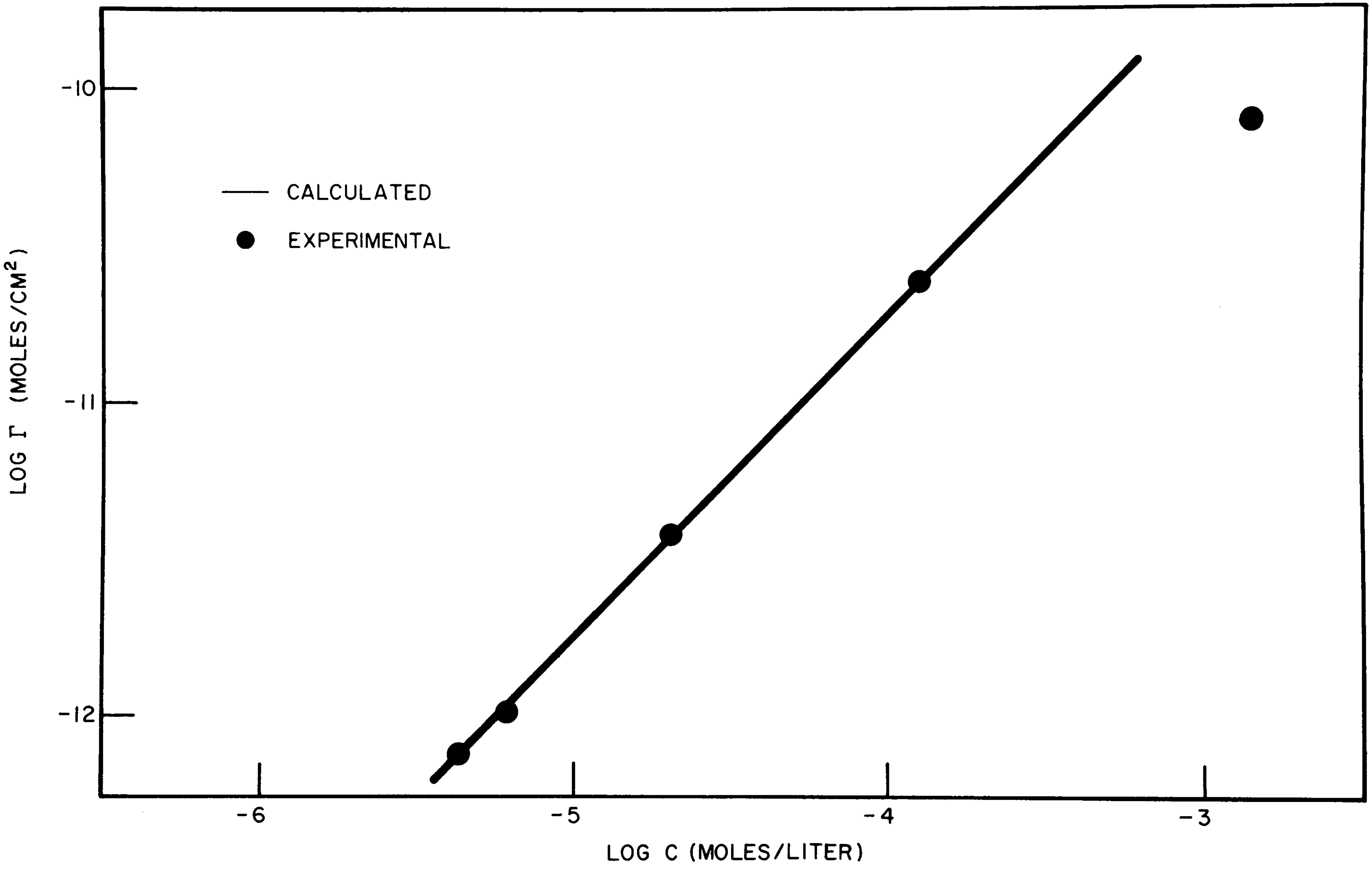

Fig.14 - THEORETICAL AND EXPERIMENTAL Γ VALUES FOR N-DECYLBENZENE SODIUM SULFONATE.

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GMS MM

It has been implicitly assumed that the time during which the jet was in contact with air was sufficient to reach equilibrium at the jet/air interface. For 10 cm distance between pipette and cutting edge, and 100 cm of water pressure, this time is about 0.05 seconds. The good agreement with theory indicates that for these solutions equilibrium is established in this interval, except possibly at 10^{-3}M where the deviation may be in part due to a lack in equilibrium. However, the ability to vary the distance from capillary tip to cutting edge makes it possible to look for effects of time to equilibrium.

It was thus shown that the skimming apparatus is basically sound and is capable of giving correct results

To obtain an indication of the applicability of the skimmer with electric fields, the surface concentration of sodium-2-phenyl-decane sulfonate was measured, with and without electric field. The field was applied between the hypodermic needle tip and a metal cylinder air electrode, isolated and surrounding the solution jet. This arrangement is equivalent to a field applied perpendicular to the solution/air interface, the tip being in contact with solution, provided the solution is a good conductor. This is certainly true with NaCl solutions of appreciable concentration, but is questionable for dilute solutions of surfactants. In the present case the field was probably rather distorted and the results given in Table I are mostly for orientation purposes.

It is seen that the influence of the field is much more pronounced with the air electrode negative. Again the main effect of the field seems to be on the positive sodium ions. This corroborated our findings with the surface energy balance, so it was concluded that the skimming apparatus can be used with confidence for experiments with applied fields.

TABLE I

SURFACE CONCENTRATION OF SODIUM-2-PHENYL-DECANE SULFONATE

Concentration (bulk)	Field Strength v/cm	Air Electrode	Γ Measured (moles/cm^2) x 10^{12}
3×10^{-5}	0		3.2
	1000	Negative	4.9
	4000	Negative	12.8
	1000	Positive	4.5
	4000	Positive	6.8
3×10^{-6}	0		1.8
	1000	Negative	2.0
	4000	Negative	4.9
	1000	Positive	1.9
	4000	Positive	3.9

C. Measurements With NaCl

The prime obstacle to obtaining surface concentration measurements of NaCl solutions is the difficulty of having to distinguish in the ppm range between two comparatively concentrated solutions. A survey of methods of analysis for NaCl showed that conductivity measurements would be the most accurate means for our purpose. Conductivity cells giving readings independent of liquid volume were constructed according to Mysels (Figure 15) (19). The conductivity was measured with an "esi" Impedance Bridge Model 250-DA. To obtain maximum precision, two cells were used, one connected between the "R" terminals containing the unknown, the other connected between "C" and "D-Q" ground containing a standard. Both cells were thermostated at 29.60 ± 0.01°C. A calibration curve is shown in Figure 16. It is seen that the deviation of the measured points from the curve corresponds to about 0.0005 in 0.6. With this one obtains as an upper limit using Equation (29)

$$\Gamma = -3.5 \times 10^{-11} \text{ moles/cm}^2$$

with

$$c_s - c_B = 0.0005 \times 10^{-3} \text{ moles/cm}^3$$
$$R = 200$$
$$r = 0.029 \text{ cm.}$$

This value of Γ is of the order of magnitude that would be expected from theoretical consideration.

Correspondingly, in our experiments, using skimming ratios of up to 1:200 with both positive and negative fields, no concentration change could be detected in the skimmed solutions as compared to bulk solutions.

To obtain a direct surface concentration measurement with tolerable limits of error of ± 10% the method of analysis would have to be 10 times more accurate. It should be pointed out again that the problem is not one of measuring small chloride concentrations

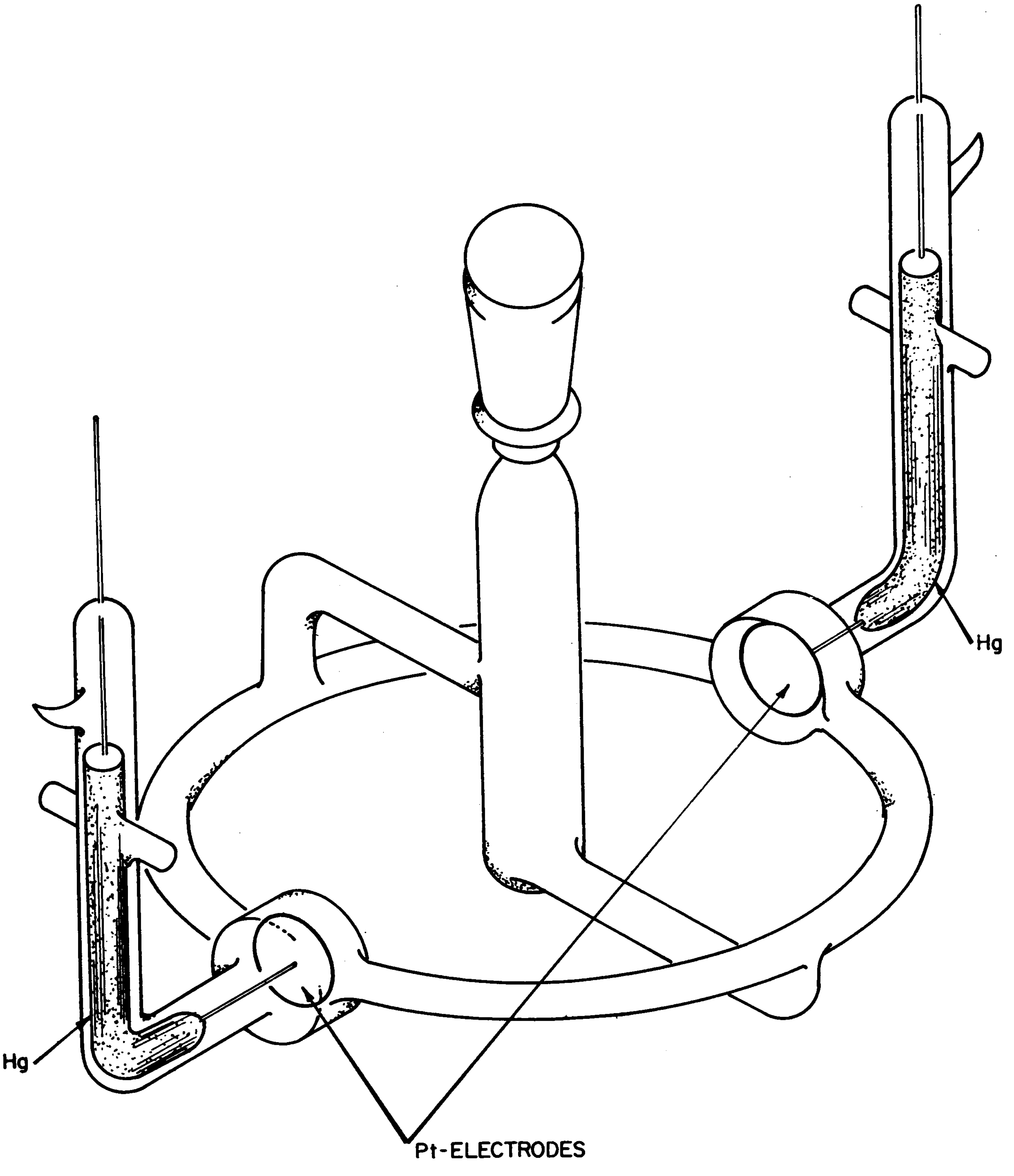

Fig. 15—CONDUCTIVITY CELL

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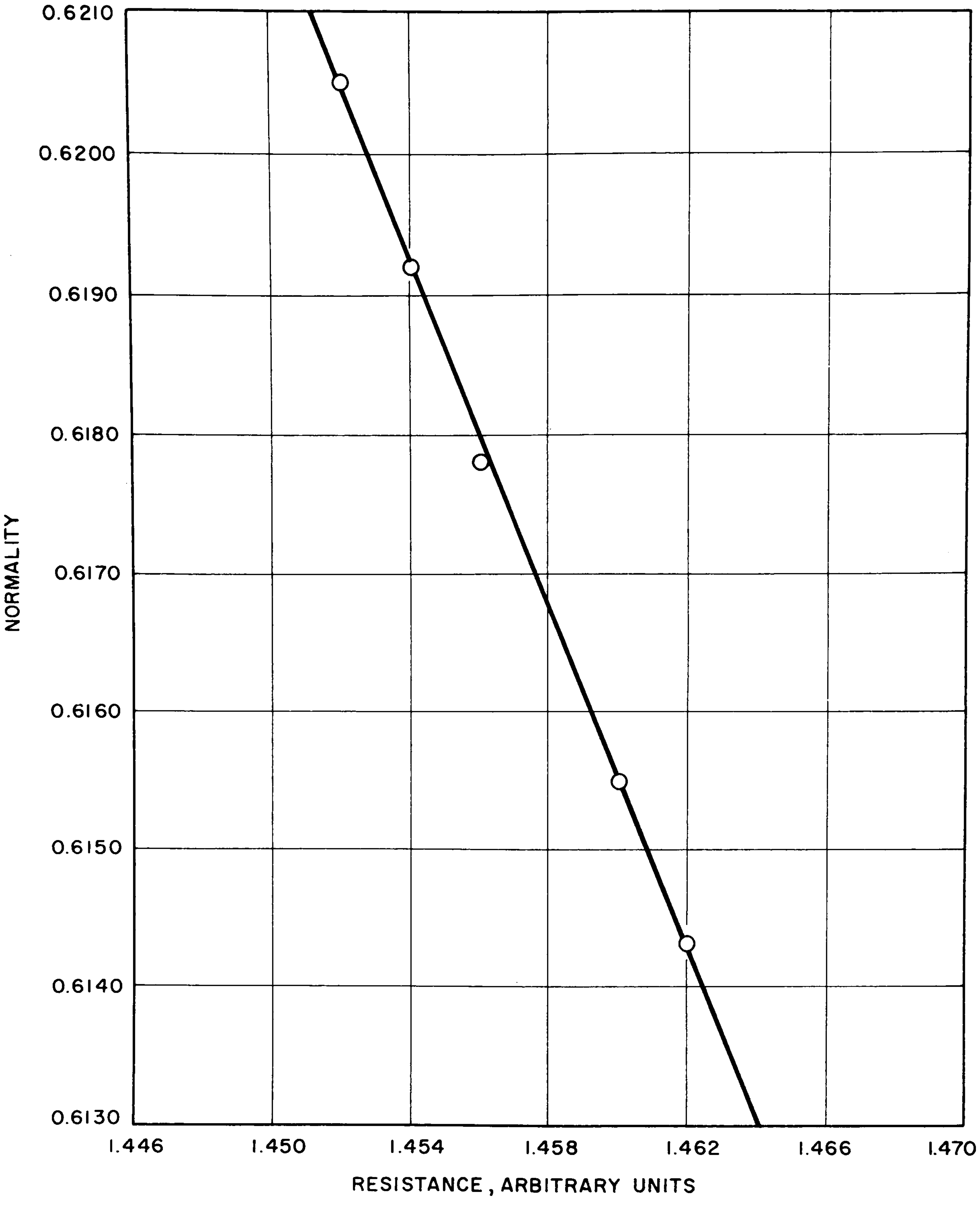

Fig.16–CALIBRATION CURVE NORMALITY VS RESISTANCE

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but rather that of determining small differences between large concentrations. The former presents no particular problems; concentrations down to 0.1 ppm can be determined chromatographically. As far as the latter is concerned, to our knowledge, we have reached a limit with the means available today.

In any case it can be concluded that the surface concentration change of NaCl solutions up to 3.5% due to the application of positive or negative electric fields up to 4000 v/cm is increased by less than one order of magnitude. The effect is small and precludes application in practical desalination of sea water.

IV. EXPERIMENTS ON THE EFFECTS OF ELECTRIC FIELDS ON VAPORIZATION AND FREEZING PROCESSES

Results with the surface energy balance indicate that the application of an electric field across the salt solution/air interface results in a lowering of surface tension by increased orientation of water dipoles. This effect should be reflected in a change in the rate with which a salt solution establishes equilibrium with its environment. For example, the rate at which water molecules cross the solution vapor interface in a vaporization process, or the rate with which water dipoles become aligned for inclusion in an ice crystal in a freezing process, should be affected by the presence of a field.

Several simple experiments were performed to determine if an electric field changed the rate of vaporization of water from a 0.6 M(3.5%) salt solution. The apparatus used consisted of a covered Plexiglass tray equipped with a pair of electrodes, one above and one below the solution surface, as shown in Figure 17. Dry nitrogen was passed over the surface of a salt solution and then dried in a drying tube with $Mg(ClO_4)_2$. The rate of evaporation was calculated from the weight gain of the drying tube. In all experiments the gas flow rate was sufficiently high that saturation of the gas with water vapor was not attained; also, the total amount of water evaporated was low enough that the change in temperature of the solution was negligible.

Experiments were performed without an electric field and with applied fields up to 7000 v/cm at which arcing between the vapor electrode and solution surface occurred. A comparison of results obtained shows that there is no marked difference in the rate of vaporization of water when an electric field of either polarity is applied across the vapor-solution interface.

The effects of electric fields on the purity of water from ice separated from freezing brine were also studied briefly. The interface in this case is solid/liquid, rather than liquid/air as

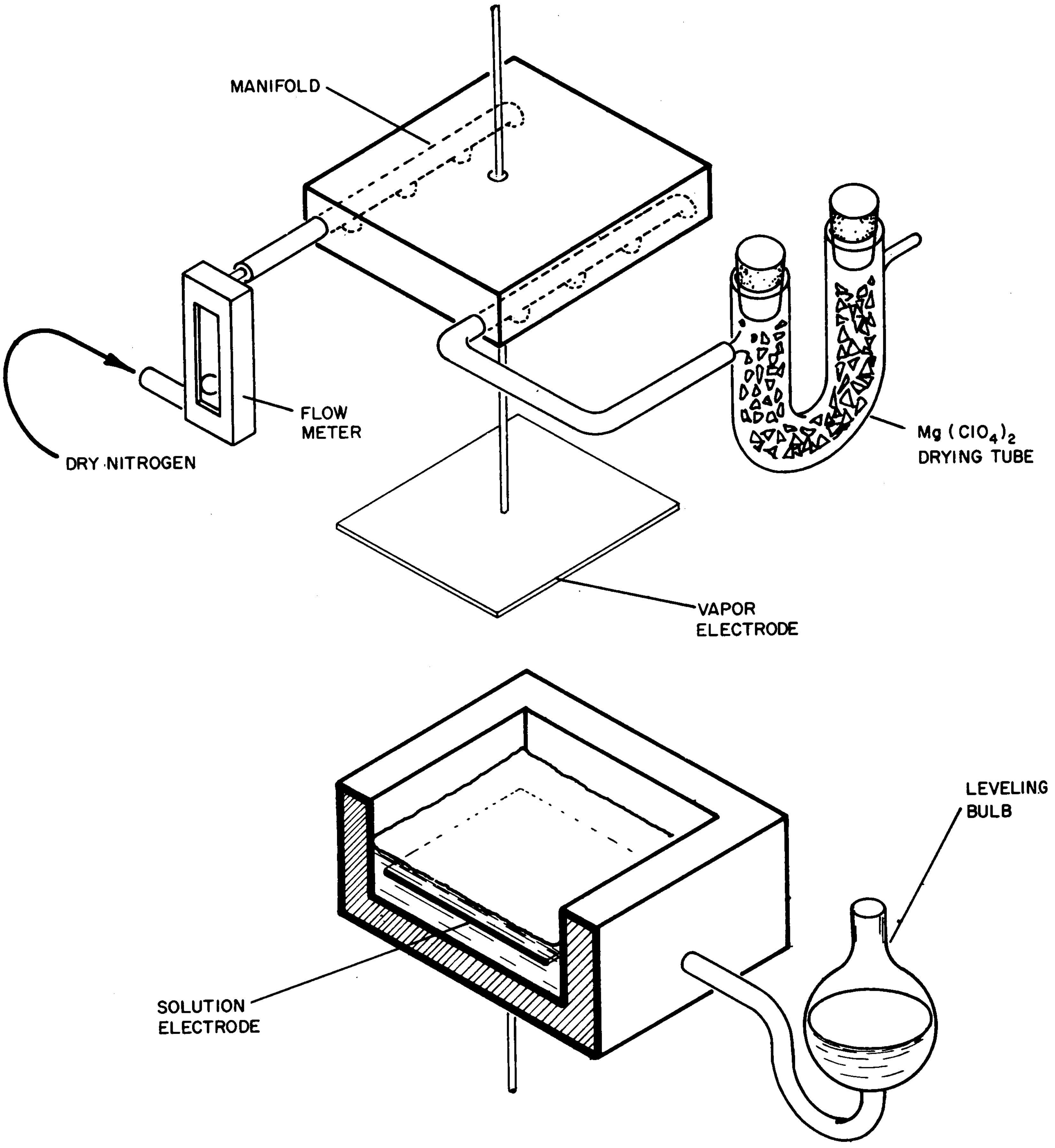

Fig. 17 — APPARATUS FOR DETERMINING THE RATE OF VAPORIZATION OF WATER

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GMS/JRR

studied with the surface energy balance and skimmer. The kinetics of the formation of ice crystals depend on the properties of the ice/water interface which, in turn, is largely characterized by the dipole nature of water molecules. One would expect then that a change in the orientation of water molecules by the interaction of water dipoles at the ice/water interface with an electric field would affect, to some degree, the rate of heat transfer across the interface and/or the nature of the ice crystal grown in an electric field. Workman and Reynolds (20) have shown that voltages of up to 250 v are established between an electrode in a growing ice crystal and another in the liquid phase. The voltage disappeared when growth of the ice crystal was stopped.

The apparatus used in our freezing experiments is shown in Figure 18. In accordance with Workman and Reynolds, voltages were observed between the two electrodes while ice was freezing on the brass block from distilled water. However, no measurable voltages were observed with ice freezing from 3.5% salt water. Although Workman and Reynolds observed potentials in salt solutions, the concentrations employed were only of the order of 10^{-4}N while solutions used in our experiments were 0.6N. The greatest difficulty in these experiments is the establishment of an electric field across the ice/solution interface because of the tendency to form an electrolytic contact between the two electrodes by the salt solution. In attempts to obtain a steady applied electric field, pure water was first frozen on the block, and the salt water, chilled to 0^{o}C, then added until the solution electrode was covered. These attempts failed because of conductivity along the vessel wall and inbibition of salt water by the ice, as evidenced by gas generation on the freezing block.

Attempts were also made to coat the lower electrode by freezing a layer of pure ice from salt water, however, appreciable conductivity through the ice occurred in every case due to inclusion of salt water in the ice. The amount of included salt was

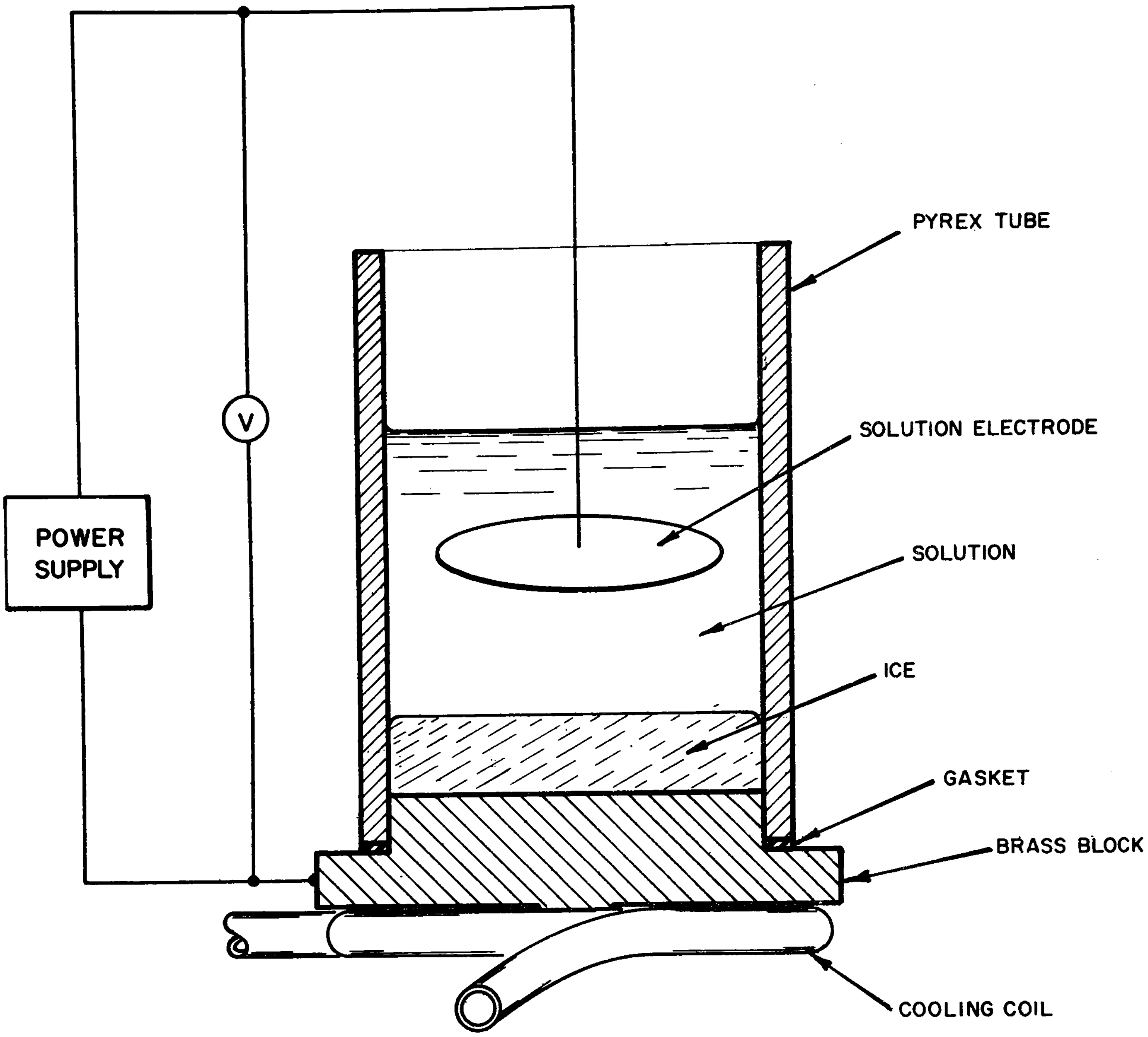

Fig. 18 – APPARATUS FOR THE STUDY OF THE EFFECTS OF ELECTRIC FIELDS ON THE FORMATION OF ICE

DWG. A4500-45
GMS - JRR

determined for various freezing rates, and the results obtained are shown in Table II. Inversion of the apparatus, so that drainage of the concentrated brine from the advancing ice interface was facilitated, lowered the concentration of included salt by a factor of 2. Increasing the freezing time also had a large effect in lowering the salt concentration of the ice. In each case, the ice was drained well but not washed before measuring the salt concentration. Concentration of salt in the ice was determined by the Volhard method.

TABLE II

EFFECTS OF ORIENTATION AND FREEZING TIME ON THE SALT CONCENTRATION IN ICE

Direction of Growth	Time to Freeze, 4 ml, Hrs.	NaCl Conc. (N)
up	.5	.594
down	.5	.378
down	.5	.326*
down	.67	.398
down	2.0	.278
down	3.0	.200

The salt retained by the ice was apparently due to inclusion in small pockets because crushing the ice and washing with chilled pure water had only a small effect in lowering the salt concentration obtained.

It is concluded that a more refined experimental technique than that used here will be required to investigate the effects of applied fields on growth and drainage of ice crystals.

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*Ice from this experiment was washed with chilled pure water before analysis

V. SUMMARY

Electrostatic fields of up to 6700 v/cm, positive and negative, have been applied to air/NaCl-solution interfaces and the surface tension changes measured with a surface energy balance. The NaCl solution concentration ranged from 0 to 3.5%.

It was found that either field direction lowers the surface tension of all investigated solutions. A positive air electrode lowers the surface tension of pure water less than a negative air electrode. This is taken as evidence that the field at the air-water interface is considerably smaller than the 10^7 v/cm previously thought present, that the orientation of the water dipoles at the interface is only slight, and that the predominant small orientation present is with the hydrogen atoms facing the air.

The Gibbs equation has been used to calculate the surface deficiency of NaCl solutions under applied electric fields The data show that a positive air electrode increases the surface deficiency and a negative air electrode decreases it. This behavior can be explained by assuming the electric field to be either exclusively or predominantly effective on the Na^+ ions alone, due to their smaller diameter. The conclusion is drawn that the difference in the adsorption energy, W(x), of the Onsager-Samaras treatment for cations and anions can not be neglected.

It is shown that the assumption of a diffuse double layer in the Lewis equation leads to a surface deficiency which is about two orders of magnitude too high. One obtains the right order of magnitude, however, by neglecting the diffuse layer and making the calculations on the basis of an inner double layer only. This causes the difficulty of having to assume cations to be adsorbed in the inner layer. However, most of the experience, which has led to the conclusion that cations are not usually adsorbed in the inner layer, has been obtained from studies of solid-solution interfaces. No data are available for air/solution interfaces.

An apparatus is described which skims a thin surface layer off a solution jet with or without an electric field applied perpendicular to the jet. It is shown that the apparatus gives good results for the surface concentration of surface active substances.

The usefulness of the apparatus rests on the ability to analyze the skimmed and unskimmed position with the required accuracy. This has not been possible for NaCl solutions up to 3.5%. It can be concluded, however, that the surface concentration of NaCl solutions under fields of up to ±4000 v/cm is of the order of the surface concentration of the solution without the field, and that the change from bulk concentration is too small to form the basis of a fractional desalination process.

Experiments on the vaporization of water showed that an electric field applied across the solution/air interface has little, if any, effect on the rate of transfer of water molecules across the interface.

An apparatus for freezing water from 3.5% NaCl solutions on an electrode was built; however, electric fields could not be applied across the ice/solution interface because of formation of an electrolytic contact between the electrodes by the brine. Orientation of the ice and time required for freezing are controlling factors in the inclusion of salt in the ice. The amount of included salt in the ice in inversely proportional to the time required for freezing a given amount.

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